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Study of the removal of heavy metals (Cu,Cd, and Zn) by chemical precipitation

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Abstract

In this research the efficiency of chemical precipitation was studied for the removal of toxic heavy metals (copper(II), cadmium(II), and zinc(II)). Lime ($\text{Ca}(\text{OH})_2$), caustic soda (NaOH), and soda ash (Na_2CO_3) are the used commercial precipitating agents. In addition, calcined eggshell ($\text{CaO}_{\text{Eggshells}}$) was also used as a synthetic comparative precipitant to conventional lime. $\text{CaO}_{\text{Eggshells}}$ was produced by calcination of Eggshell powder (CaCO_3) at 800°C for 7 h.

For the individual metal removal ($\text{Cu}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Zn}(\text{II})$), about 99.99 % of total removal was obtained for $\text{Cu}(\text{II})$ and $\text{Cd}(\text{II})$, and more than 97 % for $\text{Zn}(\text{II})$ using 400 mg/L of commercial precipitants. The optimum pH (O_{pH}) slightly varied from one metal to another. Around 9.33 of final pH (pH_f) was enough to reach the maximum removal of $\text{Cu}(\text{II})$, but for the maximum $\text{Cd}(\text{II})$ removal, at least 10.5 of pH_f was required. While, raising the pH to 10.86 was needed to reach the maximum removal of Zn . Among all the commercial precipitants, NaOH was the suitable one for the individual metal removal.

To make the medium more complex, the heavy metals ($\text{Cu}(\text{II}) + \text{Cd}(\text{II}) + \text{Zn}(\text{II})$) were combined. The removal efficiency of combined metals remains significant, with over 99 % reached for all metals by using 400 mg/L of precipitants. Na_2CO_3 is the best agent for the removal of combined metals at $O_{\text{pH}} \leq 10$. It has the advantage of removing metals at lower pH compared to other hydroxide agents. The $\text{CaO}_{\text{Eggshells}}$ is also a good choice to remove the combined heavy metals, especially for $\text{Cu}(\text{II})$ by 99 % of removal and about 97 % for $\text{Cd}(\text{II})$ and $\text{Zn}(\text{II})$. In the combined metals system, it is difficult to control the range of pH in order to achieve maximum removal of the three metals simultaneously.

The sludge analysis of combined heavy metals indicates that the sludge volume produced by hydroxide precipitants was more significant than carbonate precipitates due to their gelatinous form. In contrast, the mass of carbonate precipitates was higher than that of the hydroxide precipitates.

To confirm the good efficiency of chemical precipitation in synthetic solution of distilled water, chemical precipitation was applied at two different industrial wastewaters charged with heavy metals. The *ENICAB* industrial wastewater (Biskra city, Algeria) contained important concentrations of $\text{Cu}(\text{II})$ (18.10 mg/L) and $\text{Zn}(\text{II})$ (10.21 mg/L). After the treatment using $\text{Ca}(\text{OH})_2$, NaOH and Na_2CO_3 , the process removed more than 99 % of $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ at $\text{pH}_f = 9.21$ and 9.96 using 300 mg/L of precipitating agent. Sludge characterization showed that the average particle size of carbonate precipitates was larger than hydroxide precipitates. However, their sludge volume was smaller. In *Galvanic Wastewater* (Padova city, Italy), charged largely on $\text{Cu}(\text{II})$ (51.55 mg/L) and $\text{Ni}(\text{II})$ (36.66 mg/L), 1600 mg/L of $\text{Ca}(\text{OH})_2$ and $\text{CaO}_{\text{Eggshells}}$ removed about 93% of $\text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$ at a very basic pH (> 12). While, this removal was not conform to maximum concentration standards. Sludge volume produced by using $\text{Ca}(\text{OH})_2$ was higher than that produced by using $\text{CaO}_{\text{Eggshells}}$. The opposite was happened with precipitant mass. SEM and EDX results were discussed at three different precipitating agent doses, in the purpose of following the chemical precipitation stages by showing the different changes in the structure of precipitates and the appearance of new mineral elements at each stage.

Key words: Heavy metals, chemical precipitation, $\text{Ca}(\text{OH})_2$, NaOH , Na_2CO_3 , $\text{CaO}_{\text{Eggshells}}$ industrial wastewater.

في هذا البحث درست أبعاد وكفاءة عملية الترسيب الكيميائي لإزالة المعادن الثقيلة السامة (النحاس (II)، الكاديوم (II) والزنك (II)). الجير والصودا الكاوية ورماد الصودا هي عوامل الترسيب التجارية المستخدمة. بالإضافة إلى ذلك، تم استخدام قشور البيض المكلس أيضًا كمسبب اصطناعي تتم مقارنته بالجير التقليدي. تم إنتاج مسحوق قشور البيض المكلس بتكليس كربونات الكالسيوم CaCO_3 عند درجة حرارة 800 درجة مئوية لمدة 7 ساعات.

بالنسبة لإزالة المعادن الفردية النحاس (II)، والكاديوم (II)، والزنك (II)، فقد تم الحصول على إزالة كاملة (حوالي 99.99%) للنحاس (II) والكاديوم (II) باستخدام 400 مغ/لتر من المرسلات التجارية، وإزالة أكثر من 97% من الزنك (II). تختلف قيمة درجة الحموضة (pH) المثالية قليلاً من معدن إلى آخر، حوالي 9.33 من درجة الحموضة (pH) كان كافياً للوصول إلى الحد الأقصى لإزالة النحاس (II)، ولكن لإزالة الكاديوم (II) نحتاج درجة حموضة 10.5 على الأقل؛ بينما نحتاج إلى رفع قيمة ال pH إلى 10.86 للوصول إلى الحد الأقصى لإزالة الزنك. من بين جميع المواد المرسبة، كانت الصودا الكاوية هي المادة المناسبة لإزالة المعادن الفردية.

لجعل الوسائط أكثر تعقيداً، تم الدمج بين المعادن السابقة ((Cu(II) + Cd(II) + Zn(II)). النجاعة لا تزال كبيرة، أكثر من 99% لإزالة جميع المعادن باستخدام 400 مغ/لتر من رماد الصودا، وهو أفضل عامل لإزالة المعادن المجمعة بحيث ان درجة الحموضة المثلى لم تتجاوز 10. يتمتع رماد الصودا بميزة إزالة المعادن عند درجة حموضة أقل مقارنة بعوامل الهيدروكسيد الأخرى. تعد قشور البيض المكلس أيضاً خياراً جيداً لإزالة المعادن الثقيلة المجمعة، خاصة بالنسبة للنحاس (II) بنسبة ازالة 99% وحوالي 97% للكاديوم (II) والزنك (II). في نظام الجمع المعدني، من الصعب التحكم في مجال ال pH من أجل الحصول على أقصى إزالة للمعادن الثلاثة في وقت واحد.

يشير تحليل الحمأة (الرواسب) للمعادن الثقيلة مجمعة إلى أن حجم الحمأة الناتجة عن مرسلات الهيدروكسيد أعلى من رواسب الكربونات بسبب شكلها الجيلاتيني. في المقابل، كانت كتلة رواسب الكربونات أكبر من كتلة رواسب الهيدروكسيد.

لتأكيد نجاعة تقنية الترسيب الكيميائي في محاليل الماء المقطر، قمنا بتطبيق هذه الطريقة على اثنين من مياه الصرف الصحي الصناعية المختلفة المشحونة بالمعادن الثقيلة. تحتوي مياه الصرف الصناعي ل ENICAB (مدينة بسكرة، الجزائر) على تراكيز مهمة من معدني النحاس (II) والزنك (II) (18.10 مغ/ل و 10.21 مغ/ل تواليًا)، بعد المعالجة باستخدام عوامل الترسيب التالية: الجير Ca(OH)_2 و هيدروكسيد الصوديوم NaOH و كربونات الصوديوم Na_2CO_3 ، أزلت العملية أكثر من 99% من Cu(II) و Zn(II) عند قيمة 9.21 و 9.96 pH باستخدام 300 مغ/لتر من العوامل المرسبة. أظهرت خصائص الحمأة أن متوسط مقاس الجزيئات لرواسب الكربونات أكبر من مقاس جزيئات رواسب الهيدروكسيد، في حين ان حجمها كان أقل.

في مياه الصرف الصحي الجلفانية (النفايات السائلة الصناعية في مدينة بادوفا، إيطاليا)، الملوثة إلى حد كبير بالنحاس (II) (51.55 مغ/ل) والنيكل (II) (36.66 مغ/ل)، 1600 مغ/لتر من Ca(OH)_2 و $\text{CaO}_{\text{Eggshells}}$ مكنت من ازالة 93% من النحاس (II) و النيكل (II) في درجة حموضة تجاوزت (12 > pH). ومع ذلك، الإزالة لم تتوافق مع المعايير القصوى لازالة المعادن الضارة. بالنسبة لنظام الحمأة، كان حجم الحمأة الذي ينتجه Ca(OH)_2 أعلى من حجم الحمأة التي تنتجها $\text{CaO}_{\text{Eggshells}}$ ، في حين ان العكس حدث مع كتلة الحمأة. تمت مناقشة نتائج SEM و EDX في ثلاث تركيبات مختلفة من عوامل الترسيب بغرض متابعة مراحل الترسيب الكيميائي من خلال إظهار التغيرات المختلفة في بنية الرواسب وكذلك ظهور عناصر معدنية جديدة في كل مرحلة.

الكلمات المفتاحية: المعادن الثقيلة، الترسيب الكيميائي، الجير، الصودا الكاوية، رماد الصودا، قشور البيض المكلس، مياه الصرف الصناعي.

Résumé

Dans cette recherche, l'efficacité de la précipitation chimique a été étudiée pour l'élimination des métaux lourds toxiques (cuivre(II), cadmium(II) et zinc(II)). La chaux ($\text{Ca}(\text{OH})_2$), la soude caustique (NaOH) et le carbonate de soude (Na_2CO_3) sont les agents précipitants commerciaux utilisés. En outre, la coquille d'œuf calcinée ($\text{CaO}_{\text{Eggshells}}$) est également utilisée comme précipitant synthétique comparatif avec la chaux conventionnelle. Les $\text{CaO}_{\text{Eggshells}}$ est produit par calcination de poudre de coquille d'œuf (CaCO_3) à 800°C pendant 7 heures.

Pour l'élimination des métaux individuels ($\text{Cu}(\text{II})$, $\text{Cd}(\text{II})$ et $\text{Zn}(\text{II})$), on a obtenu une élimination totale d'environ 99,99 % pour $\text{Cu}(\text{II})$ et $\text{Cd}(\text{II})$ en utilisant 400 mg/L de précipitants commerciaux, et plus de 97 % d'élimination de $\text{Zn}(\text{II})$. Le pH optimal (OpH) variait légèrement d'un métal à l'autre, environ 9,33 de pH_f était suffisant pour atteindre l'élimination maximale de $\text{Cu}(\text{II})$, mais pour l'élimination maximale de $\text{Cd}(\text{II})$, au moins 10,5 de pH_f était nécessaire ; tandis que on devait augmenter le pH à 10,86 pour atteindre l'élimination maximale de Zn . Parmi tous les précipitants, NaOH était celui qui convenait le mieux à l'élimination des métaux individuels.

Pour rendre le milieu plus complexe, les métaux lourds ($\text{Cu}(\text{II}) + \text{Cd}(\text{II}) + \text{Zn}(\text{II})$) ont été combinés. L'efficacité d'élimination des métaux combinés reste significative, avec plus de 99 % d'élimination pour tous les métaux en utilisant 400 mg/L de précipitant. Na_2CO_3 est le meilleur agent pour l'élimination des métaux combinés à $\text{OpH} \leq 10$. Na_2CO_3 a l'avantage d'éliminer les métaux à un pH plus faible que les autres agents hydroxydes. Le $\text{CaO}_{\text{Eggshells}}$ est également un bon choix pour éliminer les métaux lourds combinés, en particulier pour le $\text{Cu}(\text{II})$ avec 99 % d'élimination et environ 97 % pour le $\text{Cd}(\text{II})$ et le $\text{Zn}(\text{II})$. Dans le système de combinaison de métaux, il est difficile de contrôler la gamme de pH afin d'obtenir une élimination maximale des trois métaux simultanément.

L'analyse des boues de métaux lourds combinés indique que le volume des boues produites par les précipitants d'hydroxyde est plus élevé que celui des précipités de carbonate en raison de leur forme gélatineuse. En revanche, la masse des précipités de carbonate est plus importante que celle des précipités d'hydroxyde.

Afin de confirmer la bonne efficacité de la précipitation chimique en solutions synthétiques d'eau distillée, on a appliqué la précipitation chimique à deux eaux usées industrielles différentes chargées en métaux lourds. L'eau usée industrielle ENICAB (ville de Biskra) contient des concentrations importantes de $\text{Cu}(\text{II})$ (18.10 mg/L) et $\text{Zn}(\text{II})$ (10.21 mg/L), après le traitement utilisant $\text{Ca}(\text{OH})_2$, NaOH et Na_2CO_3 , le processus a éliminé plus de 99 % de $\text{Cu}(\text{II})$ et $\text{Zn}(\text{II})$ à $\text{pH}_f = 9,21$ et $9,96$ en utilisant 300 mg/L d'agent de précipitation. La caractérisation des boues a montré que la taille moyenne des particules des précipités de carbonate était supérieure à celle des précipités d'hydroxyde. Cependant, leur volume de boue était plus faible. Dans l'eau usée galvanique (ville de Padoue, Italie), chargée en grande partie en $\text{Cu}(\text{II})$ (51.55 mg/L) et $\text{Ni}(\text{II})$ (36.66 mg/L), 1600 mg/L de $\text{Ca}(\text{OH})_2$ et de $\text{CaO}_{\text{Eggshells}}$ ont éliminé environ 93% de $\text{Cu}(\text{II})$ et $\text{Ni}(\text{II})$ à un pH très basique (>12). Alors que, cette élimination n'est pas conforme aux normes de concentration maximale. Pour le système de boues, le volume de boues produit par $\text{Ca}(\text{OH})_2$ était plus élevé que celui produit par $\text{CaO}_{\text{Eggshells}}$, l'inverse s'est produit avec les masses des précipités. Les résultats SEM et EDX ont été discutés pour trois doses différentes d'agent précipitant dans le but de suivre les étapes de la précipitation chimique en montrant les différents changements dans la structure des précipités ainsi que l'apparition de nouveaux éléments minéraux à chaque étape.

Mots clés : Métaux lourds, précipitation chimique, $\text{Ca}(\text{OH})_2$, NaOH , Na_2CO_3 , $\text{CaO}_{\text{Eggshells}}$, eaux usées industrielles.

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DEDICATION

I dedicate this humble work to:

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My brothers and sisters;

All my small and large family;

All my friends of the class 2017/2018;

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**LIST OF
ABBREVIATIONS AND
ACRONYMS**

LIST OF ABBREVIATIONS AND ACRONYMS

Abbreviation and acronyms	Meaning
Cu(II)	Copper ion
Cd(II)	Cadmium ion
Zn(II)	Zinc ion
Ni(II)	Nickel ion
WHO	World Health Organization
JORA	Journal Official Republic Algeria
MCL	Maximum Contamination Level
ENICAB	Entreprise National Des Industries Du Câble De Biskra = Cable Industry National Company Of Biskra
Ca(OH) ₂	Lime (Calcium Hydroxide)
NaOH	Caustic soda
Na ₂ CO ₃	Soda ash (Sodium carbonate)
CaO _{Eggshells}	Calcined eggshells
CaO	quick lime
EDX	Energy Dispersive X-Ray Analysis
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
K _{sp}	Solubility Product Constant
OD	Optimum Dose
OpH	Optimum pH
PM	Precipitant Mass
R%	Removal Efficiency
RM	Residual Metal Concentration
V _s	Volume of Sludge

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GENERAL INTRODUCTION

General Introduction

Heavy metals are inorganic substances related to the elements, which have a higher density and are toxic even at low concentration. Heavy metals are non-biodegradable and their solubility in the aquatic environments leads to bio-accumulation in aquatic life and human body, causing various diseases and disorders, damaging central nervous function, lungs, kidneys and liver. Certain heavy metals are essential components for human body, but large doses of heavy metals cause acute or chronic toxicity. The increasing level of heavy metals in the environment represents a serious risk to human health, living resources, and ecological systems (Carolin et al., 2017 ; Dai et al. 2017 ; Ghosh et al., 2011)

The heavy metals in water could be derived from both natural (weathering and erosion of bedrocks and ore deposits) and anthropogenic activities (mining industries, wastewater irrigation and agriculture activities), which are the main source of heavy metals (Benhaddya et al., 2020). Wastewaters contain high levels of heavy metals, which are discharged into the environment inappropriately and indiscriminately and have disastrous effects on surface water, groundwater, sediments, and soil (Benalia et al., 2022 ; Chen et al., 2018). Industrial activities (paper industries, pesticides, tanneries, metal plating, smelting, battery manufacturing, dyeing, plastics and mining operations, etc...) and urban activities that produce toxic heavy metals, such as cadmium, copper, zinc, nickel, arsenic, chromium, and mercury have been categorized as hazardous and non-biodegradable in environment (Benalia et al., 2022 ; Samiullah et al., 2018 ; Khalid et al., 2018 ; Carolin et al., 2017)

Among these elements, copper (Cu(II)) and zinc (Zn(II)) are two of the most common metals found in effluents from a wide range of industries, Cd(II) is also considered one of the most toxic metals (Dai et al., 2017 ; Ye et al., 2016). Cu(II) is an essential trace element for all living organisms because it is an important part of the complex of respiratory enzymes and cytochrome c oxidase, it plays an important role in bone formation. However, if Cu(II) cannot be maintained at an appropriate physiological concentration, it causes serious syndrome diseases (Dai et al., 2017 ; Ye et al., 2016 ; Fu et al., 2011). Zn(II) is a trace element that is necessary for the functioning of various enzyme systems, and its deficiency affects body development in humans and animals. It is also important for the physiological

functions of living tissue and regulates many biochemical processes. However, too much zinc can lead to serious health problems when it accumulates in the human body (Dai et al., 2017 ; Ye et al., 2016 ; Fu et al., 2011). Cd(II) plays a major role in industries, such as plating, cadmium-nickel battery, phosphate fertilizers, stabilizers, and alloys. Even at low concentration, the cadmium compounds are hugely harmful and gets concentrated in the ecosystem (Carolin et al., 2017).

For all these considerations, the removing of these hazardous heavy metals is compulsory in order to preserve the human health, the fauna and flora, and the environment. Heavy metals can only be removed by separation or converted to a chemically inert state for that a large number of technologies have been employed so far including chemical precipitation, adsorption, ion exchange, coagulation/flocculation, ion flotation, and membrane filtration (Benalia et al., 2022 ; Chen et al., 2018, Ghosh et al., 2011 ; Chen et al. 2009). Of these methods, chemical precipitation is the most widely used method due to its simplicity of use and it is considered to be the most economical. It is commonly used for the removal of heavy metals. (Benalia et al., 2022 ; Chen et al., 2018 ; Youcef et al., 2014 ; Chen et al., 2009).

The aquatic system in Algeria is threatened by heavy metal pollution due to anthropogenic activities. For example, acid mine drainage (AMD) resulting from mining and metallurgical activities, soil contamination by oil from petroleum industries located in the Sahara (e.g. Hassi Messaoud) can contribute to groundwater pollution, and other industrial activities such as the paper, plastic, battery, cable and pigment industries, etc., can also contribute to pollution....etc (Benhaddya and Hadjel, 2014)

In this study, the removal of three hazardous heavy metals Cu(II), Cd(II) and Zn(II) will be investigated by a chemical precipitation process. The thesis will be presented in two main sections: the bibliographical part and the experimental part.

The first part is based on the literature review, presented in two chapters. Chapter I includes all the important information on the three heavy metals (Cu, Cd and Zn), focusing on their physical and chemical characteristics, occurrence and sources, uses in different industries, toxicity and consumption limits. This chapter also discusses the presence of heavy metals in certain Algerian sites, based on the results of Algerian research projects. However, Chapter II summarises all the knowledge about the chemical precipitation process, the definition and the

different properties, the chemicals used, the kinetics, the different types of precipitation, and the stages of the process from pre-treatment to sludge disposal.

The second part describes the protocol and the results of the tests carried out in the laboratory. This part is presented in three chapters. In chapter I, the material and methods used for chemical precipitation process will be described, starting with the preparation of synthetic solution composed from heavy metals and precipitating agents. Four precipitates will be used, two hydroxides (lime ($\text{Ca}(\text{OH})_2$) and caustic soda (NaOH)), one carbonate (soda ash (Na_2CO_3)) and synthetic precipitant prepared using eggshells ($\text{CaO}_{\text{Eggshells}}$). The physico-chemical characterisation of two different industrial wastewaters (ENICAB and Galvanic industrial effluents) will be described. The method for preparing $\text{CaO}_{\text{Eggshells}}$ will be explained step by step in this chapter. In addition, the precipitation process will be described, including Jar tests and, sludge analysis.

Then, in chapter II, the process described in chapter I will be applied to study the possibility of removing heavy metals ($\text{Cu}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Zn}(\text{II})$) from synthetic solutions in two different ways, separately (each metal alone) and in combination (three metals together) using: $\text{Ca}(\text{OH})_2$, NaOH and Na_2CO_3 , respectively. The efficiency of the combined metals removal will also be tested using the synthetic precipitant ($\text{CaO}_{\text{Eggshells}}$). To better understand the mechanism of this process, tests will be focused on the effect of different parameters: the dose of precipitating agent, the Heavy metal content, the initial pH, the precipitate settling time, the volume and the mass of the sludge and the mineral composition of the sludge.

Finally, in Chapter III, the same experiments tested previously will be applied in synthetic solution to two real industrial wastewaters (ENICAB and Galvanic). The ENICAB wastewater contains high levels of $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ exceeding the standards and the second (Galvanic) contains very high levels of $\text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$. Various analyses such as XRD, SEM and EDX will be used to characterize the final produced sludge.

BIBLIOGRAPHIC PART

CHAPTER I

GENERALITY ABOUT HEAVY

METALS (COPPER, CADMIUM,

AND ZINC)

I.1 Introduction

There are multiple ways to define heavy metals. The well-known definition states that heavy metals create positive ions in solution and have a density five times that of water. They are toxic elements (Haynes, 2017 ; Sharma et al., 2014 ; Wang et al., 2009). A heavy metal is also defined as an element with an atomic weight between 63.5 and 200.6 and a specific gravity greater than 5.0 (Carolin et al., 2017 ; Srivastava and Majumder 2008).

Heavy metals in the environment occur as natural or anthropogenic origin (Figure 1) (Zamora-Ledezma et al., 2021 ; Srivastava et al., 2017).

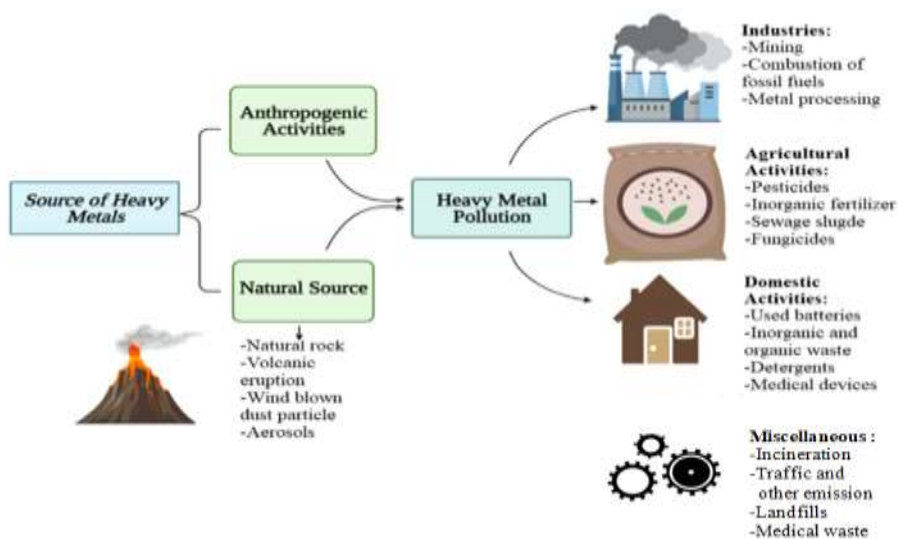


Figure 1 Sources of pollution caused by heavy metals -The figure is a combination of the schemes shown in Srivastava et al., (2017) and Zamora-Ledezma et al., (2021).

Excessive concentrations of any of these heavy metals are dangerous and have adverse effects on human health, symptoms and diseases presented in (Figure 2) (Zamora-Ledezma et al., 2021 ; Nordberg et al., 2015; Sarkar, 2002).

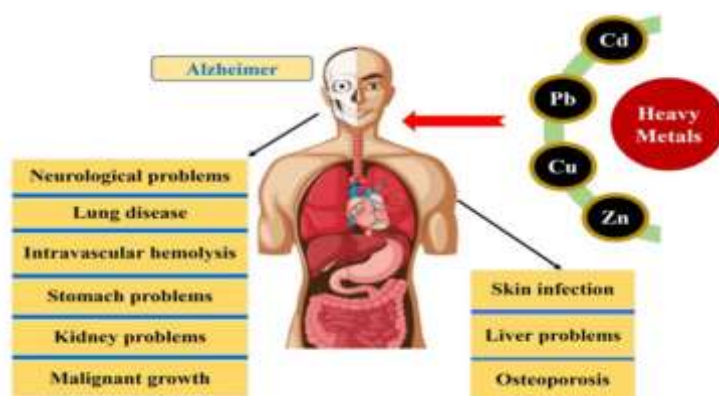


Figure 2 Heavy metals and their toxic effects on human health (Hama Aziz et al., 2023).

In this chapter, the chemical and physical properties, compounds, sources, nature occurrence, production, uses, toxicity and, limit consumption of selected heavy metals (Cd, Cu and Zn) are discussed.

I.2 Generality about Cadmium

I.2.1 Physical and chemical properties

Cadmium with symbol (Cd) is a transition metal in group II-B of the periodic table (Figure 3) (like Hg and Zn). The naturally occurring isotopes are 106 (1.22%), 108 (0.88%), 110 (12.9%), 111 (12.75%), 112 (24.07%), 113 (12.6%), 114 (28.86%), and 116 (7.5%) (Nordberg et al., 2015 ; Dean, 2005 ; Bradl, 2005 ; Sarkar, 2002 ; Weast and Astle, 1988). The main physical properties are shown in the Table 1.

Table 1 Different physical cadmium properties (Haynes, 2017 ; Dean 2005; Schulte Schrepping and Piscator, 2000)

Propertie	Unity	Value
Atomic number		48
Atomic weight	g.mol ⁻¹	112,411
Density (25 °C)	g.cm ⁻³	8,69
Oxidation state		+2
Melting point	°C	321,069
Boiling point	°C	767 ± 2
Electronic configuration		[Kr] 4d ¹⁰ 5s ²
Electrical resistivity, at 18 °C	μΩ.cm	7.5
at 22 °C		7.27

Cadmium is chemically similar to zinc, it was identified as an impurity in zinc carbonate, changed color on heating due to cadmium impurities, and has no defined taste or odor. Cd is commonly occurring in small concentrations in zinc ores, such as sphalerite (ZnS). Majority of Cd is obtained as a by-product of copper, lead and zinc ore (Haynes, 2017; Sarkar, 2002).

Cadmium is silver-white metal that is easy to cut with a knife, malleable shiny, it is also soft, ductile and has a relatively high vapor pressure (Sharma et al., 2014 ; Wang et al., 2009). Cd is a relatively volatile element, and it is a member of Group 12 (Zn, Cd, Hg) of the

Periodic Table (Figure 3), having a filled d shell of electrons $4d^{10}5s^2$. Cd, Zn, and Hg having no oxidation state higher than +2 (Cotton et al., 1995; Merian et al., 2004; Herron 2003).

Cadmium forms hydroxides and complex ions with ammonia and cyanide, and also a variety of complex organic amines, sulfur complexes, chloro-complexes, and chelates. Cd forms precipitates with carbonates, arsenates, phosphates, oxalates, and ferrocyanides. It is readily soluble in nitric acid and is not soluble in bases; it reacts readily when heated in O_2 to produce oxides. Cd reacts with halogens and non-metals such as S, Se, and P, and may also form numerous alloys (Bradl, 2005 ; Merian et al., 2004 ; Adriano, 2001).

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

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Figure 3 Periodic Table of Elements (showing the position of heavy metals and their different properties) (<https://ptable.com> by Michael Dayah, 2022).

I.2.2 Cadmium Compounds

Among several inorganic Cd compounds, several are fairly soluble in water (e.g. cadmium acetate, cadmium chloride, and cadmium sulfate). Cadmium oxide and cadmium carbonate may be soluble at basic pH (Nordberg et al., 2015). Properties of the most important cadmium compounds are listed in Table 2.

Table 2 Cadmium compounds properties (Dean, 2005 ; Herron, 2003)

Cadmium Compounds	Formula	Molecular weight	Melting point, °C	Boiling point, °C	Density (d ^{°C})	Solubility in g/100 g H ₂ O
Cadmium carbonate	CdCO ₃	172.42	500 d	N/A	5.026	N/A
Cadmium chloride	CdCl ₂	183.32	568	964	4.05 ²⁵	120 ²⁵
Cadmium hydroxide	Cd(OH) ₂	146.43	H ₂ O ,130	CaO, 200	4.79	0.00015 ²⁰
Cadmium Oxide	CdO	128.41	1540	1559 sp	8.15 cubic	N/A
Cadmium sulfate	CdSO ₄	208.474	1000	N/A	4.69	76.7 ²⁵

N/A : Not Available

I.2.2.1 Cadmium Carbonate

CdCO₃ is obtained only when ammonium carbonate is used to precipitate the white prismatic crystals from cadmium ion solutions (Herron, 2003 ; Sneed and Brasted, 1961). Cadmium oxide slowly absorbs carbon dioxide to form the normal carbonate.

I.2.2.2 Cadmium Chloride

The hydrates are CdCl₂ · H₂O , CdCl₂ · ½ H₂O, and CdCl₂ · 4 H₂O. The pentahydrate 2CdCl₂ · 5 H₂O is the most common commercial form of the chloride and exists as colorless crystals (Herron, 2003 ; Richardson 2002). CdCl₂ is produced by reaction of molten cadmium and chlorine gas at 600 °C or by dissolving cadmium metal in hydrochloric acid, subsequently vaporizing the solution (Herron, 2003 ; Richardson, 2002).

I.2.2.3 Cadmium Hydroxide

Cd(OH)₂ is a colorless powder. The best way to prepare Cd(OH)₂ is by adding a solution of cadmium nitrate to a boiling solution of sodium or potassium hydroxide. The

hydroxide is precipitated from salt solutions by the addition of bases (Richardson, 2002). $\text{Cd}(\text{OH})_2$ is insoluble in bases and easily dissolves in dilute acids and solutions of ammonium ions, ferric chloride, alkali halides, cyanides, and thiocyanates forming complex ions (Merian et al., 2004 ; Herron, 2003).

I.2.2.4 Cadmium Oxide

The amorphous form is yellow red, brown red, or brown black, the color depending on the particle size and the stoichiometry. Cadmium vapor burns in air to produce the dark brown oxide CdO , or it is formed by pyrolysis of the carbonate or nitrate (Merian et al., 2004 ; Herron, 2003 ; Richardson, 2002). The amorphous oxide is insoluble in water or alkalies and bases but is readily soluble in dilute acids, ammonia, ammonium salt solutions, sodium cyanide solutions and forms a variety of soluble complexes (Herron, 2003 ; Richardson, 2002).

I.2.2.5 Cadmium Sulfate

$\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ the colorless monoclinic crystal, is the normal form of cadmium sulfate is also soluble in water. It is prepared by crystallizing solutions obtained by dissolving cadmium metal, oxide, sulfide, hydroxide, or carbonate in sulfuric acid. The monohydrate $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ is produced by evaporating a cadmium sulfate solution above $41.5\text{ }^\circ\text{C}$ (Richardson, 2002) . Anhydrous CdSO_4 is prepared by oxidation of the sulfide or sulfite under carefully controlled oxidizing atmospheres at high temperature (Herron, 2003).

I.2.3 Natural occurrence and environmental levels

Cadmium is widely dispersed in the environment. It is found in natural deposits as ores containing other elements (Wells, 2012 ; Wang et al., 2009 ; Bradl, 2005 ; Hiatt and Huff, 1975). Cd occurs in nature in the form of various inorganic compounds and as complexes with naturally occurring chelating agents; organo-cadmium compounds are unstable and have not been detected in the natural environment.

I.2.3.1 Cadmium occurrence in Food

The presence of cadmium in plants can result from the deposit of cadmium-containing aerosols directly on plant surfaces and from cadmium absorption by roots. Plants vary in their sensitivity to cadmium in the soil and in their ability to accumulate it (Wang et al., 2009).

Data from analyses carried out in different countries indicate that most food stuffs have Cd concentrations in the range 0.005-0.100 mg/kg (Table 3). Certain foods (e.g. kidney and oysters) may contain much higher concentrations (Nordberg et al., 2015).

Table 3 Cadmium Concentrations (Mean Values) in Various Food stuffs (Nordberg et al., 2015 ; Nordberg et al., 2002 ; Adriano, 2001 ; WHO/IPCS, 1992)

Food	Cd (mg/kg wet weight)
Potatoes	0.01 - 0.06
Spinach	0.043 - 0.15
Carrots	0.016 - 0.030
Wheat grains	0.005 - 0.08
Milk	0.00017 - 0.002
Oysters	0.1 - 4.7
Beef kidney	0.2 - 1.3
Beef meat	0.005 - 0.02
Fish meat other than crab	0.04 - 0.1

I.2.3.2 Cadmium occurrence in soil and water

In natural soils, Cd concentration is influenced by the amount of Cd in the parent rock. Soils derived from igneous rocks contain the lowest amount of Cd (0.10 to 0.30 ppm), soils derived from metamorphic rocks should have a medium concentration (0.10 to 1.0 ppm) and soils derived from sedimentary rocks contain the highest amount of Cd (0.30 to 11 ppm) (Adriano, 2001 ; Lund et al., 1981). Average Cd concentrations in surface soils in many parts of the world range from 0.07 to 1.1 mg/kg. In non-polluted areas, Cd concentrations in soil are generally less than 1 mg/kg (Nordberg et al., 2015).

In natural waters, the main sources of cadmium are bottom sediments and suspended particles; its concentration in the aqueous phase is small. In non-polluted natural waters, Cd concentrations are usually low (Nordberg et al., 2015).

I.2.3.3 Cadmium occurrence in ambient Air

Cadmium is present in the air as a result of the incineration of household waste, emissions from industry, including mining and power generation based on coal combustion. Cd particles can be transported in the air over a wide area, so soil and water can be contaminated far from the source of emission (Sarkar, 2002).

I.2.4 Cadmium uses

The significant use of cadmium is primarily in plating in order to protect steel, iron, copper, brass, and other alloys from corrosion. Cd is also used in batteries (rechargeable Ni-Cd batteries, silver-cadmium batteries solar batteries), photography, lithography, rubber curing and as a fungicide (Nordberg et al. 2015 ; Wang et al., 2009 ; Bradl, 2005 ; Sarkar, 2002 ; Adriano, 2001) .

CdS colorants is used in the semiconductor industry (McCabe et al., 1996), in high-quality paints, plastics, soaps, rubber, paper, glass, printing inks, ceramic glazes, textiles, and fireworks. It is also extensively used as a pigment. The pigments available are generally yellow, orange and red up to bordeaux red. They are prepared from Cd metal or metal salts and are insoluble in water. (Merian et al., 2004 ; Herron, 2003).

New applications include electric and hybrid vehicles, remote energy storage systems and solar cells. (Nordberg et al., 2015). The use of Cd has been limited worldwide for environmental reasons (Bradl, 2005).

I.2.5 Environmental contamination

Cd(II) and solutions of its compounds are toxic and hazardous elements for environment (water and soil) and all living beings, it means for plants , animals and human health (Haynes, 2017; Sharma et al., 2014 ; Nordberg et al., 2015 ; Bradl, 2005 ; Adriano, 2001).

I.2.5.1 Contamination of water

Drinking water contamination can be caused by cadmium impurities in the zinc of galvanised pipes or Cd-containing welds in fittings, water heaters, water coolers and taps. Infiltration of Cd into groundwater from discharged Cd oxide sludge can also be a route of drinking water contamination (Nordberg et al., 2015).

Cadmium pollution comes mainly from industrial and municipal waste. The solubility of cadmium in water is largely influenced by the acidity of the medium (Wang et al., 2009).

In freshwater, the calcium content of the water (i.e. hardness) and pH play important roles in cadmium's toxicity, Cd bioavailability and toxicity have been shown to decrease with decreasing pH and increasing hardness (Lawrence et al., 1989). The free and dissolved cadmium ions (Cd^{2+}) are the most toxic (Nordberg et al., 2015).

I.2.5.2 Contamination of agricultural soil and plants

Cd is toxic for plants at very small concentrations. Phytotoxicity depends on the plant species and the concentration of Cd in the medium. Cd has negative effects such as stunted growth, damage to internal and external root structures, reduced hydraulic conductivity of root water, interference with nutrient uptake, reduced chlorophyll content, interference with enzymatic activities related to photosynthesis (Bradl, 2005).

Most people's exposure to cadmium comes mainly from the plant matter that makes up our basic food (especially potatoes, cereal products and rice), and from increased cadmium concentrations in agricultural soils (main sources: atmospheric deposition and phosphate fertilizers) (Nordberg et al., 2015).

Taking the example of some Japanese regions where pollution by Cd is suspected, levels ranging from 1 to 69 mg/kg have been found in the topsoil of rice paddies. The Cd related to the itai-itai epidemic disease (see details below) came mainly from rice-field soil contaminated by Cd-polluted irrigation water (Nordberg et al., 2015 ; Bradl, 2005).

I.2.6 Ecotoxicological effects of cadmium

I.2.6.1 Impacts on animals

Cd(II) is considered toxic to several animals because of its capacity to combine with sulphhydryl groups (SH groups "R-SH"). These groups have important functions, notably the formation of disulfide bridges and the resulting conformational changes in proteins (Merian et al., 2004). Cd(II) affects renal causing the renal dysfunction (Prodan, 1932 ; Wilson et al., 1941).

I.2.6.2 Impacts on human health

Consumption of agricultural products represents the most important mode of Cd exposure in the general population. Four main sources of Cd can contaminate food: agricultural technology (pesticides, phosphate fertilizers, sewage sludge, etc.), industrial pollution, geological sources and food transformation (food additives, chemical and physical contact with equipment and containers). Dietary intake of Cd varies from country to another, due to the quantities and types of food consumed, among foods which contain Cd are animal organs (kidney and liver) (Adriano, 2001). Drinking water, tobacco are another sources of exposure to Cd. Cigarette tobacco contains about 1 ppm of Cd (Sharma et al., 2014).

Industrial exposure is mainly via inhalation and oral exposure to cadmium-containing fumes. The symptoms that may affect people are: headache, sleep disorders, memory deficits, throat dryness, cough, chest pain, nausea and vomiting. Cd affects the organs such as lungs, kidney, and bone as well as pulmonary and neurologic systems, leading to chemical pneumonitis and death possibility (Sharma et al., 2014 ; Bradl, 2005). In the past, Potts have registered three out of eight deaths in 74 nickel-cadmium battery workers with at least 10 years' exposure to cadmium oxide dust to be from cancer of the prostate (Nordberg et al., 2015).

Cd has a long biological half-life (17-30 years) in humans, accumulating mainly in the liver and kidneys. (Nordberg et al., 2015).

In the mid-1970s, Japanese researchers focused on the detection of bone diseases (Itai-itai disease). Itai-itai disease is characterized by kidney damage manifested by tubular and glomerular dysfunction and bone lesions. The cause was attributed to the effluent influx from zinc mine located in the upper reaches of the Jinzu River. Residents were then exposed to Cd through the ingestion of rice and other crops grown in the area. (Figure 4) (Nordberg et al., 2015).

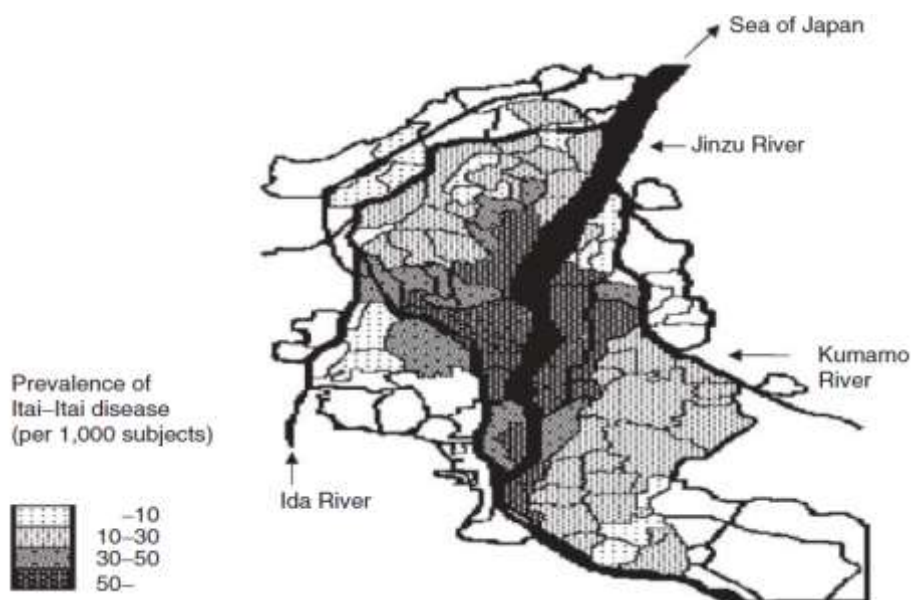


Figure 4 Distribution of Itai-itai disease in the Jinzu river basin (Nordberg et al., 2015).

I.2.7 Cd limit consumption

The drinking water quality guidelines published by the WHO have been reviewed from 5 to 3 $\mu\text{g/L}$ as the maximum allowable limit (Nordberg et al., 2015). The EPA (Environmental

Protection Agency) standard for maximum concentration of Cd in drinking water is 5 $\mu\text{g/L}$. However, the FDA (Food and Drug Administration) has authorized the presence of Cd in food colorants up to 15 $\mu\text{g/L}$ (Sharma et al., 2014). In Algeria, 0.2 mg / L is the maximum allowed value for industrial liquid effluent (JORA, 2006). For specific industries, the cadmium limit value has been fixed as follows: 0.5 mg/L for the mechanical industry and 0.07 mg/L for the non-metallic mining industry (ceramics, glass, cement, plaster, and lime) (JORA, 2006).

I.3 Generality about copper

I.3.1 Physical and chemical properties

Copper with symbol (Cu): belongs to group I-B of the periodic table (Figure 3); it is placed in the first transition series (period 4). Its electron configuration is $[\text{Ar}] 3d^{10} 4s^1$. Copper has two stable isotopes, ^{63}Cu and ^{65}Cu , with natural occurrences of 69.2% and 30.8% respectively. It has also nine synthetic radioactive isotopes with atomic masses between 58 and 68. ^{67}Cu having the longest half-life at 58.5 hours. However, the radioactive isotope ^{64}Cu has a short half-life of just 12.8 hours and is used as a tracer (Haynes, 2017 ; Nordberg et al., 2015 ; Bradl, 2005 ; Richardson, 2002). Copper is reddish in colour, has a bright metallic sheen, is malleable, ductile and an excellent conductor of heat and electricity (Haynes, 2017). The most important physical thermal and electrical properties are given in the Table 4 below.

Table 4 Different Physical Copper properties (Haynes, 2017; Dean, 2005 ; Richardson, 2002).

Propertie	Unity	Value
Atomic number		29
Atomic weight	g.mol^{-1}	63.546
Density	g.cm^{-3}	8,96
Oxidation state		0 +1 +2 +3
Melting point	$^{\circ}\text{C}$	1084
Boiling point	$^{\circ}\text{C}$	2560 ± 1
Electronic configuration		$[\text{Ar}] 3d^{10} 4s^1$
Electrical resistivity, at 20 $^{\circ}\text{C}$	$\mu\Omega.\text{cm}$	1.7241×10^{-2}

Copper can assume oxidation states 0, +1, +2, and +3. Cu(0) is very stable, but can dissolve in acids such as sulfuric and nitric acids (Haynes, 2017 ; Nordberg et al., 2015).

Cu(II) , $[\text{Ar}]3d^9$, is predominantly blue or green, and the unpaired 3d electron results in magnetic phenomena. It is the most abundant oxidation state in environments, the ion is stable in most environments, and it is isomorphous with Zn^{2+} , Mg^{2+} , and Fe^{2+} ions (Nordberg et al., 2015 ; Richardson, 2002).

The most abundant Cu mineral is chalcopyrite (CuFeS_2), which contains 34% of Cu (Bradl, 2005).

Copper is very stable in fresh water and also in sea water or alkali metal hydroxide solutions. Wastewater containing organic sulfur compounds can be corrosive to copper (Richardson, 2002).

Pourbaix has developed potential – pH equilibrium diagrams for metals in dilute aqueous solutions. Figure 5 shows the behavior of copper at room temperature and atmospheric pressure. The Cu – H_2O system contains three fields of different character (Richardson, 2002):

- ✓ Corrosion, in which the metal is attacked.
- ✓ Immunity, in which reaction is thermodynamically impossible.
- ✓ Passivity, in which there is no reaction because of kinetic phenomena.

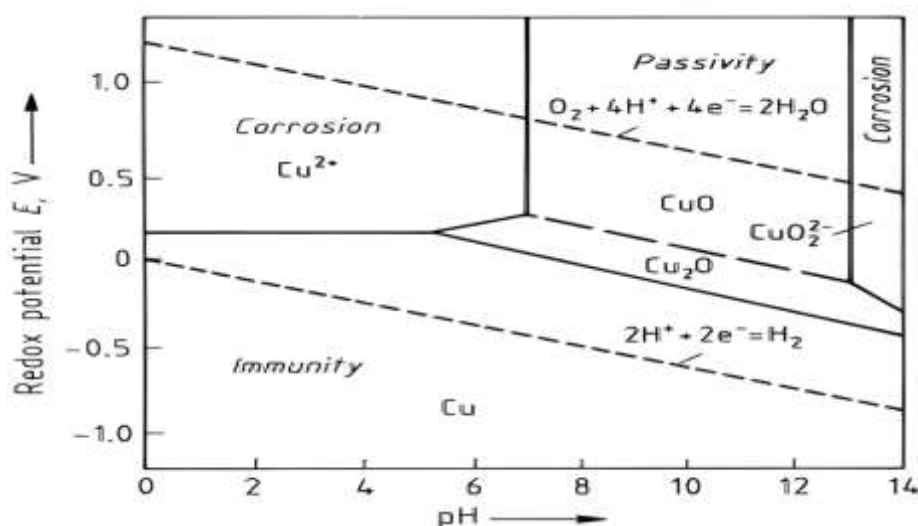


Figure 5 Pourbaix diagram for copper behavior (Richardson, 2002).

I.3.2 Copper compounds

There are lots of copper compounds, each one has his own properties. [Table 5](#) resumes different physical and chemical properties of the important copper compounds. Among the important copper compounds: copper oxide, copper hydroxide, copper carbonate hydroxide, copper chloride and copper sulfate, and they are the most useful in industrial companies ([Richardson, 2002](#)).

Table 5 Copper compounds properties ([Dean, 2005](#)).

Copper Compounds	Formula	Molecular weight	Melting point, °C	Boiling point, °C	Density (d ^{°C})	Solubility in g/100 g H ₂ O
Copper(I) chloride	CuCl	98.99	423	1490	4.14	0.0047 ²⁰
Copper(I) oxide	Cu ₂ O	143.091	1244	1800 dec	6.0	N/A
Copper(I) sulfide	Cu ₂ S	159.157	1129	N/A	5.6	N/A
Copper(II) carbonate	CuCO ₃	123.555	N/A	N/A	N/A	N/A
Copper(II) carbonate hydroxide	CuCO ₃ ·Cu(OH) ₂	221.116	200 dec	N/A	4.0	N/A
Copper(II) chloride	CuCl ₂	134.452	598	993	3.4	75.7 ²⁵
Copper(II) chloride dihydrate	CuCl ₂ ·2H ₂ O	170.483	100 dec	N/A	2.51	75.7 ²⁰
Copper(II) hydroxide	Cu(OH) ₂	97.561	N/A	N/A	3.37	N/A
Copper(II) nitrate	Cu(NO ₃) ₂	187.555	255	subl	N/A	145 ²⁵
Copper(II) oxide	CuO	79.545	1227	6.31	N/A	N/A
Copper(II) sulfate	CuSO ₄	159.609	560 dec	N/A	N/A	22.0 ²⁵
Copper(II) sulfate pentahydrate	CuSO ₄ ·5H ₂ O	249.685	110 dec	2.286	22.0 ²⁵	22.0 ²⁵

N/A: Not Available

I.3.2.1 Copper Oxide

➤ Copper(I) Oxide

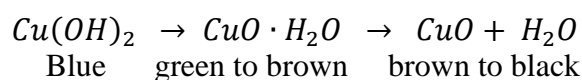
Cu₂O Cuprite, with cubic or octahedral crystal morphology, decomposes above 1800°C. In nature, it appears as a red or reddish-brown mineral (Richardson, 2002).

➤ Copper(II) Oxide

CuO occurs in nature as the black minerals tenorite and paramelaconite. CuO is stable to air and moisture at room temperature. It is insoluble in water or alcohols, and it is dissolved by alkali metal cyanides and by strong acid solutions (Richardson, 2002).

I.3.2.2 Copper(II) Hydroxide

Cu(OH)₂, decomposes over 100 °C or over 50 °C in the presence of an excess of alkali. Also it decomposes in hot water to form more stable copper(II) oxide and water (Richardson, 2002).



Cu(OH)₂ is practically insoluble in water (0.003 mg/L), and it is readily soluble in mineral acids and ammonia solution. When freshly precipitated, it is soluble in concentrated alkali, with the formation of [Cu(OH)₃]⁻ or [Cu(OH)₄]²⁻. Cu(OH)₂ is naturally unstable but can be kinetically stabilized by a suitable production method (Richardson, 2002).

I.3.2.3 Copper(II) Carbonate

CuCO₃, is practically insoluble in water, but dissolves in aqueous solutions of ammonia and alkali metal cyanide. It dissolves rapidly in mineral acid and hot acetic acid solutions, with formation of Cu(II) salt (Richardson, 2002).

I.3.2.4 Copper Chloride

➤ Copper(I) Chloride

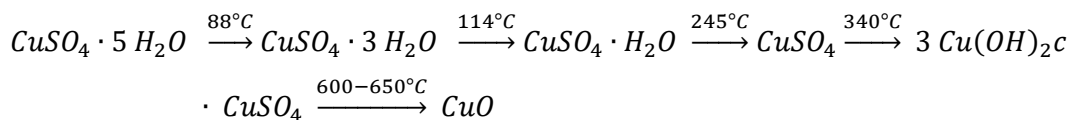
CuCl, is slightly soluble to insoluble in water, with values from 0.001 to 0.1 g/L being reported. It is easily hydrolyzed to copper(I) oxide by hot water. CuCl is insoluble in dilute sulfuric and nitric acids, but it quickly dissolves in hydrochloric acid (Richardson, 2002).

➤ Copper(II) Chloride

The more common commercial form of CuCl₂ is the dihydrate. Its solubility characteristics are approximately the same as those of the anhydrous form (Richardson, 2002).

I.3.2.5 Copper Sulfates

$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, is found in nature as the mineral chalcantite, blue trichlinic crystals
Thermal analysis of the pentahydrate gives the following:



Copper(II) sulfate pentahydrate is the most widely used copper compound, due to its economy and availability (Richardson, 2002).

$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ is prepared by the reaction of a basic Cu(II) compound with a sulfuric acid solution (100 – 200 g/L H_2SO_4), eg: $\text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_{4(\text{aq})} + \text{H}_2\text{O}$

There are different commercial methodes for the production of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ for e.g: Harike process, two-tower process, the trickle method , by solvent extraction and byproduct Recovery (Richardson, 2002) .

I.3.3 Natural occurrence and environmental levels

Copper is ranked 26th in crustal abundance behind Zn with average crustal concentrations of 24 to 55 ppm (Bradl, 2005) and $2.5 \times 10^{-4} \text{ mg kg}^{-1}$ in the sea (Merian et al., 2004). It occurs naturally in many minerals such as cuprite (Cu_2O), malachite ($\text{Cu}_2\text{CO}_3 \cdot \text{Cu}(\text{OH})_2$), azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), chalcopyrite (CuFeS_2), chalcocite (Cu_2S), and bornite (Cu_3FeS_4) (Haynes, 2017). Table 6 presents average global copper emissions from natural sources, estimated by (Nriagu, 1989). Average copper concentrations in the air in rural zones vary from 5 to 50 ng m^{-3} . In uncontaminated areas, the copper content of seawater is 0.15 mg L^{-1} , while that of freshwater ranges from 1–20 mg L^{-1} (Nriagu, 1979). Average copper concentrations in uncontaminated soil were 30 mg kg^{-1} (range 2 to 250 mg kg^{-1}) (Merian et al., 2004).

Table 6 Worldwide emissions of copper from natural sources (Merian et al., 2004 ; Nriagu 1989).

Copper emissions	Typical range ($\times 10^3$ tons)
windblown dusts	0.9 – 15
forest fires	0.1 – 7.5
biogenic processes	0.1 – 6.4
sea salt spray	0.2 – 6.9

Table 7 shows the concentrations of copper usually found in various environmental media. Natural uptake of copper by micro-organisms, plants and animals from the surrounding environment (water, sediments, soil and food) is defined as "bioaccumulation" (Nordberg et al., 2015).

Table 7 Copper concentrations (ppm) in various environmental media (Bradl, 2005).

Material	Average Concentration	Range
Igneous rocks	125	80 – 200
Sandstone	30	6 – 46
Limestone	6	0.6 – 13
Shale and clay	35	23 – 67
Coal	17	1 – 49
Fly ash	185	45 – 1452
Soils	30	2 – 250
Freshwater (($\mu\text{g/L}$))	3	0.2 – 30
Seawater (($\mu\text{g/L}$))	0.25	0.05 – 12

I.3.3.1 Copper occurrence in food

The copper content of organ meats is very high, particularly in the liver and kidneys. In addition, of all foodstuffs, fish, fruit, cereals, nuts and green vegetables are good sources of copper (Nordberg et al., 2015 ; De Romaña et al., 2011 ; WHO, 2000).

I.3.3.2 Copper occurrence in water

Concentrations of copper in seawater generally range from less than 1 to 5 $\mu\text{g/L}$, occurring at higher levels near the continental shelf than in the open sea.

$\text{Cu}(\text{OH})_2^0$ is the predominant copper species in seawater (~90%), while free copper ions represent less than 1% of the total amount of copper. Uncontaminated freshwater resources exhibit highly variable copper concentrations (0.2-30 $\mu\text{g/L}$), with a world median value of 3 $\mu\text{g/L}$. Nevertheless, copper has a strong binding affinity with organic chelators such as humic and fulvic substances, so dissolved organic matter content will influence copper speciation. (Nordberg et al., 2015).

In drinking water, copper concentrations can vary considerably depending on the type of water, e.g. hardness and pH. Copper content is higher in acidic water. It has been estimated that food contributes over 90% of copper intake in adults at low copper concentrations in water (< 0.1 mg/L), and that drinking water consumption contributes up to 50% at higher concentrations (> 1 to 2 mg/L) (De Romaña et al., 2011). Dissolved Organic Carbon (DOC) is a significant modifier of copper toxicity in aquatic environments (Nordberg et al., 2015).

I.3.3.3 Copper occurrence in air and soil

Wind-blown copper increases air concentrations. Mean air concentrations are generally between 5 and 200 ng/m³. However, higher levels may be occurred in urban or other contaminated areas (Merian et al., 2004).

Average copper concentrations in uncontaminated surface soils range from 6 to 80 mg/kg dry weight. Copper mine waste is one of the main sources of copper in soil. Sewage sludge can also contain significant quantities of copper (Nordberg et al., 2015).

I.3.4 Copper uses

Copper is an important alloying element, the most famous copper alloys being brass (copper-zinc) and bronze (copper-tin). Other applications are kitchenware, for chemicals and pharmaceutical equipment; as a pigment and as a precipitant of selenium, water delivery systems, fertilizers, bactericides and fungicides, feed additives and growth promoters (Nordberg et al., 2015 ; Bradl, 2005 ; Merian et al., 2004). The most important uses of copper are in electrical wires (~9.75 x 10⁶ tons) and cables for the transmission of electricity. Electronic industry, as well as water pipes and tubes are other important applications (Nordberg et al., 2015 ; Merian et al., 2004).

CuCO₃ is used as a precursor in the production of copper salts and soaps. It is also used for animal feed as a source of copper, and in electroplating for pH control (Richardson, 2002).

CuSO₄ has multiple uses, as an algacide and molluscicide in water; together with lime as a fungicide for plants; as a mordant in electroplating; as a component of Fehling's solution and for the estimation of reduced sugars in urine. CuSO₄ is also used to inhibit algae growth in municipal reservoirs, in irrigation equipment and pipes, as well as in swimming pools and industrial cooling systems (Merian et al., 2004) .

I.3.5 Copper importance

Cu is a constituent of several plant enzymes, which are responsible for a range of physiological processes in plants, such as photosynthesis, respiration, cell wall metabolism, seed production ...etc. (Bradl, 2005).

In animals, It is responsible for oxidation processes and is found in numerous proteins such as phenolase, hemocyanin and galactose oxidase and others (Richardson, 2002) .

In humans, Copper is an essential component of many biological processes, mainly as an integral part of enzymes (Nordberg et al., 2015 ; Bradl, 2005). Its importance as a nutrient for development and growth is increasingly being studied in medicine. Copper is also used to produce new copper-based antibiotics and anti-inflammatories. For humans, the recommended daily copper requirement is 2.5 to 5 mg (Richardson, 2002).

In humans, Cu deficiency leads to anemia, bone and cardiovascular disorders, mental and nervous system deterioration, hair keratinization defects and reduced levels of the neurotransmitters dopamine and norephedrine. However, Cu toxicity in humans is very rare, and is generally associated with chronic ingestion or malnutrition in babies and young children (Bradl, 2005).

I.3.6 Ecotoxicological effects of copper

I.3.6.1 Effects on Animals

In contrast to the terrestrial environment, the aquatic environment is less tolerant of copper concentration variability, concentrations above 0.1 mg L⁻¹ in water are toxic to fish. However, concentrations of 0.8 mg L⁻¹ are survivable by some fish (Merian et al., 2004).

The liver in avian species appears to be the main organ of copper distribution. Ruminants are also highly susceptible to copper toxicity. In sheep, copper toxicity can develop on forage with a normal copper content of 8-10 mg kg⁻¹. The principal effects are on the liver and blood, with fatal cases of hepatitis and hemolytic anemia (Merian et al., 2004).

I.3.6.2 Implications for Human Health

Copper is an essential element for humans, but large quantities can be lethal. Copper salts are considered more toxic than the metal itself. The lowest Lethal Dose (LD_{Lo}) for acute oral toxicity in man is around 100 mg/kg. However, recovery has been observed after ingestion of doses up to 600 mg/kg. The total biological half-life of ⁶⁷Cu varies from 13 to 33 days depending on age group, and is shorter in women than in men. (Nordberg et al., 2015).

➤ Acute Effects

Soluble salts of copper could be toxic, when they are ingested with malicious and suicidal intent, or when used as medical treatment on severely burned skin. In the first instances, gram quantities of copper sulfate lead to nausea, vomiting, diarrhea, renal, and liver damage, increased blood pressure and respiratory rates. In cases of serious intoxication, the clinical profile becomes more severe, including lethargy, convulsions, coma, and death. (Merian et al., 2004).

➤ Chronic Effects

Exposure to copper dust can cause skin irritation and discoloration of skin and hair. In addition, long-term exposure led to atrophic changes in the mucous membranes. Although there is some evidence of copper accumulation in the liver (Richardson, 2002).

I.3.7 Cu limit consumption

Since copper is both an essential element and also potentially toxic, there is a risk to living beings if the environment contains too much or too little of it. (Haynes, 2017 ; Nordberg et al., 2015 ; Merian et al., 2004 ; Organization, 1998).

The recommended daily intake of copper in food is 0.5 – 0.7 mg for children in the first year of life, and 2.0 – 3.0 mg for adults (Merian et al., 2004).

The ECG (European Council Guideline) sets a limiting value of 0.04 mg/L of Cu for waters inhabited by salmon and trout. The Cu limit for drinking water is (1.5 mg/L) in Switzerland, (1 mg/L) is the value confirmed by the USPHS (US Public Health Service), WHO (0.05 mg/L) (Merian et al., 2004). However, the maximal allowed value by the Algerian authorities for the industrial wastewater was fixed at 0.5 mg/L of Cu (JORA, 2006). For specific industries, the copper limit value has been fixed as follows: 0.7 mg/L for the mechanical industry; 1.5 mg/L for metal transformation industry and 0.1 mg/L for the non-metallic mining industry (glass, cement, plaster and lime) (JORA, 2006).

I.4 Generality about Zinc

I.4.1 Physical and chemical properties

The important physical properties of Zinc with symbol (Zn) are shown in the Table 8 below. It is delicate at ordinary temperatures, but malleable between 100 and 150 °C. It is also a good conductor of electricity and burns in air at high red temperatures, releasing white clouds of oxide.

Natural zinc has five stable isotopes, ^{64}Zn (49%), ^{66}Zn (28%), ^{68}Zn (19%), ^{67}Zn (4.1%), and ^{70}Zn (0.62%). Twenty-five other unstable isotopes and isomers are recognized (19 known radioactive isotopes). The half-life of ^{65}Zn is 243.8 days and that of ^{69}Zn is 13.8 h. In nature, zinc has only one oxidation state, which is II, while the Zn^{2+} ion is colorless. (Haynes, 2017 ; Nordberg et al., 2015 ; Bradl, 2005 ; Adriano, 2001).

Table 8 Different Physical Cadmium properties (Haynes, 2017 ; Nordberg et al., 2015 ; Ley et al., 2010)

Propertie	Unity	Value
Atomic number		30
Atomic weight	g.mol^{-1}	65.38
Density	g.cm^{-3}	7.13
at 20C°		
at mp		6.83
Oxidation state		+2
Melting point	°C	419.53
Boiling point	°C	908 ± 2
Electrical resistivity	$\text{m}\Omega^{-1}.\text{mm}^{-1}$	18.1
at 0 °C		
at 25 °C		16.82
at 100 °C		12.17

Zinc forms complexes with ammonia, amines, cyanide and halide ions. In basic solutions, the hydroxide, $\text{Zn}(\text{OH})_2$, is precipitated and the zincate ion, $\text{Zn}(\text{OH})_4^{2-}$, is formed in an excessively basic solution. Zn forms water-soluble chlorates, chlorides, sulfates, and nitrates, while the oxides, carbonates, phosphates, silicates and organic complexes are insoluble or slightly soluble (Bradl, 2005 ; Ley et al., 2010).

It is amphoteric and forms stable, non-conductive, non-magnetic, and white or colorless salts, with the exception of those containing a chromophoric group, such as zinc chromate (ZnCrO_4). At medium pH, it forms hydroxides ($\text{Zn}(\text{OH})_2$) that are sparingly soluble in water, while its solubility increases at extremely basic pH, releasing Zn ions at low pH and zincate at high pH (Nordberg et al., 2015).

I.4.2 Zinc compounds

Table 9 lists some of the most important zinc compounds, details about the important compounds are given below.

I.4.2.1 Zinc Chloride

Zinc chloride, $ZnCl_2$, generally occurs as a white powder, highly soluble in water. It is also soluble in alcohols, ether, acetone, ethyl acetate, glycerine, pyridine, amines and nitriles (Ley et al., 2010).

Technical-grade zinc chloride is usually produced by leaching zinc oxides or zinc-containing waste such as zinc dross or ammonium chloride slags with HCL (Ley et al., 2010).

I.4.2.2 Zinc Sulfate

$ZnSO_4$ is very soluble in water, and forms hydrates with 1, 2, 4, 6, and 7 molecules of water of crystallization. The hepta-, hexa-, and monohydrates are industrially produced (Ley et al., 2010). Zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$), transformed into the hexahydrate at 39 °C. Mixed crystals are formed with the sulfates of Fe, Mg, Mn, Co, and Ni. It is very soluble in glycerine, but only slightly soluble in other organic solvents (Ley et al., 2010).

I.4.2.3 Zinc Carbonate

Smithsonite, zinc spar, or calamine, $ZnCO_3$, has the theoretical composition 52.14% Zn, 35.10% CO_2 . The color is yellowish or reddish to brown, rarely colorless. Minerals with higher impurity contents include manganese zinc spar (up to 15% $MnCO_3$), iron zinc spar (up to 53% $FeCO_3$), copper zinc spar (up to 6% $CuCO_3$), zinc lead spar (up to 1% PbO), and cadmium zinc spar (up to 7% $CdCO_3$) (Ley et al., 2010).

Table 9 Zinc compounds properties (Haynes, 2017 ; Dean, 2005)

Zinc Compounds	Formula	Molecular weight	Melting point, °C	Boiling point, °C	Density ($d^{°C}$)	Solubility in g/100 g H_2O
Zinc carbonate	$ZnCO_3$	125.418	140 dec	N/A	4.434	0.000091 ²⁰
Zinc carbonate hydroxide	$3 Zn(OH)_2 \cdot 2 ZnCO_3$	549.107	N/A	N/A	N/A	N/A
Zinc chloride	$ZnCl_2$	136.315	325	732	2.907	408 ²⁵
Zinc hydroxide	$Zn(OH)_2$	99.424	125 dec	N/A	3.05	0.000042 ²⁰
Zinc nitrate	$Zn(NO_3)_2$	189.418	N/A	N/A	N/A	120 ²⁵
Zinc nitrite	$Zn(NO_2)_2$	157.42	N/A	N/A	N/A	N/A
Zinc oxide	ZnO	81.408	1974	N/A	5.6	N/A
Zinc sulfate	$ZnSO_4$	161.472	680 dec	N/A	3.8	57.7 ²⁵

N/A : Not Available

I.4.3 Natural occurrence and environmental levels

Zn is the 24th most commonly found element in the earth's crust (70 ppm average value) (Bradl, 2005). The principal ores of zinc are sphalerite or blende (sulfide), smithsonite (carbonate), calamine (silicate), franklinite (zinc, manganese, iron oxide), and hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$) (Haynes, 2017 ; Bradl, 2005). The availability of zinc in various minerals is affected by the Zn concentration of the magma and premetamorphic rock (Adriano, 2001). The data presented in the Table 10 represents the Zn concentrations usually found in various environmental media.

Table 10 Zinc concentrations (ppm) in various environmental media (Bradl, 2005).

Material	Average Concentration	Range
Igneous rocks	65	5 – 1070
Sandstone	30	5 – 170
Limestone	20	< 1 – 180
Shale	97	15 – 1500
Fly ash	449	27 – 2880
Soils	90	1 – 900
Freshwater	15	< 1 – 100
Seawater	5	< 1 – 48

I.4.3.1 Zinc occurrence in food

Foods have very different amounts of zinc (Table 11). The world's poorest people primarily obtain their Zn from cereals and legumes. It is estimated that 30% of dietary zinc in the USA comes from cereals and legumes. In general, legumes have more zinc than processed cereals. For instance, cooked mature black beans have 1.9 mg of zinc per cup (172 g) but boiled chickpeas have 2.5 mg per cup (164 g) (Nordberg et al., 2015).

Table 11 Zinc content of foods (Nordberg et al., 2015).

Average Zn concentration (mg)	Kind of food
> 15	Oyster Peanut Butter Crunch
5-10	Beef , Lamb , Duck , King Crab , Wheaties
4-5	Beef liver, Pork, Lamb, Captain Crunch, Quaker Oats
3-4	Veal , Turkey dark meat, Blue Crab, Rice Chex, Corn Chex, Cheerios, Whole-wheat flour
2-3	Lobster, Clams, Yogurt, Skim milk, White beans, Chick peas, Lentils, Corn meal
1-2	Pork loin,, Chicken dark meat, Swordfish, Shrimp,

	Mushroom, White wheat flour, Navy beans, Black bean, Pinto beans, All Bran, Nuts
< 1	Chicken breast, Chicken liver, Salmon, Tuna, Other finfish, Vegetables, White rice, Eggs, Tofu, Cheddar cheese, Blue cheese, Cottage cheese

I.4.3.2 Zinc occurrence in air

In atmosphere, zinc is primarily found in oxidised aerosol form. About 45,000 tonnes of zinc are occurred naturally each year as a result of volcanic emissions, fires, and windborne dust (Nriagu, 1989 ; Nordberg et al., 2015). Urban and industrial regions typically have the highest quantities of zinc (Nordberg et al., 2015).

I.4.3.3 Zinc occurrence in water

Zinc is commonly found in particles larger than 450 nm in water. It can be found as hydrated metal ions, such as $Zn(H_2O)_6^{2+}$, simple inorganic complexes, ex. $Zn(H_2O)_5Cl^+$, simple organic complexes, like citrate, stable inorganic complexes, such as Zn sulphide, stable organic complexes, as Zn humate, both adsorbed on organic colloids to generate Zn^{+2} - humic acid and on inorganic colloids to form $Zn^{2+}Fe_2O_3$. The majority of freshwaters have a pH that promotes zinc adsorption onto particles (Nordberg et al. 2015).

Natural zinc content in surface waters are typically below 10 $\mu g/L$, although it can range from 10 to 40 $\mu g/L$ in groundwater (Nordberg et al., 2015).

I.4.3.4 Zinc occurrence in soil

The concentrations of Zinc are significantly affected by the process of rock weathering, with approximately 75% of these rocks are sedimentary in nature (Alloway, 2008). It should be note that about 915,000 tonnes of water-soluble Zn compounds are released each year by weathering (Nordberg et al., 2015). The values of non-contaminated soils ranged from 1–2000 mg/kg, with an average of 40–90 mg/kg (Adriano, 2001).

I.4.4 Production and uses

With regard to annual global use of metals, zinc comes in fourth place after iron, aluminium, and copper. It is mostly applied to steel and iron as a protective coating. Zinc is widely used to prevent corrosion on a variety of metals. Among the more significant alloys are those made of brass, nickel silver, commercial bronze, and aluminium solder. Zinc is also used to galvanise other metals, like iron. Galvanised metals are employed in a wide range of industries, including appliance, transportation, and building (Haynes, 2017 ; Adriano, 2001).

Zinc and its compounds are found in a wide range of home products, such as paints, varnishes, rubber, powders, cosmetics, cutlery, and astringents. Inorganic Zn compounds are also used to make glass, laptop screens, car tires, TV screens, dry cell batteries, and electrical equipment. Other uses include pesticides, textile printing, and drying, as well as agricultural micronutrient fertilizers. In addition, they serve as a wood preservative, a flux in metallurgical processes, and an adhesive production process (Adriano, 2001). On the other hand, organic Zn compounds are used extensively in the fields of lubricants, topical antibiotics, and fungicides (Nordberg et al., 2015).

I.4.5 Zinc importance and effects of its deficiency

In plants, zinc plays a role in a number of metalloenzymes, the integrity of cytoplasmic ribosomes, and the plasma membrane of root cells. It also catalyzes the conversion of carbohydrates into proteins and oxidation (Haynes, 2017).

Zn is also a very important element for animals' growth. According to tests, animals lacking in zinc need 50% more food to reach the same weight as animals that get enough zinc. (Nordberg et al., 2015).

Zn plays a vital role in the majority of bodily processes, if not all of them. Growth, skin integrity and function, immunocompetence, wound healing, and a number of metabolic activities including the production or breakdown of proteins, carbohydrates, lipids, and nucleic acids. It is a necessary coenzyme-like component that keeps over 70 metallo-enzymes functioning. Zinc is redox neutral and quickly attaches to proteins with the right amino acid patterns (Nordberg et al., 2015 ; Ley et al. 2010).

Particularly the prostate gland contains the maximum concentration of Zn (87 $\mu\text{g/g}$ wt weight), while the average concentration throughout the body is 33 $\mu\text{g/g}$ wet weight. There are 10.7 – 22.9 mmol/L in serum, 17.4 ± 1.8 mmol/L in plasma, 184 – 198 mmol/L in erythrocytes, and 3.30 ± 1.33 mmol/g in hair (Nordberg et al., 2015 ; Thane et al., 2004 ; Henderson et al., 2003).

Insufficient consumption of Zn in the diet, particularly during times of development, pregnancy, and lactation, can lead to a deficiency. Dermatitis, anemia, delayed wound healing, hypogonadism, and cognitive impairment are among the clinical signs of zinc deficiency (Bradl, 2005).

I.4.6 Ecotoxicological effects of Zinc

According to Nordberg et al., (2015), zinc metal and the majority of its compounds are considerably less toxic than many of heavy metals. There are certain variations in the toxicity of zinc salts, which are mostly caused by the toxicity of the compound's anionic component. The carcinogenic nature and elevated toxicity of zinc chromate (ZnCrO_4) can be attributed to the anionic CrO_4^{2-} component rather than Zn^{2+} (Rohe and Wolf, 2000).

I.4.6.1 Acute effects

Zinc and its components lead to intoxications, which can happen by eating food tainted with zinc that has leached from food containers or from breathing in dust containing zinc or zinc oxide while working (Rohe and Wolf, 2000).

Abdominal pain, nausea, diarrhea, and gastrointestinal distress are signs of acute intoxication. Symptoms like fatigue and trouble writing also occur when there is an excess of elemental zinc. Other symptoms include sweating, metallic taste in the mouth, fast breathing, coughing, fever, chest and leg discomfort, exhaustion, and thirst go away 24 to 48 hours after exposure (Rohe and Wolf, 2000).

I.4.6.2 Chronic effects

Ingestion of potable water contaminated with 40 ppm Zn has been associated with the development of chronic toxicity. The symptoms are comparable to those of acute poisoning, but are less prominent (Rohe and Wolf, 2000).

In humans, 3–5 g of ZnCl_2 is the Lethal Dose (LD). Zinc sulfate, ZnSO_4 , is less hazardous than zinc chloride because it is less caustic (Rohe and Wolf, 2000).

I.4.7 Zn limit consumption

The MAK value (Maximale Arbeitsplatz Konzentration : maximum workplace concentration) of zinc oxide, ZnO , is 5 mg ZnO/m^3 , measured as total fine dust. The same TLV (total locked value) has been set in Hungary, Japan, Poland, Sweden, and by the WHO, while it is 10 mg ZnO/m^3 in Bulgaria, Romania, and Pennsylvania (US); it is 15 mg ZnO/m^3 in Finland (Rohe and Wolf, 2000). In Algeria, the maximal allowed value for the industrial wastewater was fixed at 3 mg/L of Zn (JORA, 2006). For specific industries, the Zinc limit value has been fixed as follows: 2.5 mg/L for the mechanical industry; 1.5 mg/L for metal transformation industry and 2 mg/L for the non-metallic mining industry (glass, cement, plaster and lime) (JORA, 2006).

I.5 Heavy Metals in Algeria (sources and hazardous)

Many Algerian researches take in consideration the dangerous effect of heavy metals, natural and anthropogenic occurrence. In this section the most important researches, which studied the availability and the risks of the presence of heavy metals in natural water have chosen.

Ahmed A. Alomary and Soraya Belhadj, focused on the distribution and bioavailability of 6 hazardous heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) in 18 different sites along the coasts of Algeria (Southwestern Mediterranean Sea) were collected during the first week of August 2005 (Figure 6, Table 12).

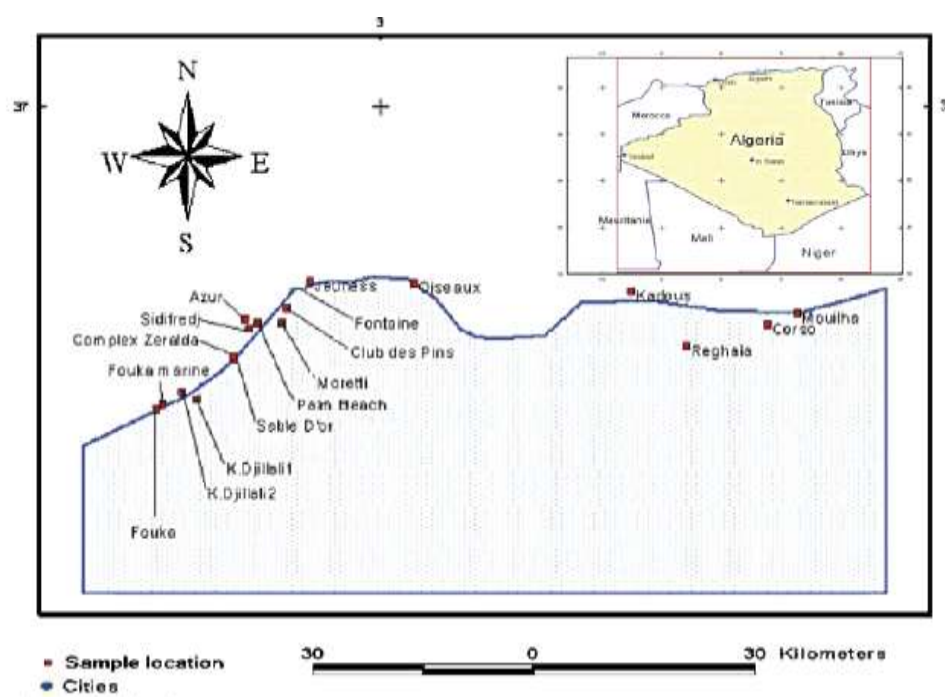


Figure 6 Location of sampling points (Alomary and Belhadj, 2007).

Based on the data presented in Table 12, it can be observed that, with the exception of Cd, the mean concentrations and maximal values of the metals are all below the average values observed in the Earth's crust. This does not rule out the occurrence of an anthropogenic part of metals in the analyzed samples. It was observed that the Fouka site has the highest metal content while the Kadous site has the lowest.

Table 12 Heavy metals concentration in different sampling Mediterranean sites (Alomary and Belhadj, 2007)

Sample #	Site name	Heavy metals concentration ($\mu\text{g/L}$)					
		Cd	Cr	Cu	Ni	Pb	Zn
1	Mouilha	0.6	9.2	2.1	3.8	5.9	11.9
2	Corso	0.3	8.9	2.3	2.4	3.9	13.9
3	Reghaia	0.3	9.2	1.3	1.6	5.9	6.0
4	Kadous	0.1	6.7	1.1	0.8	2.5	5.3
5	Oiseaux	1.2	9.5	10.4	11.9	5.5	36.1
6	Jeuness	0.3	6.4	1.6	1.3	5.3	6.1
7	Fontaine	0.4	5.2	2.5	1.5	1.3	11.7
8	Club des Pins	0.6	5.0	1.7	2.9	2.8	8.7
9	Moritti	1.1	2.6	2.0	5.2	5.4	8.5
10	K.Djillali1	1.2	6.0	9.7	9.4	6.5	35.3
11	K.Djillali2	1.7	6.6	5.2	7.0	7.2	25.8
12	Fouka marine	1.3	5.6	6.5	8.3	9.3	25.5
13	Fouka	2.3	8.8	8.6	9.0	6.0	45.7
14	Palm Beach	1.3	10.8	5.2	27.4	11.5	24.6
15	Sidifredj	1.3	17.4	4.9	54.9	6.6	20.3
16	Azur	1.9	7.4	4.5	9.3	6.3	25.1
17	Sable D'or	1.9	14.2	7.7	42.5	5.2	30.8
18	Complex zeralda	1.6	18.9	7.1	51.0	4.7	25.6
	Average	1.1	8.8	4.7	13.9	5.7	20.4
	Crust	0.2	200	70	80	16	132

In Table 13, Alomary and Belhadj made a comparison between his study shown before (Table 12 and Figure 6), with another Algerian results of another researches, studying the same metals occurrence in another localisations in the Mediterranean sea.

Table 13 Concentrations of certain heavy metals compared to other sites in the Mediterranean Sea.

Heavy metals	Concentration range ($\mu\text{g/g}$)		
	Southwestern Med.Sea ^a Algeria	Rhumel river ^b Algeria	Algiers Bay ^c Algeria
Cd	0.1 – 2.3	1.5 – 3.6	
Cr	2.6 – 18.9	15 – 101	15 – 159
Cu	1.1 – 10.4		9 – 87
Ni	0.8 – 54.9		
Pb	1.3 – 11.5	50 – 206.25	4 – 69
Zn	5.3 – 45.7		58 – 274

^a (Alomary and Belhadj, 2007)

^b (Afri-Mehnaoui et al., 2004)

^c (Benamar et al., 1999)

The results reported by [Alomary and Belhadj](#) for Cr, Cu, Pb, and Zn are regarded as extremely low when compared to the amounts discovered by the studies listed in [Table 13](#); this may represent a very small contamination of Cr, Pb, and Zn at the analyzed locations. These heavy metals concentrations are very low compared to the Algerian standards ([JORA, 2006](#)), so they didn't cause any serious problems for humans and environment .

[Yasmine Ait Ouaisa et al., 2012](#) studied the removal of hexavalent Chromium Cr (VI, +6 valence states) from effluent tannery in Rouiba, Algeria. By using three different processes electro-coagulation (EC), adsorption (AD) and their integration (EC + AD), the final results were presented in [Table 14](#). The effluent tannery contains 232 µg/L, this concentration is small but still cause some dangerous effect for human lives and for the environment because it is superior than the Maximum Contamination Level (MCL). Note that the Maximum allowed value of Cr (VI) = 100 µg/L, according to the Algerian Standards ([JORA, 2006](#)), and it is equal to 50 µg/L, according to the American Protection Agency ([Ouaisa et al., 2012](#)).

Table 14 Comparison of the removal efficiency (R%) and residual metal concentration (RM) of Cr(VI) by electrocoagulation, adsorption and their integration. $C_0 = 232 \mu\text{g/L}$ ([Ouaisa et al., 2012](#)).

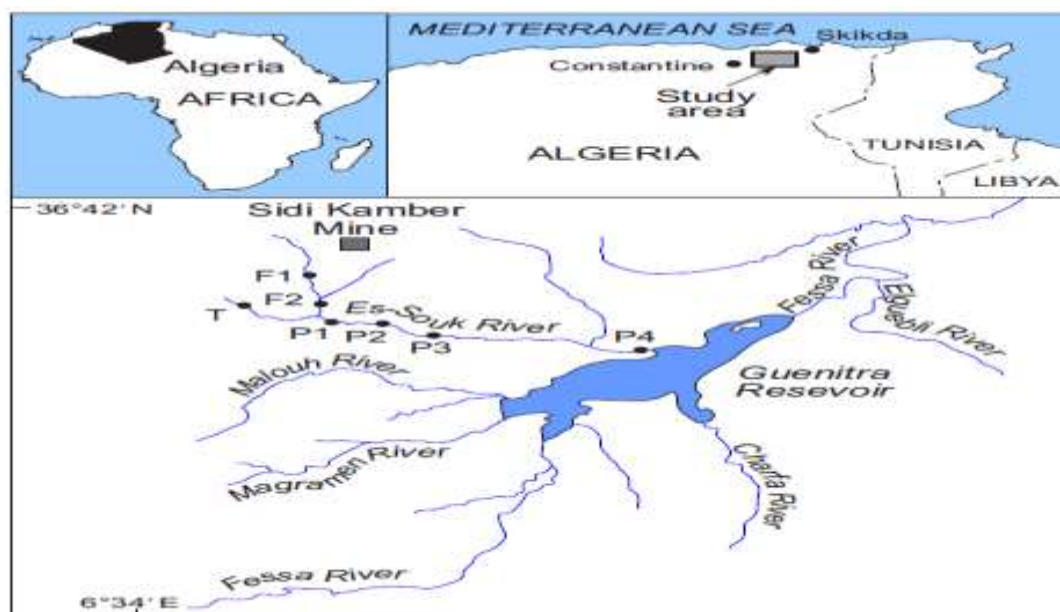
Heavy Metal	Processes		
	EC	AD	EC + AD
R_{Cr(VI)} %	24.6	77	92
RM (µg/)	175	53	19

From analyzing the Cr(VI) removal results presented in [Table 14](#), it was clear that the combination between the two processes gave a better Chromium removal, just 19 µg/L of remaining Cr(VI), this concentration is inferior than the MCL of Algerian and USA standards.

Another important research, did it by [Chahrazed Boukhalfa](#) studied the pollution of Oued Es-Souk river, Souk Ahras (North-eastern Algeria), caused by mine activities of the abandoned Sidi kamber mine. In this work, samples taken from 7 different localization, T situated in the upstream of the mine effluent, F1 and F2 represent sampling sites of the mine water during low flows (June) and high flows (January), P1-P4 located in the downstream of the mine effluent ([Figure 7](#) and [Table 15](#)).

Table 15 concentration of dissolved parameters in water downstream Sidi Kamber mine during two different season (Boukhalfa, 2007).

Sample point	Period	pH	Conductivity ($\mu\text{s/cm}$)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)	Pb (mg/L)	Cd (mg/L)
T	/	7	537	0.24	0.22	1.44	ND	ND
F1	June 1989	2.2	22600	4143	-	5062	0.6	10.8
	January 1990	2.2	13979	3993	7.79	1429	1.4	11.3
F2	January 1990	3.6	7700	1990	33.6	-	0.55	0.41
P1	June 1989	3.3	1850	3.7	-	18.8	3.2	0.18
	January 1990	3.2	5436	979	25.62	448.54	0.76	0.62
P2	June 1989	3.0	2270	17.1	-	20.7	3.2	0.24
	January 1990	4.85	1841	473	5.18	78.61	ND	0.24
P3	June 1989	3.2	2320	14.2	-	13.0	3.8	0.25
	January 1990	4.7	1929	148	4.48	76.26	ND	0.22
P4	June 1989	8.65	561	0.15	-	0.9	ND	0.05
	January 1990	4.6	1901	26.7	7.44	55.86	0.71	0.2

**Figure 7** Sidi Kamber Mine location and seven sampling sites at Es-Souk River (T, F1, F2, P1, P2, P3 and P4) (Boukhalfa, 2007).

From analyzing the results of table, the water characteristics changed from site to other. In the upstream river (Site T) the water quality was not contaminated, with a neutral pH and very low heavy metals concentrations. However, in Sidi Kamber mine station (F1 and F2) the

water was too much polluted, at station F1, the effluent has very acidic pH, high conductivity and contains a huge amount of heavy metals, this properties changed from wet (January) and dry (June) season, the Zn was too much higher in the dry season compare to the wet season. At station F2, presented as ground water, the properties became less polluted, its pH being less acidic and the heavy metals concentration decreasing expect Mn, due to buffering reactions with hydroxide, carbonate and aluminosilicate minerals present in the aquifers (Boukhalifa, 2007).

The river water downstream in P1 station mixed with the mine water exiting F2 station, changing the water's properties. The overall difference in river water quality downstream revealed that pH values increased with increasing distance from the mine, but specific conductivity and lead concentrations decreased. Cadmium and zinc, on the other hand, stayed in solution. In comparison to low flow, the pH values were more acidic during the wet season. The specific conductivity values were higher during the dry period; it is possible that the dissolved elements were removed more effectively by adsorption and precipitation than by stream water evaporating. The importance of iron and zinc solubility during the wet season was demonstrated by their high quantities, which is associated with the low pH observed during this time (Boukhalifa, 2007).

A comparative analysis of the overall water quality at the head of the Guenitra reservoir (station P4) and upstream of the mine (station T) in the Oued Es-Souk demonstrates that, even with the impacts of dilution, adsorption, and precipitation, the river water has acquired novel attributes including an elevated specific conductivity, acidic pH, and substantial metal concentrations. Also the degree of pollution decreased from station P1 to station P4 because of heavy metals decreasing and pH value increasing.

It should be noted that the dissolving of metals during wet periods becomes quite substantial if such phenomena are activated during dry seasons. So it was necessary to consider these conditions when the Sidi Kamber mine was abandoned (Boukhalifa, 2007).

I.6 Conclusion

In this chapter, a general study of three important heavy metals, cadmium, copper, and zinc, has been carried out, including physical and chemical properties, focusing on their important compounds that play a considerable role in heavy metal toxicity.

Cu, Cd, and Zn have different naturel sources and their occurrences in nature were very low, the anthropogenic sources (agriculture, domestic and industrial activities) still the important source of heavy metals toxicity, such as mining industries, metallurgy, chemical manufacturing, steel industries, printing circuit, electroplating industries, paints, and fertilizers etc...

The Cu and Zn are essential elements for plants, animals, and humans, they are necessary for most of physiological functions, they play also a vital role in enzyme synthesis, bone development, and in tissues. The deficiency of these two metals can cause several biologic problems. However, the use of important quantities (above the standard limit value) can cause serious health and environment hazards. The Cd is one of the most toxic metals (after the Mercure) even in small concentration.

These toxic metals are exposed to human and environment, when they discharged inappropriately. The accumulation of non-biodegradable ions can cause severe damage to mucus tissues and intestinal tract, central nervous and reproductive systems.

Finally, the removal of heavy metals is mandatory in order to preserve the environment and the human health by the application of different treatment processes, such as chemical precipitation.

CHAPTER II

CHEMICAL PRECIPITATION –

OVERVIEW

II.1 Introduction

Wastewater containing heavy metals discharged into the environment has terrible effects on soil, groundwater, sediment, and surface water (Chen et al., 2018 ; Ye et al., 2017). Based on their toxicity, these substances can cause serious health and environmental problems as shown in the previous chapter.

Before releasing industrial wastewater, the amount of heavy metals must be decreased to below the MCL (Maximum Contaminant level). Several treatment techniques, including chemical precipitation (Benalia et al., 2022 ; Chen et al., 2018 ; Ouanoughi, 2004), adsorption (Svobodová et al., 2024 ; Bouaziz et al., 2021; Youcef and Achour, 2014), ion exchange (Jasim and Ajjam, 2024 ; Bashir et al., 2019), coagulation/flocculation (Skotta et al., 2023), ion flotation (Hu et al., 2024 ; Polat and Erdogan, 2007) , and membrane filtration (Zamora-Ledezma et al., 2021 ; Ates and Uzal, 2018), have been employed to remove heavy metals from the contaminated wastewater (Khawar et al., 2018 ; Carolin et al., 2017 ; Ghosh et al., 2011) .

In the present chapter, chemical precipitation has selected for the removal of Cu(II), Cd(II) and, Zn(II). This method is the most commonly used process in the industry. In this chapter, the useful information about the chemical precipitation have explored, such as physical/chemical properties, used processes, schematic designs and its advantages and limitation, the different results of previous researchers who used this approach for the removal of the studied metals (Cu, Cd, and Zn) have mentioned.

II.2 Overview of processes for removing heavy metals from water

A wide range of approaches have been applied to remove heavy metals from water (Zamora-Ledezma et al., 2021 ; Barakat, 2011) :

- ***Non-conventional treatments*** or emerging removal methods (Figure 8), such as Fenton reactions, nanotechnology methods, and microbial fuel cells, have greater implementation costs as a major drawback. One of the greatest ways to clean water of many impurities, including heavy metals, is through adsorption. Its benefits included relatively low energy consumption, a high removal capacity, and technical requirements for operation (Zamora-Ledezma et al., 2021 ; Burakov et al., 2018).
- ***Conventional treatments*** as membrane technologies, ion exchange, and electrochemical removal exhibit numerous drawbacks, such as high energy

requirements, partial removal, and the creation of toxic sludge. The financial and technical requirements for installation, operation, and maintenance may present additional challenges. Therefore, it is imperative to create solutions that are both sustainable and effective. (Tavker et al., 2021 ; Zamora-Ledezma et al., 2021). **Coagulation–flocculation** is a successful physicochemical technique for removing heavy metals (Xu et al., 2019). This method reduces a significant quantity of effluent pollutants by agglomerating fine particles and colloids into larger particles. (Teh et al., 2016). **Chemical precipitation** is a useful method for removing heavy metals, mostly from the wastewater of certain industries like the electroplating and paper industries...etc. By adjusting the pH, heavy metal ions are transformed into less soluble substances like carbonate, sulfide, and hydroxide, which can then be eliminated through physical processes like filtration, flotation, or sedimentation. These processes depend on the size, density and surface charge of the particles to be removed (Wang et al., 2005 ; Chen et al., 2018 ; Zamora-Ledezma et al., 2021).

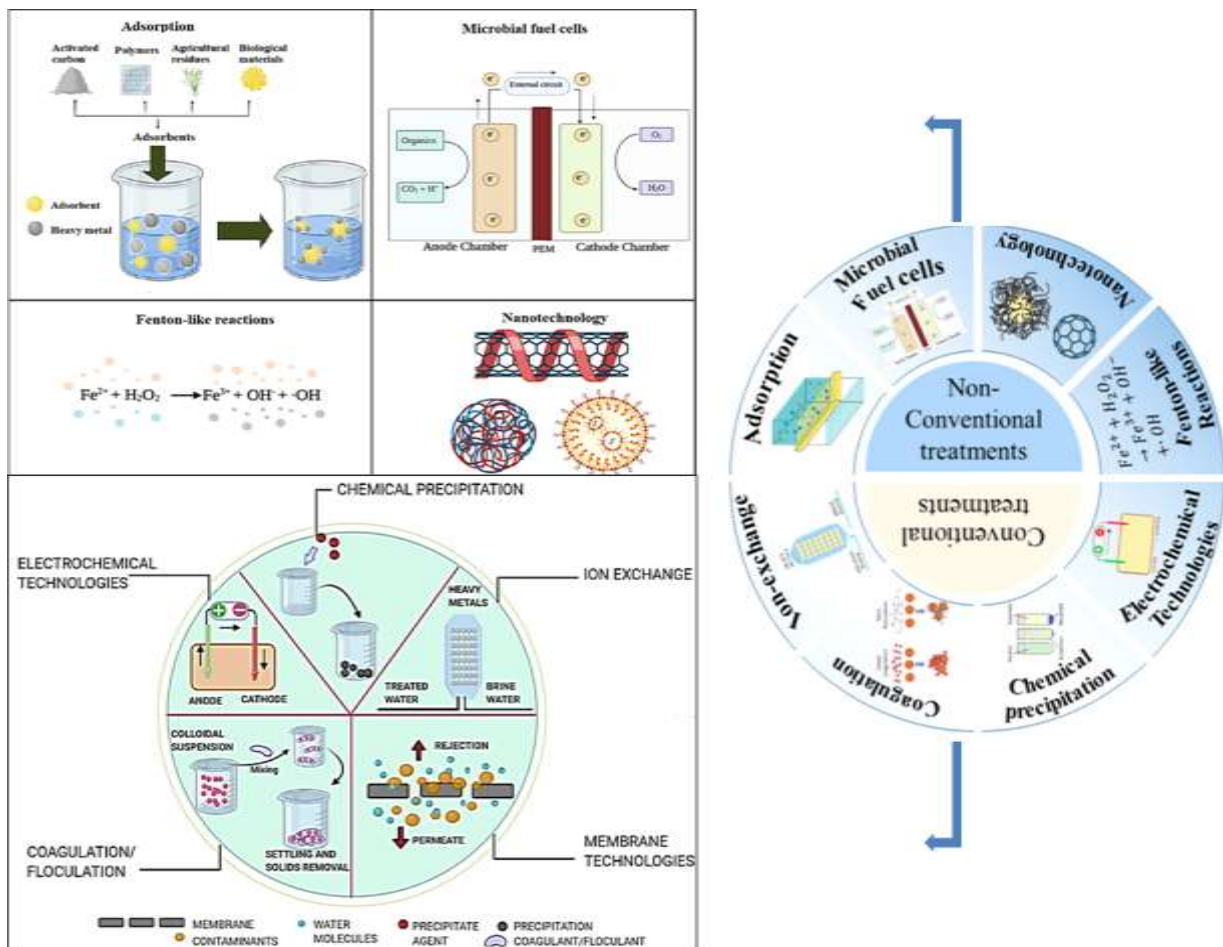


Figure 8 Non-conventional and conventional treatments for removing heavy metals from wastewater (Zamora-Ledezma et al., 2021)

II.3 Definition and properties of chemical precipitation

Chemical precipitation is a physico-chemical simple process and is one of the oldest and most prevalent methods for converting soluble metallic ions, and specific anions that are undesirable to effluent or water into an insoluble form. It is a frequently employed treatment method for hardness, phosphorus, and heavy metal removal. For example, wastewater that comprises hazardous metals (Azimi et al., 2017 ; Wang, L. K., et al., 2005). This technique is employed in many industries to remove significant amounts of metal ions and is thought to be a cheap and efficient technology, that works well at a variety of temperatures. Nevertheless, this approach is inappropriate when the concentration of metal ions is minimal (Chen et al. 2018 ; Carolin et al., 2017 ; Chen et al., 2017).

The precipitation process produces extremely fine particles. Following the isolation of these precipitates, the residual solution is either discharged or employed for other reasons (Chen et al., 2018 ; Azimi et al., 2017 ; Carolin et al., 2017 ; Fu and Wang, 2011).

The success of this process depends on the solubility of the precipitated metal compounds, if a metal can form an insoluble compound, the compound can be removed. (BrbootI et al., 2011).

Heavy metal precipitation behaviors vary depending on the pH, as the solubility of metals is influenced by pH (Chen et al., 2018 ; Wang et al., 2018 ; Sis and Uysal, 2014). The pH depends on the contaminants in wastewater and the precipitant dosage, which needs to be continuously checked and adjusted during the precipitation process (Chen et al., 2018).

II.3.1 Chemicals of heavy metals precipitation

Precipitation is a process that happens when the solubility of a salt in solution is exceeded. To form a metallic precipitation, chemical precipitant agents are added to the solution then they interact with the ions of heavy metals to form insoluble solid particles (Chen et al., 2018 ; Carolin et al., 2017 ; Azimi et al., 2017 ; Fu and Wang, 2011).

The most commonly used chemicals for precipitating heavy metals are: lime (Ca(OH)_2) or caustic soda (NaOH) for hydroxide precipitation, soda ash (Na_2CO_3) or sodium bicarbonate ($\text{Na(HCO}_3)_2$) for carbonate precipitation, sodium sulfide (Na_2S) or sodium hydrosulfide (NaHS) for sulfide precipitation (Chen et al., 2018 ; Azimi et al., 2017).

II.3.2 Kinetics of chemical precipitation

It is typically useful to determine the kinetics of the process. Understanding the numerous mechanisms that drive the precipitation process is also required. Figure 9 provides a summary of the mechanisms.

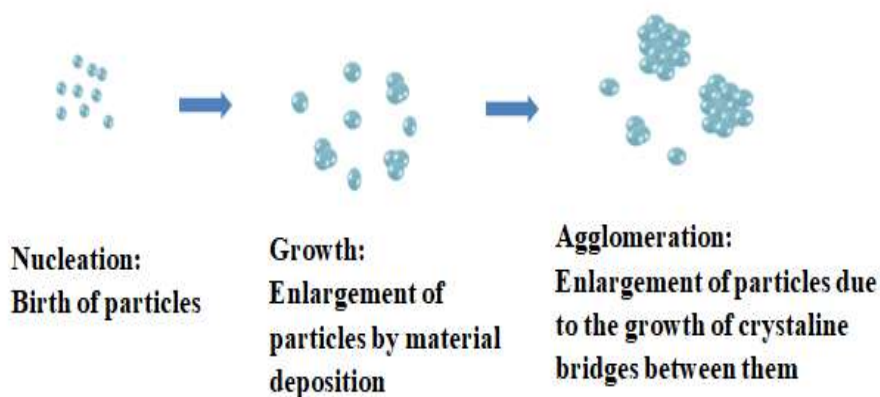


Figure 9 Three main mechanisms of precipitation: aggregation, growth, and nucleation (Lewis, 2017).

II.3.2.1 Nucleation

The first time a solid phase forms from a solution is known as nucleation. It happens when molecular or ion clusters and aggregates in a supersaturated solution reach a certain size. A solid phase is generated spontaneously from solution during primary homogeneous nucleation, whereas the introduction of foreign particles causes primary heterogeneous nucleation (Lewis, 2017; Jones et al., 2005).

II.3.2.2 Growth

Growth is the process by which crystals form as a result of the deposition of crystalline material onto an existing crystal surface. The supersaturation levels (Figure 10) determine the kind of growth that will happen: rough growth is preferred at high supersaturation levels, birth-and-spread growth is preferred at intermediate supersaturation levels, and spiral or smooth growth is preferred at low supersaturation levels (Lewis, 2017 ; Lewis et al., 2015).

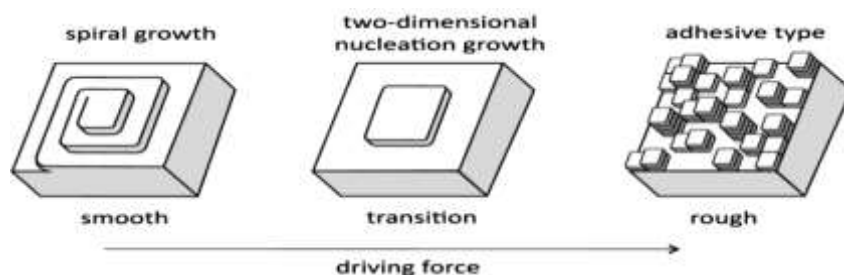


Figure 10 Relationship between growth type and supersaturation (Lewis et al. 2015)

II.3.2.3 Agglomeration

Agglomeration is the process that occurs, when two or more particles come into touch with each other and remain together enough time for a crystalline bridge to form between the particles. As a result, an agglomeration or stable particle forms. Particle agglomeration may be the only way to increase size during a precipitation process (Lewis, 2017; Lewis et al., 2015).

II.3.3 Process types

Conventional chemical precipitation processes produce insoluble precipitates of heavy metals as hydroxide, sulfide, carbonate and phosphate (Gunatilake, 2015).

II.3.3.1 Hydroxide precipitation

The metal that precipitates of the solution is usually found as hydroxide. Figure 11 illustrates the conceptual mechanism of chemical precipitation-based heavy metal removal.

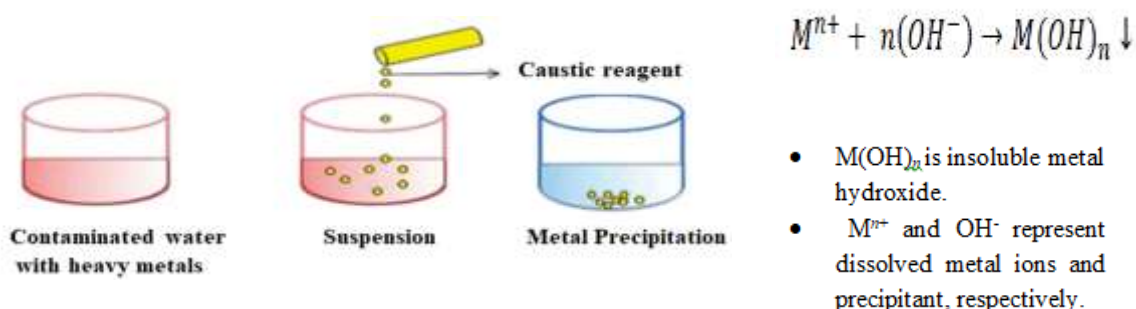


Figure 11 Conceptual mechanism of heavy metal removal by chemical precipitation

Basic chemicals like lime and caustic soda (sodium hydroxide) are commonly used reagents for hydroxide precipitation. Quicklime and hydrated lime ($\text{Ca}(\text{OH})_2$) are two forms of lime that are useful. Typically, lime is converted into 'milk of lime' (or sludge) before being

added to the treatment system (Wang et al., 2009). The typical procedure in small plants involves manually loading bagged hydrated lime into a batch mixing tank. A solution feeder is then used to feed the resulting "milk of lime" into the treatment process and then it transfers the lime to the point of application. After that, the sludge is diluted with lime milk and added to the process either by pumping or gravity. Caustic soda, added to the treatment system as a 6 - 20 % aqueous solution, does not necessitate the use of distribution or mixing tools (Wang, L. K., et al., 2005).

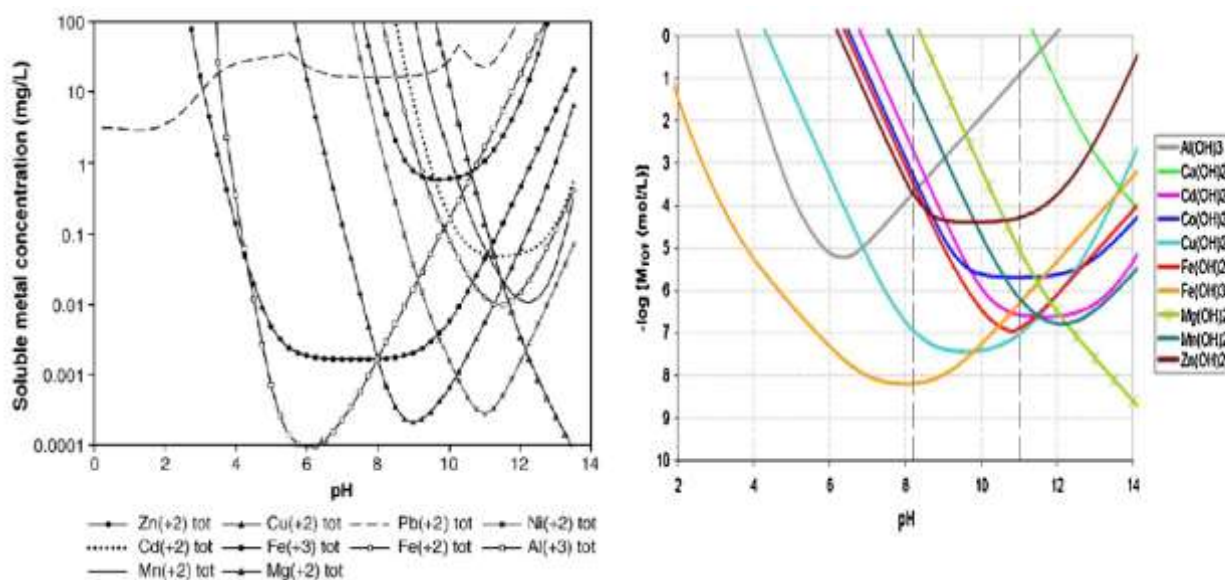
a) Advantages

Of all chemical precipitation procedures, metal hydroxide precipitation is the most commonly employed for treating water, because it is cost-effective, simple to use, and easy to control by adjusting pH. (Gunatilake, 2015). Water treatment methods have conventionally focused on chemical neutralization through the use of bases such calcium oxide (CaO), hydrated lime (Ca(OH)₂), limestone (CaCO₃), or the hydroxides of Mg, Na, and NH₄⁺. The reaction between a base and a solution containing dissolved metal ions results in the precipitation of the metals as metal hydroxides (Lewis, 2017). Limestone and lime are commonly employed due to their abundant availability and economical cost. (Carolin et al., 2017).

A specific pH is needed for hydroxide precipitation, in order to decrease the metal content below the standard values. This is more difficult to accomplish if there are several metals in the solution since each metal has a different pH of minimal solubility (Chen et al., 2017). Table 16 presents the pH ranges at which various metal species exhibit the lowest solubility, while Figure 12 illustrates the possible minimal solubilities that occur at varying pH values for several metals. The solubilities of the different metal hydroxides are reduced to the minimum at a pH of between 8.0 and 11.0 (Gunatilake, 2015).

Table 16 Minimum solubility ranges for metal hydroxides

Metal	Solubility K_{sp} (mg/L)	pH range
Al^{3+}	0.00055	6.2
Cd^{2+}	0.60	10.15_13
Cr^{3+}	0.04	7.0
Cu^{2+}	0.03	7.5_11.5
Fe^{3+}	0.00006	7.0_10.0
Pb^{2+}	16.5	10.0
Zn^{2+}	0.13	9.5

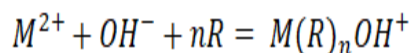
**Figure 12** Solubility of metal hydroxide as a function of pH (Lewis, 2010; Oncel et al., 2013).

b) Limitations

Hydroxide precipitation is the most common method, but it has some disadvantages:

- Lack of efficiency in decreasing sulfate in solution and the production of large amounts of sludge that need to be disposed (Lewis, 2010).
- Costly due to the necessity of employing excessive quantities of chemical for precipitation, in order to prevent resolubilization of precipitated compounds subsequent to filtration (Chen et al., 2017).

- Organic radicals have an impact on hydroxide precipitation, because they can create chelates that complicate the precipitation reaction (Gunatilake, 2015):



- The final concentration for some metals that can be attained is not very low (Grijalva, 2009).
- Amphoteric metal precipitates, such as zinc and lead, tend to re-dissolve, when the pH exceeds the optimum range. In addition, the combined metals make it difficult to use hydroxide precipitation, the fact that the optimum pH for one metal can affect the solubility of another (Chen et al., 2009; Matlock et al., 2001). As a result, the remediation of complex wastewaters comprising various heavy metals typically requires pH regulation and the use of fractional precipitation techniques (Chen et al., 2009).
- When complexing agents are in the wastewater, they inhibit metal hydroxide precipitation (Matlock et al., 2001).
- Pyrite and metal hydroxide sludge (gelatinous precipitates) are secondary byproducts of hydroxide precipitation that can be difficult to filter and thicken (Chen et al., 2017).
- The produced sludges are dangerous and need to be stored in a designated location and given particular care before disposal. The ultimate disposal of these substantial volumes of sludge and big volumes of chemicals used may be highly costly, which would increase the treatment cost (Chen et al., 2017).

c) Removal of Cu(II), Cd(II) and Zn(II) by hydroxide precipitation

Many researchers have used chemical precipitation for the removal of different toxic metals. Table 17 summarizes some results reported in previous studies on the removal efficiency of Cu, Cd, and Zn ions from synthetic solution and from wastewater (individually or in combination) using different hydroxide precipitating agents, focusing on the remaining metals and their final pH. In the Table 17, results can generally show that for the Cu(II), Zn(II), and Cd(II) removal, all the researches had a good removal efficiency more than 87 % at a pH range between 7 and 12.

Table 17 Various hydroxide precipitation researches for the removal of Cu(II), Cd(II) and Zn(II)

Aqueous Solution	Initial pH	Precipitating agent (mg/L)	Metal	Initial metal concentration (mg/L)	Remaining metal (mg/L)	pH value according to maximal removal	Reference
Effluent from plating industry	11.76-11.78	NaOH (N/A)	Cu(II)	0.0017	0.00023	10.5	(Yatim et al., 2021)
			+ Zn(II)	1.0613	0.00202		
Synthetic solution (deionized water)	N/A	Ca(OH) ₂ = 170 Na ₂ CO ₃ = 324	Zn(II)	100	0.35 0.04	11.2 9.3	(Chen et al., 2018)
		Ca(OH) ₂ = 292 Na ₂ CO ₃ = 334	Cu(II)	100	0.01 0.19	11.3 9.3	
Synthetic solution	6.0	Ca(OH) ₂ = 800	Zn(II)	100	0.13	9	(Wang et al., 2016)
		NaOH			0.16	9.2	
Synthetic selected food industrial wastewater	2.0	Ca(OH) ₂ = 220 NaOH	Cu(II)	10	0.2	9	(Abdel-Shafy, 2015)
					0.0001	11	
					0.5	9	
Coal mine drainage wastewater (CMDW)	N/A	NaOH	Zn(II)	19.3	0.02	10	(Oncel et al., 2013)
Raw acid main drainage	3.06	NaOH	Cu(II) + Zn(II)	0.46	0.035	8.2	(Balintova and Petrilakova, 2011)
				7.1	0.476		
Rayon industry waste water	6.9	CaO	Zn(II)	32	0.18	10	(Ghosh et al., 2011)
Synthetic effluents	2 – 2.7	CaO + Fly ash = 900 + 500 CaO + Fly ash + CO ₂ = 900 + 500 + CO ₂	Zn(II) + Cu(II)	100	2.5	9	(Chen et al., 2009)
					0.5	7	
					0.45	8	
Acidic soil leachate	1.9	Ca(OH) ₂ NaOH	Cd(II) + Cu(II) + Zn(II)	0.4	0.0	N/A	(Meunier et al., 2006)
				3.2	0.1 0.2		
				18	0.0 0.1 0.5		
Petrochemical industries' cooling water wastes	10.8	Ca(OH) ₂ { 2000 135 NaOH { 1336 25	Cu(II)	20.02	0.01	12	(Mirbagheri and Hosseini, 2005)
				48	0.65	12.1	
				20.02	0.99	12.2	
				48	0.53	12	
Industrial wastewater + metal reagent	6.5	NaOH CaO = 220	Cu(II)	10	0.25 0.2	9.5 9	(Krätschmer et al., 2002)
Synthesized raw wastewater	1.9	Ca(OH) ₂	Zn(II)	450	0.6	10.5	(Charentan yarak, 1999)
			+ Cd(II)	150	0.5	10.5	

N/A: Not available

II.3.3.2 Sulphide precipitation

a) Advantages

One of the best techniques for removing heavy metals from wastewater is sulphide precipitation. The most common types of sulfide precipitants are gaseous sulfide sources (H_2S), aqueous (Na_2S , NaHS , NH_4S), and solid (FeS , CaS) (Carolin et al., 2017 ; Gharabaghi 2012 ; Fu and Wang, 2011).

Its advantages include lower solubility, rapid reaction, better settling properties, and the benefit of selective metal precipitation over a wide pH range and possibly high removal efficiency. It also interferes less with chelating agents. It can be observed from Figure 13 that in alkaline solutions, the solubilities of various metal sulphides are lower than those of the hydroxide precipitate; this implies that metal removal could potentially be effective at very low concentrations. Additional advantages of having quick response rates, excellent settling capacities, and selective metal removal (Gharabaghi, 2012 ; Lewis, 2010).

More recently, metal sulphide precipitation has been effectively applied to remediate acid mine drainage by removing metals from solution, sulfate-reducing bacteria are employed in this process, which converts acidic sulfate to sulphide. Tabak et al., (2003) developed a resource recovery-based remediation process to clean up a polluted mine site in the USA. Veeken et al., (2003) used a sulphide-selective electrode as a control to study the selective precipitation of heavy metals.

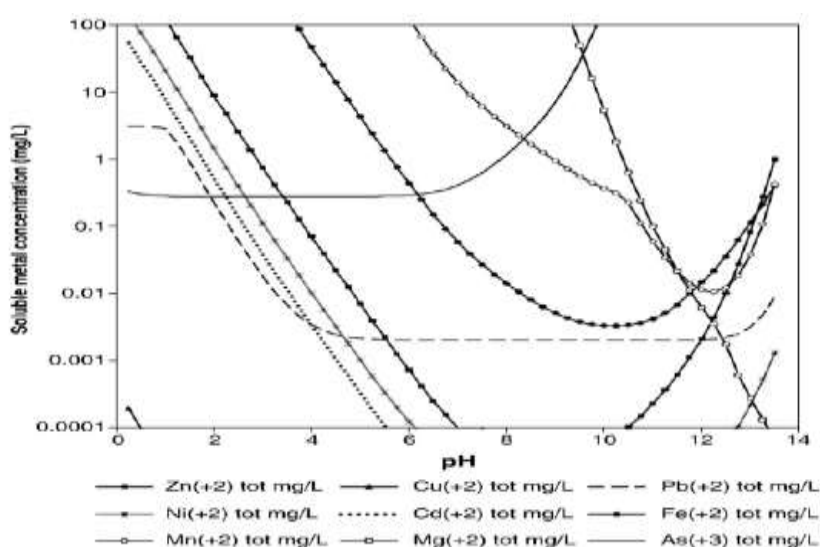


Figure 13 Metal sulphide solubility as a function of pH (Lewis, 2010)

b) Limitations

This treatment approach has been limited in chemical process applications, because of the high cost of the chemicals, as well as safety concerns about the production of hydrogen sulfide gas, especially when treating acidic effluents (Lewis, 2017; Nduna et al., 2013). Metal sulphide is still hard to use successfully for metal removal and recovery because of the particle structure of the metal sulphide precipitates, it is also difficult to control its dose. Because of the extremely low solubilities of the metal sulphide salts, this means that the process will be driven by very high supersaturations (Gharabaghi, 2012 ; Lewis, 2017).

II.3.3.3 Carbonate precipitation

Metals can be removed by carbonate precipitation, which can occur directly with the application of a carbonate reagent like calcium carbonate or indirectly by the conversion of hydroxides to carbonates with carbon dioxide. Carbonates are soluble in most metals in a range between hydroxides and sulphides, they also precipitate after during filtration (Wang et al., 2005).

➤ Advantages

- ✓ Compared to hydroxide treatment, carbonate precipitation happens at lower pH values.
- ✓ The precipitate of metal carbonate has a higher density than that of hydroxide.
- ✓ Improved solids separation and decreased volume of sludge.
- ✓ Carbonate sludge presents superior filtration properties in comparison to hydroxide sludge (Patterson, 1977).

➤ Limitations

There are a number of factors that could restrict the use of carbonate precipitation, including the presence of chelating agents and other chemical interferences during wastewater treatment chemical mixing, as well as the hazardous nature of chemical storage and handling. (Wang et al., 2005).

Chen et al. (2018) studied the possibility of removing the Cu(II) and the Zn(II) from synthetic solution by using soda ash or sodium carbonate (Na_2CO_3), for more details return to table 17.

II.3.4 Basic chemical precipitation processes

Approximately 90% of treatment systems for industrial wastewater use chemical precipitation (Lewis, 2017 ; Grijalva, 2009). This method is frequently used to remove metal from a variety of wastewaters, such as acid mine drainage and hydrometallurgical effluents. After the metals have precipitated, the residual aqueous phase can be separated from them using a filter, centrifuge, or similar technique. Furthermore, if a large precipitate forms, it has the ability to "sweep" ions and particles from the wastewater (EPA, 2000).

The fundamental steps involved in precipitating heavy metals are summarized in Figure 14 and comprise pretreatment, pH adjustment, flocculation/clarification, thickening, dewatering, disposing of sludge, and polishing effluent.

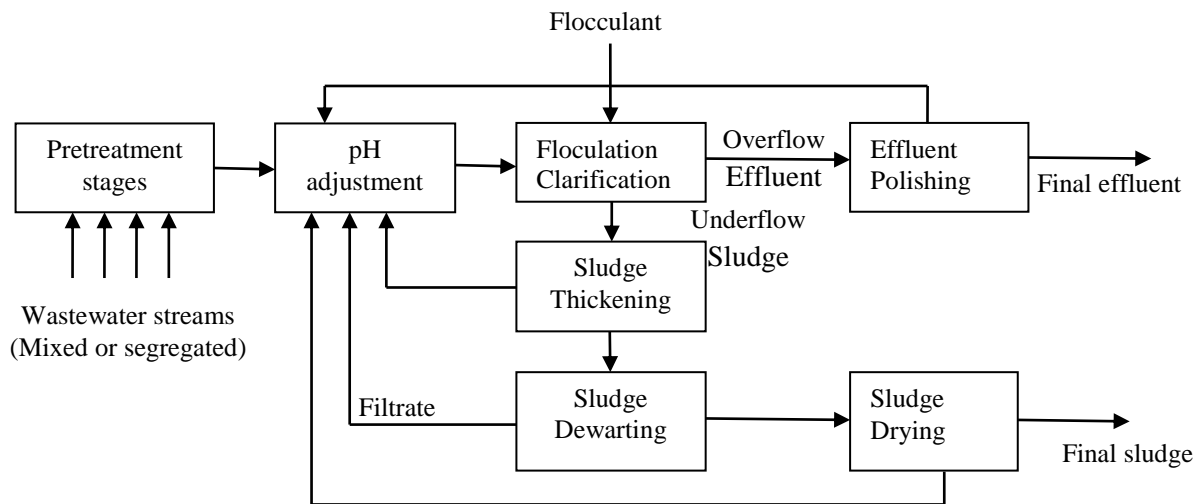


Figure 14 Basic chemical precipitation processes for wastewater treatment (Wang et al., 2009).

II.3.4.1 Pretreatment

Before sedimentation, pretreatment is used to remove substances such as oil and scum in order to increase process feasibility (Metcalf et al., 1991).

II.3.4.2 pH Adjustment

Metal precipitation happens at different pH values based on several variables. The pH level for precipitation in wastewater streams containing different heavy metals needs to be carefully selected such that the insolubility of each metal is within the acceptable range. If this is not feasible, the stream needs to be separated in order to treat the specific component metal at the right pH. Table 16 provides the average minimal pH values required for precipitation, which are determined using the metal hydroxide's solubility product K_{sp} (Skelly et al., 1973).

II.3.4.3 Flocculation/Clarification

When coupled with current separation methods, this can result in the formation of quite dense sludge, which can be processed directly in a dewatering unit. During the clarification phase, the solids (flocs) that have accumulated in the effluent stream are removed. Usually, this is a gravity settling procedure carried out in an inclined plate clarifier, also known as a Lamella clarifier, or a sedimentation tank (Wang et al., 2009).

II.3.4.4 Effluent polishing

In the polishing stage, the most common technique for removing suspended solids is filtration utilizing backwash sand in-depth filters. The filtration process is accessed by the settler/clarifier overflow. It can be released once it has passed through the granular medium. (Viessman and Hammer, 2004). An alternative method for concentrating particles in the wastewater stream and producing a clear effluent is membrane filtration. An example that might be provided is ultrafiltration (Skelly et al., 1973).

II.3.4.5 Sludge Thickening

The sludge-thickening stage often comes after the flocculation/clarification step. Typically, a sludge thickener is a conical bottom tank that collects the clarifier's underflow and offers storage for additional solids settling by gravity. About 4–6% of the solids in the sludge concentrated at the tank's bottom are solids. The benefit of using sludge with a high solids concentration is that it usually enhances the dewatering equipment's functionality and performance (Noble and Stern, 1995).

II.3.4.6 Sludge Dewatering

The Sludge dewatering or Sludge Dehydrator effect is used to separate liquids from solids. According to Wang et al., (2009), the process of dewatering concentrated sludge can be achieved with a variety of equipment, including centrifuges, rotary vacuum filters, belt presses, filter presses and others...

II.3.4.7 Sludge Disposal

Sludge management is becoming increasingly essential due to the increase in the production of industrial wastes. Recycling may be required for heavy metal sludge (Chen et al., 2018 ; Kurniawan et al., 2006).

Sludge can be disposed of in a variety of ways (landfill, ocean dumping, incineration and land application). Sludge containing metals is difficult to handle and due to its toxicity,

final disposal is often problematic and costly. If not properly disposed, these sludges can be a potential source of pollution for surface water and groundwater (Wang et al., 2009).

Numerous parameters, including the type of soil, ground water table, hydrology composition and pH of the sludge, must be taken into account when choosing the disposal location for the sludge. The possibility for the release of selenium, lead, mercury, cadmium, and chromium increases when the pH of the sludge is less than 6.5. Suitable disposal sites are areas where natural (clay, rock) or artificial means (plastic liner) can prevent excessive amounts of leachate from getting into the ground water. In cases when these requirements are not met, it could be essential to construct a collecting system at the bottom of the pond in order to collect leachate and transfer it to a treatment system for the removal of soluble metal salts (Lue-Hing et al., 1992).

II.3.5 Overview of different schematic designs for chemical precipitation

From 1980 to 2023, Chemical precipitation has been selected by researchers as an efficient method for heavy metal removal employing several schematic designs. Figure 15 shows five distinct designs for hydroxide and sulfide precipitation.

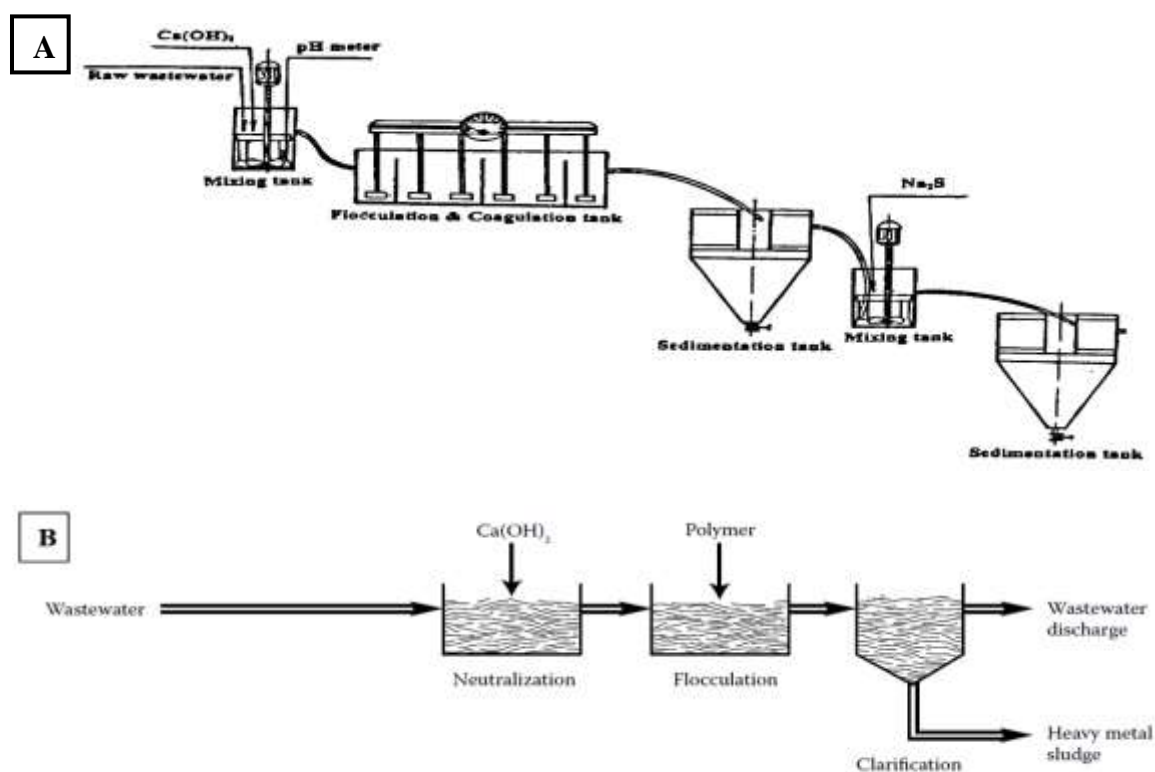


Figure 15 Different schematic designs of the chemical precipitation process used by researchers from 1999 to 2018. (A , B, C and E).

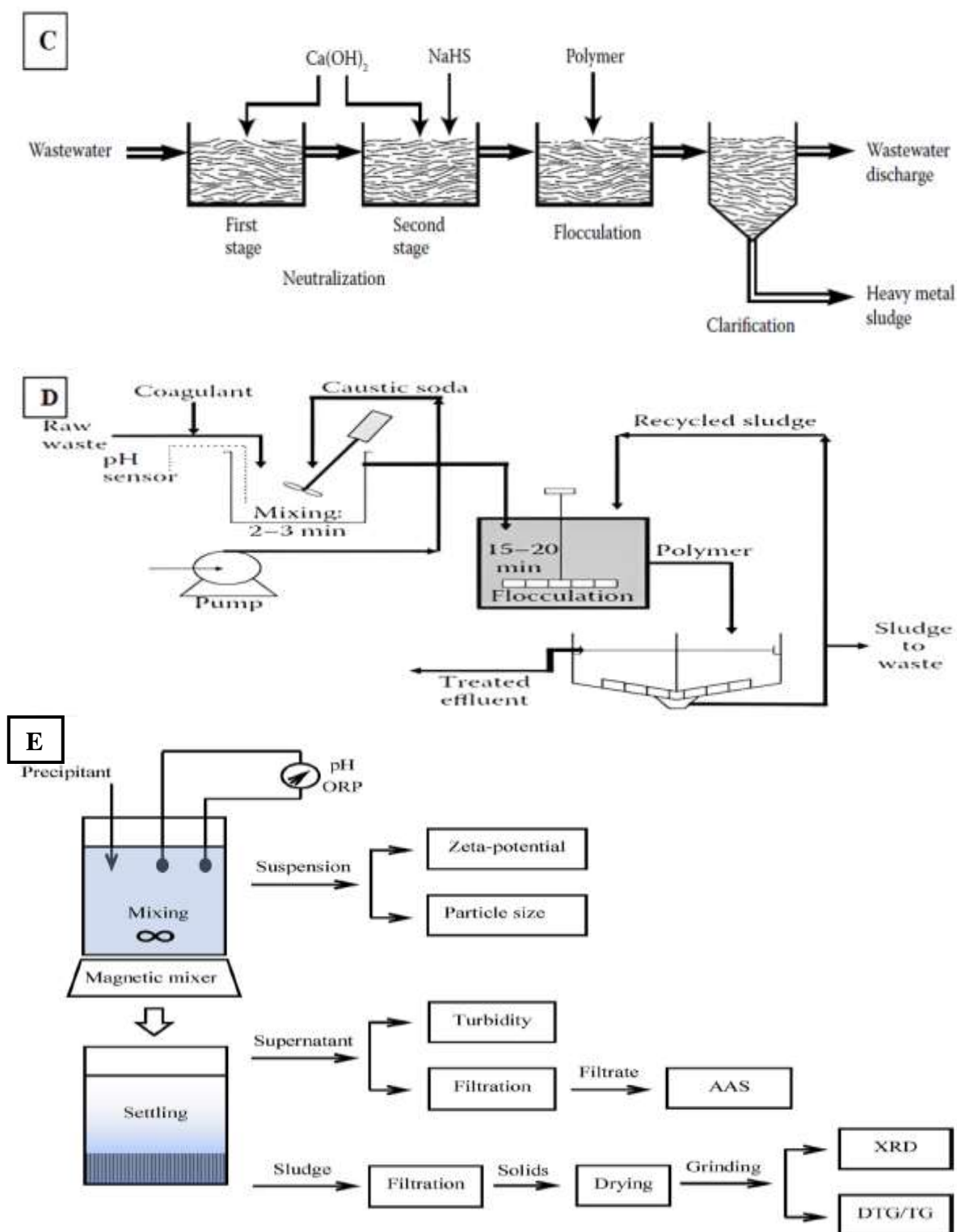


Figure 15 Different schematic designs of the chemical precipitation process used by researchers from 1999 to 2018. (A , B, C and E) (Continued).

Figure 15.A represents a design used by the researcher [Lertchai Charentanyarak](#), which composed by two rapid mixing tank with pH monitors, baffles, a stirrer with speed of 100 rpm , a coagulation and flocculation tank with the stirrer at asped of 40 rpm , and two

sedimentation tanks. Lertchai Charentanyarak used a synthesized raw wastewater, with important concentrations of zinc, cadmium, manganese and magnesium, he used the both hydroxide and sulfide precipitation (Charentanyarak, 1999).

Figure 15.B and C show two different designs used in electroplating industry, (B): Hydroxide precipitation, (C): sulfide precipitation, in order to remove different metals (Cadmium, Chromium, Zinc, Copper, Silver, Nickel, Mercury and Lead). This system was composed by different steps using 3 tanks in (B), the neutralization tank by adding $\text{Ca}(\text{OH})_2$, flocculation tank and sedimentation tank. In sulfide precipitation (C) they added another neutralization tank by adding Na_2S (Chen et al., 2017).

The continuous treatment shown in Figure 15.D was discussed by Wang et al., (2009) and is useful for large volumes of wastewater with consistent properties. An equalization tank, with a detention period of several hours to a day is typically included in continuous-flow treatment systems to balance out variations in the wastewater's properties and supply a uniform feed to the treatment system.

The initial stage of the procedure involves adjusting the pH by adding acid or alkali to the right amount to achieve the best possible precipitation. After passing through a sedimentation basin, the waste water is treated to remove any metal particles that may have settled to the bottom. The treated overflow is then released into the receiving water body. (Wang et al., 2009).

Figure 15.E shows a new precipitation design used by Chen et al., (2018) to remove copper, Zinc and lead, focusing on the characteristics of precipitates. The schematic of this experiment composed by multi steps as follow:

- * Jar tests with a series of beakers using 3 different precipitants ($\text{Ca}(\text{OH})_2$, $\text{Na}(\text{OH})$, and Na_2S).
- * Mixing tank (fast stirred for 3 min followed by gentle stirring for 7 min), after stirring they have measured the particle size of precipitates.
- * Settling tank (used volumetric method to estimate the volume of decanted sludge)
- * Filtration after that measuring pH and remaining metal from supernatant.
- * Filtration to separate solid from liquid, for the sludge examination (XRD, potential Zeta and thermal analyses) (Chen et al., 2018).

II.4 Conclusion

Chemical precipitation is our choice for the removal of heavy metals particularly Cu(II), Cd(II), and Zn(II) from industrial wastewater for many reasons, mainly because its easy handling and its low cost, also its effective process over a wide range of temperature. The pH and the solubility of precipitated metal compounds play the important role in this method's success.

Heavy metal precipitation treatment procedures typically involve: pretreatment, pH adjustment, flocculation/clarification, effluent polishing, sludge thickening, sludge dewatering and sludge disposing.

The kinetics of chemical precipitation gives an idea of the formation of precipitates, starting from a small particle, then the growth of crystals, and finally the agglomeration of particles to form settleable flocs (particle size is very important in the settling stage).

Hydroxide precipitation, Carbonate precipitation, and sulphide precipitation are the most important types of chemical precipitation and like all the strategies; these processes have advantages and drawbacks.

Chemical precipitation is a widely used method by many researchers, many of them achieved good removal efficiency with low concentration of remaining metal (compatible with MCL), especially for copper ions. However, they had some difficulties in reaching the maximum point for Cd(II) and Zn(II) removal. Perhaps because it is difficult to reach a Cd(II) concentration conforming to MCL, and the problem of Zn solubility outside the pH range of precipitation.

EXPERIMENTAL PART

CHAPTER I

MATERIAL AND METHODS

I.1 Introduction

In this chapter, the protocol followed for the preparation of the treated solutions, as well as the important details of the industrial liquid effluent samples will be explained. In addition, the preparation of the precipitating agents, the description of the chemical precipitation tests and all the materials used will be presented. Finally, the method for analyzing the sludge produced (recovery and examination) will be described.

I.1 Solutions treated

Three different solutions were used (synthetic solution, ENICAB wastewater, and Galvanic wastewater) to study the possibility of removing heavy metals by chemical precipitation.

I.1.1 Synthetic solution

Aqueous solutions of copper, zinc, and cadmium were prepared in the laboratory from metal sulfates or chlorides: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and CdCl_2 (ALDRICH + 99% of purity).

Each metal salt was dissolved in distilled water (de-ionized water) at a concentration of 100 mg/L, for precipitating agent effect and for pH adjustment. However, for metal concentration effect, a concentrated solution of 1000 mg/L was prepared.

I.1.2 Industrial wastewaters

In order to apply the selected treatment process, two industrial liquid effluents containing levels of heavy metals in excess of the discharge standard were sampled. Physico-chemical parameters (Table 29 and Table 33/34 from Chapitre III) of wastewaters were determined by standard methods of analysis (Rodier, 2009), or by the methods described in the user guides of the equipment.

I.1.2.1 Industrial wastewater (ENICAB)

The industrial wastewater of the Algerian cable industry company (ENICAB) was used without any metal reagents and prior treatment (Figure 16). Electrical cable manufacture is handled by ENICAB, an Algerian corporation that produces a broad variety of products, such as medium-voltage cables, bare high-voltage cables, industrial cables, and low-voltage cables.

ENICAB wastewater was charged with two different metals Cu(II) and Zn(II), by an average values: $\text{Cu(II)} = 18.10 \text{ mg/L}$; $\text{Zn(II)} = 10.21 \text{ mg/L}$.

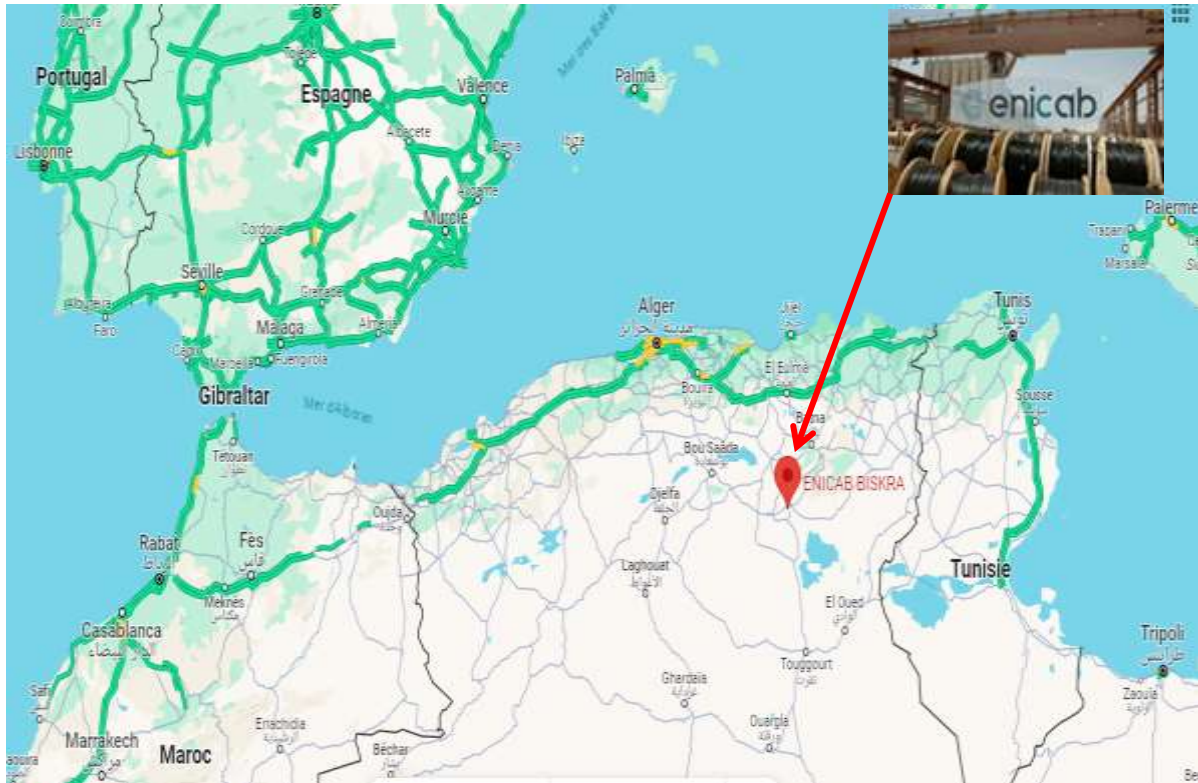


Figure 16 ENICAB company location (modified from [google maps](#))

I.1.2.2 Galvanic wastewater

The factory (electroplating company) in Padova, Italy, is the source of galvanic wastewater. Chemical and electrochemical methods for nickel and copper plating are used in this electroplating company. Two independent samples were taken from the storage tank that contained all raw industrial effluent generated in the plant. Wastewater 1 (WW1) charged with Cu(II) and Wastewater 2 (WW2) charged with Ni(II), by an average concentration : Cu(II) = 51.55 mg/L and Ni(II) = 36.66 mg/L.

I.2 Precipitating agents preparation

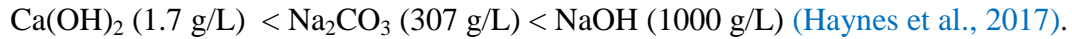
I.2.1 Conventional precipitants

For the purpose of removing heavy metals from synthetic solutions and treating industrial effluent, the precipitating agents lime ($\text{Ca}(\text{OH})_2$), caustic soda (NaOH), and hydrated soda ash ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) have been selected. Note that all of them were of analytical grade quality.

✓ $\text{Ca}(\text{OH})_2$: ALDRICH , > 95% of purity .

- ✓ NaOH : Riedel-de Haën , Germany ; very high purity.
- ✓ Na₂CO₃ · 10H₂O : Cheminova International. Madrid, Spain ; 99.5% of purity.

The following precipitating agents were dissolved in distilled water to create concentrated solutions: lime (10 g/L), soda ash (10 g/L), and hydrated caustic soda (40 g/L). These reagents are soluble in water at a temperature of 25 °C as follows:



I.2.2 Preparation of CaO using eggshells

For precipitation experiments, calcined eggshells (CaO_{Eggshells}) have been used for the treatment of combined heavy metals in synthetic solutions and the treatment of galvanic wastewater.

Eggshell is composed mainly of CaCO₃, it is mostly waste material in poultry farms and it is largely produced from house, restaurant and bakery. The composition of chicken eggshell is shown in Figure 17.

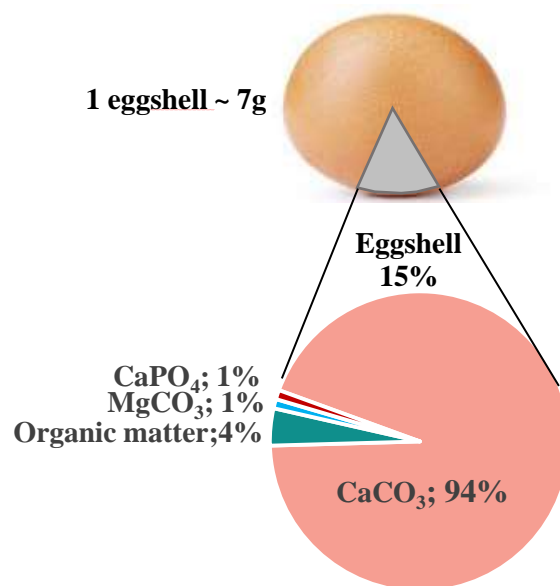


Figure 17 Chicken eggshell characteristics and compositions (eggshell composition mentioned by Puspitasari et al. 2019).

Chicken eggshell samples were collected from restaurants in Biskra city in Algeria. In order to eliminate contaminants and interfering materials like salts and organics, the eggshells were rinsed several times with de-ionized water and dried in open air for 48 hrs. After that the

eggshells were crushed using mortar and pestle for 30 minutes (an electric grinder can be used for more performance) (Ashok et al., 2014). On the basis of the studies of (Park et al., 2007), note that the primary constituent of the sample proved to be pure CaCO_3 , operating within a temperature range of 0-640°C. The two components of the sample that were found to be significant were quick lime (CaO) and limestone (CaCO_3) at temperatures between 670 and 750°C. Then calcination of the sample of eggshells was performed in the furnace at 800°C for 7 h. The gaseous state CO_2 was evaporated and forms pure calcium oxide CaO , which is similar to the commercial lime in the general structure, white and soft. It should be noted that about ~19 g/L of CaCO_3 is required to get 10 g/L of $\text{CaO}_{\text{Eggshells}}$.

Method of preparation was modified from the researches of Ashok et al., 2014 and Park et al., 2007, eggshell calcinations steps are presented in Figure 18.



Figure 18 Steps followed in the process of preparing the CaO from Eggshells at the laboratory.

I.3 Description of Jar Tests and analytical Methods

Figure 19 shows the procedures that were followed in order to complete the precipitation tests (sludge analysis and the Jar test).

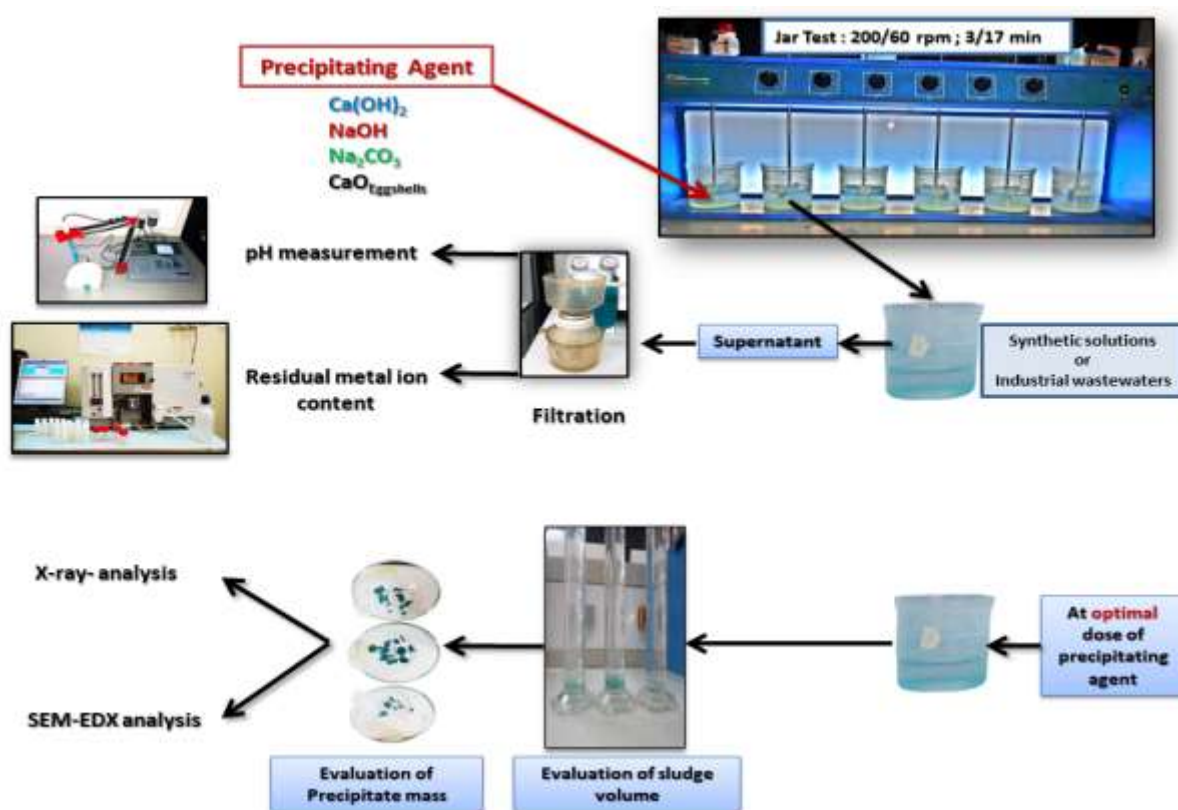


Figure 19 Chemical precipitation process (Jar tests + Sludge analysis).

A laboratory flocculator (11198-fisher Bioblock scientific flocculator) was used for the jar tests experiments (Figure 19). The impact of two reaction parameters, initial pH and precipitant doses, on heavy metal removal was examined using a series of solutions in 500 mL polyethylene beakers at room temperature (24 ± 1 °C). A specific doses of lime (Ca(OH)_2), caustic soda (NaOH), soda ash (Na_2CO_3), or $\text{CaO}_{\text{Eggshells}}$ were introduced into each solution. Such beakers were rapidly stirred at 200 rpm for 3 minutes, followed by slow stirring at 60 rpm for 17 minutes to generate coagulation and agglomeration, respectively. 50 mL of the supernatant from each beaker was filtered through a $0.45 \mu\text{m}$ membrane after settling for 30 minutes. The pH values were measured using a digital laboratory pH meter. (INOLAB instruments model pH 7310P) (Figure 19). Nitric acid was added to these solutions to acidify them after the final pH measurement, in order to determine the residual metal. Atomic absorption spectrophotometer was used for Cu(II) , Zn(II) , Cd(II) , and Ni(II) measurements (Figure 19). During the performance of the precipitation tests and depending on the availability of the apparatus, different absorption spectrophotometer for the measurement of the content of the heavy metals tested were used : Shimadzu AA-6200 (In the pedagogical laboratory of the department of agronomy, University of Biskra), XplorAA, Dual GBC (ISTE- Gabes-Tunisia), and PerkinElmer PinAAcle 900 T (CRSTRA-Biskra

research centre). During galvanic wastewater treatment, Ni(II) and Cu(II) concentrations were measured at Padova University (Italy). Each measurement was done using an air/acetylene flame. The operating parameters were set up in accordance with the manufacturer's guidelines.

The removal efficiency of the metal was calculated as:

$$\text{Metal Removal (R \%)} = \frac{C_i - C_f}{C_i} \times 100$$

Where: C_i represents the initial metal concentration prior to precipitating agent addition.

C_f : is the final concentration of the metal following the precipitating agent's addition.

I.4 Sludge analysis

In order to determine the volume and mass of the settled sludge, a single beaker was selected for each precipitating agent. The beaker represented the optimal dose for each of the following agents: Ca(OH)_2 , NaOH, Na_2CO_3 , and $\text{CaO}_{\text{Eggshells}}$.

- After a specified settling time (between 60 and 120 minutes), the sludge volume was measured using a graduated test tube (500 mL) by directly measuring in mL /500 mL (Figure 19).
- To estimate the final precipitate mass, the recovered precipitates were dried in a furnace at 80°C for 12 hours and then weighed.
- Significant chemical compounds present in the precipitates were identified through X-ray diffraction (XRD). The X-ray particle diffraction equipment employed for this purpose was the Rigaku MiniFlex 600. The XRD was operated with the following parameters: 40 kV of voltage, 200 mA of current, and a 2θ scan range of 10°–80°. The wavelength was set at 1.54 Å.
- Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were performed on sludge samples using a scanning electron microscope (Tescan VGA3). Examination of the particle size, chemical composition, and surface morphology of sewage samples is feasible with this method.
- The ImageJ software facilitates the size distribution study and the determination of the average particle size of the sludge produced by the precipitation process by using SEM imagery. ImageJ is a widely available tool with a Java framework that offers a variety

of options to users. Various particle monitoring routines and three-dimensional particle measurements are added by plugins (Collins, 2007).

I.5 Reaction parameters investigated

In order to study the application limits of the process tested, the parameters and operating conditions listed in the Table 18 were chosen.

Table 18 Summary of all precipitation tests, conditions are mentioned		
Jar test conditions	Fast stirring at 200 rpm for 3 min followed by gentle stirring at the speed of 60 rpm for 17 min + Settling for 30 min + Filtration.	
Tests in Synthetic solutions	<i>Individual heavy metal (Cu, Cd and Zn) removal</i>	
	Effect of precipitating agent dose	-Initial concentrations of each metal = 100 mg/L -Precipitating agent tested individually (Ca(OH) ₂ , NaOH and Na ₂ CO ₃): 10 to 1000 mg/L
	Effect of metal concentration	Concentrations of each metal :10 to 200 mg/L Ca(OH) ₂ , NaOH or Na ₂ CO ₃ : 80 mg/L
	Effect of initial pH	-Initial pH : 4 to 9 -Initial content of each metal ion : 100 mg/L -Ca(OH) ₂ , NaOH or Na ₂ CO ₃ : 80 mg/L
	<i>Heavy metals combination (Cu, Cd and Zn) removal</i>	
	Effect of precipitating agent dose	-Combined metals (Cu, Cd and Zn): each [M ²⁺] = 100 mg/L -Precipitating agent tested individually (Ca(OH) ₂ , NaOH, Na ₂ CO ₃ , and CaO _{Eggshells} : 80, 100, 200, 300 and 1000 mg/L
	Effect of initial pH	-Combined metals (Cu, Cd and Zn): each [M ²⁺] = 100 mg/L -Initial pH : 3 to 9 -Ca(OH) ₂ , NaOH, Na ₂ CO ₃ or CaO _{Eggshells} : 80 mg/L
Tests in industrial wastewater	<i>Removal of heavy metals (Cu and Zn) from ENICAB wastewater</i>	
	Effect of precipitating agent dose	-The wastewater contain: Cu(II)= 18.10 mg/L and Zn (II) =10.21 mg/L -24 °C, pH ₀ = 6.08 -Ca(OH) ₂ , NaOH or Na ₂ CO ₃ : 80, 100, 200, 300 and 400 mg/L
	Effect of initial pH	-Cu(II)= 18.10 mg/L and Zn (II) =10.21 mg/L -Initial pH : 3 to 9 -Ca(OH) ₂ , NaOH, or Na ₂ CO ₃ : 80 mg/L
	<i>Removal of Cu and Ni from Galvanic wastewater</i>	
	Effect of precipitating agent dose	-The wastewater after dilution contains: Cu(II)= 51.55 mg/L and Ni (II) =36.66 mg/L -20 °C , pH ₀ = 1.77 – 2 -Ca(OH) ₂ or CaO _{Eggshells} = 600, 1000, 1200, 1400, 1600 and 1800

		mg/L
	Effect of initial pH	-Cu(II)= 51.55 mg/L and Ni (II) =36.66 mg/L -Initial pH : 2 to 11.5 - Ca(OH) ₂ or CaO _{Eggshells} : 600 mg/L

I.6 Conclusion

In this chapter, the protocol used to carry out chemical precipitation tests on heavy metals in synthetic solutions and industrial effluents has been described and explained.

In order to clarify and confirm the precipitation mechanisms of the pollutants tested, a description of the dosing techniques (pH and residual content of the metal element) and the characterization of the sludge produced (volume, mass, and particle size distribution) have been presented.

CHAPTER II

REMOVAL OF HEAVY

METALS IN SYNTHETIC

SOLUTIONS

II.1 Introduction

In the following chapter, the results of precipitation tests of heavy metals (Cu(II), Zn(II), and Cd(II)) in synthetic distilled water solutions will be presented. Firstly by studying the removal of each metal ion individually using Ca(OH)_2 , NaOH, and Na_2CO_3 , respectively. Then more complex solution will be simulated, by presenting the precipitation results of the three combined heavy metals in the synthetic solutions. The latest tests were carried out using $\text{CaO}_{\text{Eggshells}}$ (calcined eggshells), in addition to the three precipitating agents used previously.

In order to understand the mechanisms involved in the removal of these heavy metals, a number of parameters will be controlled, including the dose of the precipitating agent, the initial pH of the treated water, the precipitate settling time, the volume and the mass of the sludge, and the mineral composition of the sludge.

II.2 Individual heavy metal (Cu, Cd, and Zn) removal

II.2.1 Effect of precipitating agent dose

Jar tests using variable amounts of each precipitating agent (Ca(OH)_2 , NaOH, and Na_2CO_3) were performed at 24 °C and at $\text{pH}_0 = 4.68 \pm 0.1$ (pH of distilled water). Increased doses (10 to 1000 mg/L) of each agent are used to choose the suitable precipitant for the removal of 100 mg/L of Cu(II), Cd(II), and Zn(II) individually, in synthetic solution. Then the same experiment has repeated with each metal alone, focusing on 3 parameters (Removal efficiency, residual metal, and final pH).

In order to choose the suitable precipitant, the optimum dosage and the optimum pH correspond to the best metal removal have determined, by taking in consideration the MCL standards shown in Table 19. The results of the final pH, the remaining metal concentration and the removal efficiency of the metal for the precipitating agent doses (80, 100, 200, 400, 600 and 1000 mg/L) are presented in Table 19 and Figure 20.

It is clear from these results that the precipitation of Cu(II) starts at $\text{pH} = 5.5$. However, the precipitation of Cd(II) starts at $\text{pH} = 7$ and the precipitation of Zn(II) starts at $\text{pH} = 6$. But the best results of chemical precipitation occurred in the range of , $7 \leq \text{pH} \leq 12$ for Cu (II), $8.9 \leq \text{pH} \leq 12$ for Cd(II), and $10 \leq \text{pH} \leq 11.5$ for Zn(II). This results confirms that the pH of minimum solubility varies from metal to another (Chen et al., 2017), also each metal has its own pH range of precipitation, beyond this rang the precipitation reduces (Chen et al., 2017) (Figure 20 and Table 19).

From analyzing the Table 19 and Figure 20, the most suitable precipitant for each metal removal was selected. First, the best Metal Removal Efficiency ($R_{\text{Metal}}\%$) and the smaller Remaining Metal Concentration or Residual Metal concentration (RM_{Metal}) were selected, after that the pair (Optimum Dosage “OD”; Optimum pH “OpH”) was determined.

Table 19 Precipitation behavior of individual Cu(II), Cd(II), and Zn(II) by varying precipitating agent doses. ($\text{Cu(II)}_0 = \text{Cd(II)}_0 = \text{Zn(II)}_0 = 100 \text{ mg/L}$)

Precipitating agent	Dose (mg/L)	Final pH _{Cu}	Final pH _{Ca}	Final pH _{Zn}	Cu Removal (%)	Cd Removal (%)	Zn Removal (%)
Ca(OH) ₂	80	5.38	8.02	6.93	83.20	55.80	53.69
	100	5.92	9.35	7.00	94.18	72.30	59.52
	200	9.98	11.01	10.98	99.99	91.38	96.49
	400	10.78	11.39	12.02	99.99	99.99	93.41
	600	11.12	11.62	12.31	99.99	99.99	83.51
	1000	11.45	12.01	12.64	100	99.99	59.02
NaOH	80	5.82	7.64	6.77	72.29	98.32	58.85
	100	6.02	8.96	6.81	91.39	99.80	64.30
	200	10.54	9.94	10.44	99.99	99.99	99.04
	400	11.21	10.56	11.76	99.99	99.99	93.95
	600	11.52	10.86	11.93	99.99	99.99	91.26
	1000	11.79	11.18	12.50	99.99	99.99	65.56
Na ₂ CO ₃	80	6.91	9.55	7.11	91.45	93.35	79.13
	100	7.38	9.87	7.44	92.44	98.64	94.56
	200	9.88	10.4	10.02	99.96	99.83	96.30
	400	10.46	10.69	10.62	99.99	99.96	97.39
	600	10.66	10.86	10.99	99.99	99.97	96.96
	1000	10.87	11.02	11.07	99.99	99.98	96.95

Note: colored results referred to the best removal of each metal (Cu with bleu, Cd with yellow and Zn with green).

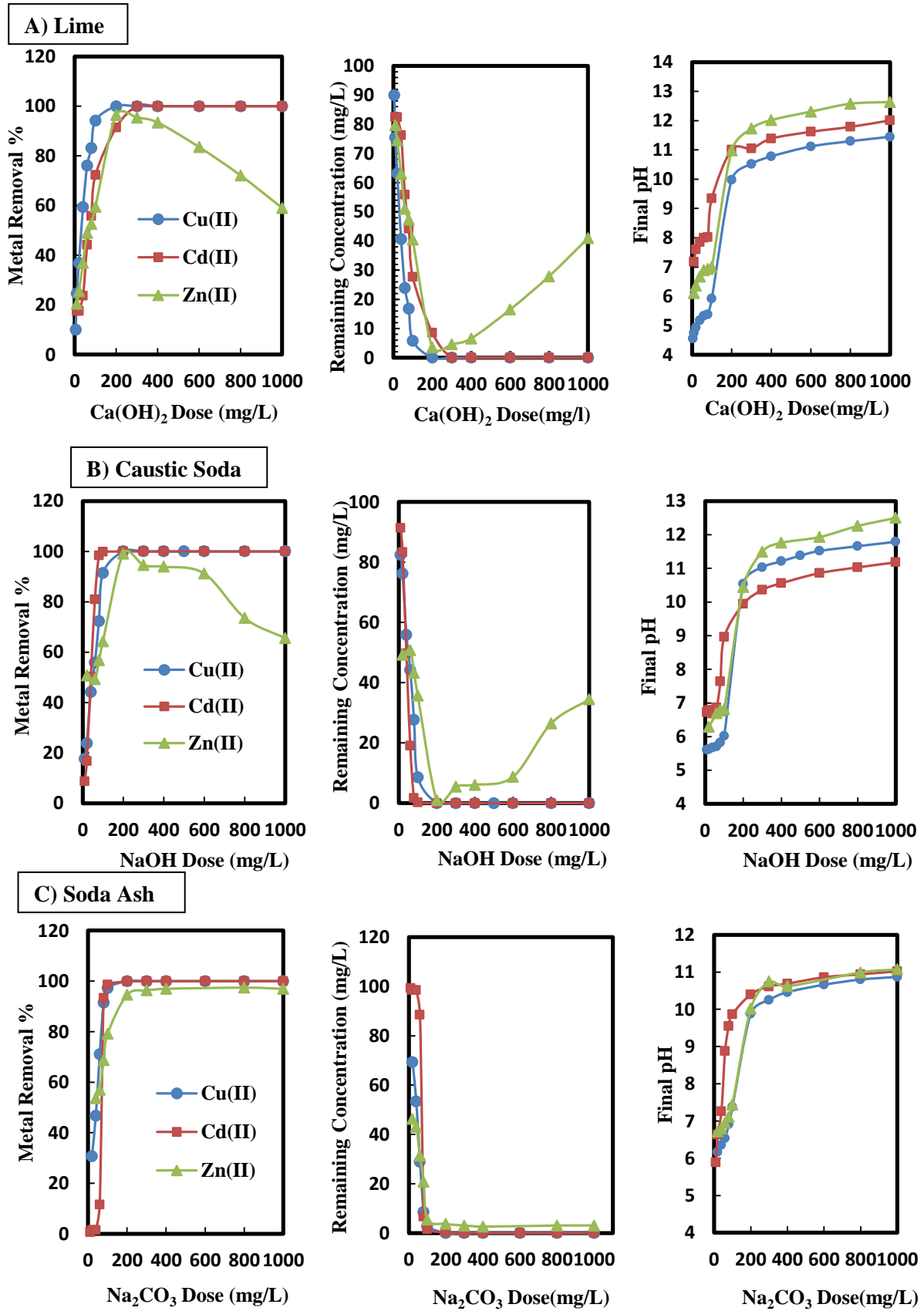


Figure 20 Effect of the precipitating agent dose (A, B and C) in the removal of 100 mg/l of individual metals (Cu(II),Cd(II) and Zn(II)).

Starting with Copper(II), it should be noted that $MCL_{Cu} = 0.5 \text{ mg/L}$ (JORA, 2006), as shown in Table 19, the results of the removal of Cu(II) were quite similar using the 3 precipitating agents by an efficiency of more than 99.99 %.

By using $Ca(OH)_2$, the Residual of Cu concentration ($RM_{Cu/Ca(OH)_2}$) was equal to $2.28 \times 10^{-5} \text{ mg/L}$, and the OD and OpH are (200 mg/L ; 9.98).

For NaOH, the $RM_{Cu/NaOH}$ was $4.78 \times 10^{-6} \text{ mg/L}$ by an OD and OpH (200 mg/L ; 10.54). However, for Na_2CO_3 , the RM_{Cu/Na_2CO_3} was $7.35 \times 10^{-3} \text{ mg/L}$ by an OD and OpH (400 mg/L ; 10.46). The RM_{Cu} using the 3 precipitating agents was conformed to the MCL_{Cu} set by the Algerian regulations. From these results, it is clear that lime and Caustic soda are the suitable precipitating agents for these two reasons:

$$OD_{Ca(OH)_2} \text{ and } OD_{NaOH} < OD_{Na_2CO_3}$$

$$RM_{Cu/Ca(OH)_2} \text{ and } RM_{Cu/NaOH} < RM_{Cu/Na_2CO_3} < MCL_{Cu}$$

Next metal is Cadmium(II), it should be noted that $MCL_{Cd} = 0.2 \text{ mg/L}$ (JORA, 2006), as can be seen in Table 19, the results of the Cd(II) removal were quite similar using the 3 precipitating agents by an efficiency of more than 99.97%.

By using $Ca(OH)_2$, the $R_{Cd}\%$ was more than 99.99%, RM_{Cd} is equal to $5.40 \times 10^{-7} \text{ mg/L}$ and the OD and OpH (400 mg/L ; 11.39).

For NaOH, the $R_{Cd}\%$ was also more than 99.99%, the RM_{Cd} was $4.78 \times 10^{-6} \frac{\text{mg}}{\text{L}}$ by an optimum dosage and pH (200 mg/L ; 9.94).

However, for Na_2CO_3 , the $R_{Cd}\%$ was not more than 99.97 % and the RM_{Cu} was 0.04 mg/L by an OD and pH (400 mg/L ; 10.69). The RM_{Cd} using the 3 agents was conform to the MCL_{Cd} . From these results, it is clear that Caustic soda is the suitable precipitant for these reasons:

$$OD_{NaOH} < OD_{Ca(OH)_2} \text{ and } OD_{Na_2CO_3}$$

$$OpH_{NaOH} < OpH_{Na_2CO_3} < OpH_{Ca(OH)_2}$$

$$RM_{Cd/Ca(OH)_2} \text{ and } RM_{Cd/NaOH} < RM_{Cd/Na_2CO_3} < MCL_{Cd}$$

The other metal is the Zinc(II), it should be noted that $MCL_{Zn} = 3 \text{ mg/L}$ (JORA, 2006) as shown in Table 19, the results of the removal of Zn(II) were different using the 3 precipitating agents, less efficiency, not like the removal of Cu(II) and Cd(II), and it was difficult to reach the maximum removal because the precipitation zone of Zn(II) is narrow, pH [9.5 ; 10.5]. A

rise in pH from 10.6 to 12 caused an increase in the dissolved Zn(II) concentration from 0.96 mg/L to more than 34 mg/L. These increases were due to the dissolution of amphoteric $Zn(OH)_2$ at a high solution pH (Wang et al., 2016).

By using $Ca(OH)_2$, the $R_{Zn}\%$ was 96.49% , the RM_{Zn} was equal to $3.51 > 3 \text{ mg/L}$ (MCL_{Zn}) and the OD and OpH is (200 mg/L ; 10.98). For NaOH, the $R_{Zn}\%$ was also more than 99.04%, the RM_{Zn} was $0.96 < 3 \text{ mg/L}$ by an OD and OpH (200 mg/L ; 10.44). For Na_2CO_3 , the $R_{Zn}\%$ was not more than 97.39 % , with $2.61 < 3 \text{ mg/L}$ of RM_{Zn} by an OD and OpH (400 mg/L ; 10.62).

The Removal of Zn, using caustic soda and soda ash, was conforming to the MCL_{Zn} ; While, the remaining Zn by using lime was superior than the MCL_{Zn} . From the previous results, it is clear that Caustic soda is the suitable precipitant for the removal of Zn(II) for these reasons:

$$OpH_{NaOH} < OpH_{Na_2CO_3} < OpH_{Ca(OH)_2}$$

$$R_{Zn/NaOH}\% > R_{Zn/Na_2CO_3}\% > R_{Zn/Ca(OH)_2}\%$$

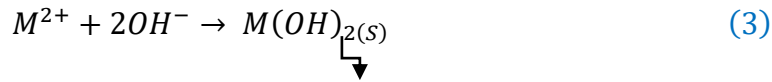
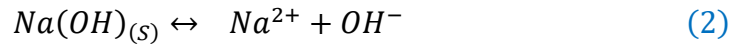
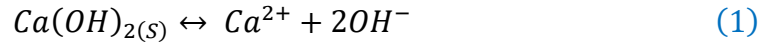
$$RM_{Cu/NaOH} < RM_{Cu/Na_2CO_3} < MCL_{Zn} < RM_{Cu/Ca(OH)_2}$$

From these experiments we conclude that:

- ✓ Caustic soda was more effective than lime and soda ash in the removal of individual metals (Cu, Cd, and Zn), this confirms that the choice of precipitating agent is very important in the heavy metal removal.
- ✓ The maximum precipitation of Zn occurred in the pH range [10 _11], in this range the solubility of the various metal hydroxides is minimized and beyond this range the hydroxide-metal complex re-solubilizes, which implies the difficulty of achieving maximum removal of all metals simultaneously (Ain Zainuddin et al., 2019 ; Wang et al., 2009).
- ✓ The use of chemical precipitation for removing Cu(II), Cd(II), and Zn(II) in synthetic solution was done successfully.

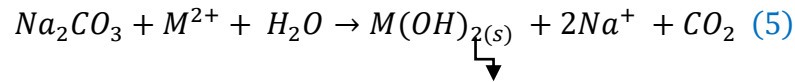
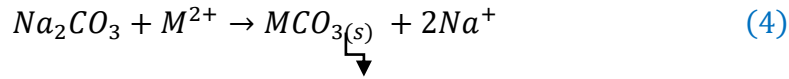
II.2.2 Mechanisms of precipitation

The principles of treatment using hydroxide precipitants (lime and caustic soda) are neutralization and precipitation of the hydroxides (Eqs. 1, 2 and 3) (Wang et al., 2016 ; Tchobanoglous et al., 2003).



↓
→ Particle growth and separation

Using Na_2CO_3 , the reaction of precipitation is shown by Eqs. (4) or (5):



Where M^{2+} represents the dissolved metal ions (Cu(II), Cd(II), and Zn(II)) and OH^{-} present the precipitating agents ($Ca(OH)_2$ and $NaOH$), while $M(OH)_2$ and MCO_3 are the insoluble metal-hydroxide and carbonate.

Eq. (4) may not occur, and the precipitation mechanism could be described by Eq. (5). According to (Chen et al., 2018), in the presence of Na_2CO_3 the removal of copper by adsorption on $CaCO_3$ is possible, but the reaction between Cu(II), OH^{-} and CO_3^{2-} would be more predominant and the formation of $Cu(OH)_2$ (94.5%) would be more remarkable by than that of $CuCO_3$ (5%).

II.2.3 Effect of metal concentration

Always with jar tests, the precipitating agent was fixed at 80 mg/L, and increases concentrations from each metal (10 to 200 mg/L) have used, then following the variation of remaining metal and final pH (Figure 21), the results of final pH, removal efficiency and residual metal were presented in Table 20.

By analyzing the results presented in Table 20 and Figure 21, focusing on the remaining metal and on the final pH. So, by increasing the metal concentration, the final pH decreases which means the remaining metal increases and the metal removal decreases.

Table 20 Effect of varying the concentration of Cu(II), Cd(II), and Zn(II), by using 80 mg/L of different precipitating agents.

Precipitating agent	M ²⁺ Content (mg/L)	Final pH _{Cu}	Final pH _{Cd}	Final pH _{Zn}	Cu Removal (%)	Cd Removal (%)	Zn Removal (%)
Ca(OH) ₂	10	9.85	10.59	10.90	99.99	99.60	61.31
	20	9.71	10.29	10.85	99.99	99.70	82.49
	40	9.17	10.16	10.31	99.99	99.82	92.97
	60	7.37	10.03	9.04	99.98	99.90	83.42
	100	5.68	8.2	6.96	83.20	59.45	60.48
	200	5.27	7.82	6.89	53.75	58.90	59.94
NaOH	10	10.29	10.79	10.65	99.99	99.78	97.70
	20	9.96	10.59	9.89	99.99	99.86	93.09
	40	9.36	10.36	9.57	99.99	99.88	91.26
	60	7.81	10.45	7.12	99.31	99.92	90.00
	100	6.17	8.33	6.77	78.87	98.36	60.43
	200	5.75	8.19	6.42	47.50	69.88	78.68
Na ₂ CO ₃	10	9.97	10.08	9.96	99.99	99.22	94.88
	20	9.90	10.10	9.89	99.99	99.64	91.72
	40	9.57	9.97	9.61	99.99	99.70	97.58
	60	8.77	9.93	9.02	99.98	99.69	95.20
	100	6.64	9.68	7.03	97.11	99.60	69.37
	200	6.17	8.97	6.86	66.12	86.70	54.02

As a conclusion from these experiments, a good efficiency of metal removal requires an important amount of precipitating agent, a precipitant deficiency occurred, which affect the precipitation process. As a result, the dosage of the precipitating agent is very important to reach the maximum metal removal.

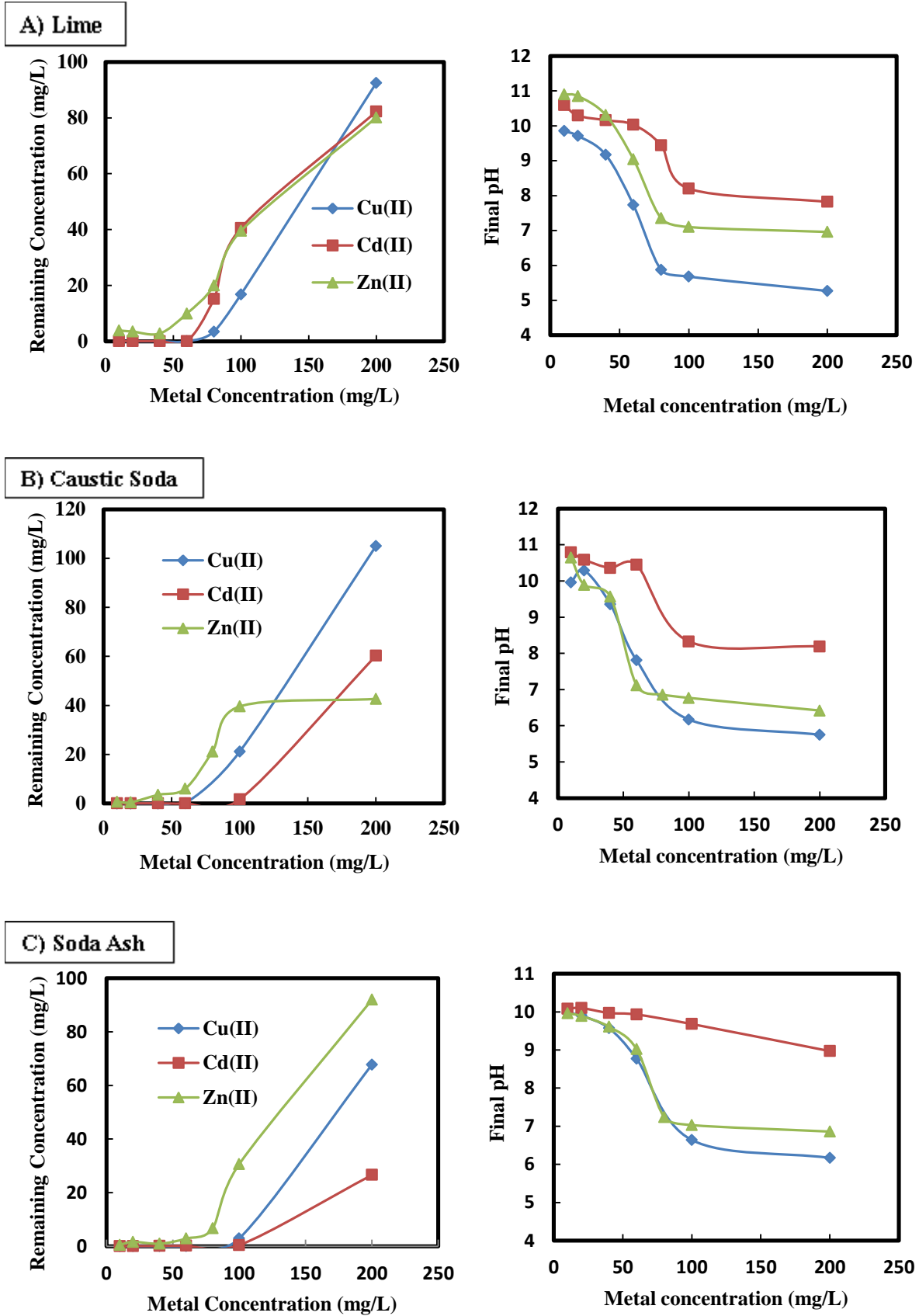


Figure 21 Studying the removal of individual Cu, Cd and Zn by the variation of metal concentration, using 80 mg/L of precipitating agents (A, B and C).

II.2.4 Effect of Initial pH

The experiments were carried out by varying the initial pH from 4 to 9 of the solutions to be treated, and by using 80 mg/L of the same precipitant. The initial content of each metal ion was set at 100 mg/L (Table 21 and Figure 22).

Table 21 Precipitation behavior of Cu(II), Cd(II), and Zn(II) by pH adjustment.

(Cu(II)₀ = Cd(II)₀ = Zn(II)₀ = 100 mg/L and 80mg/L of precipitating agent).

Precipitant	pH _i	Final pH _{Cu}	Final pH _{Cd}	Final pH _{Zn}	Cu Removal (%)	Cd Removal (%)	Zn Removal (%)
Ca(OH) ₂	4	5.54	8.38	7.52	83.87	79.00	58.65
	5	5.55	8.42	7.59	82.47	80.72	60.99
	6	9.83	8.63	7.57	99.99	95.64	67.88
	7	9.86	8.72	7.57	99.99	94.94	69.69
	8	9.91	9.49	10.50	99.99	99.32	97.42
	9	10.42	10.14	10.83	99.99	99.94	98.18
NaOH	4	5.51	8.76	7.72	80.95	90	71.82
	5	5.50	8.75	7.70	79.30	96.15	69.72
	6	9.77	9.88	7.71	99.99	99.80	78.84
	7	9.79	9.71	7.76	99.99	99.64	90.14
	8	9.86	9.85	10.86	99.99	99.82	99.05
	9	10.18	10.52	11	99.99	99.97	99.31
Na ₂ CO ₃	4	5.64	7.64	7.24	55.52	58.28	81.08
	5	5.81	7.61	7.29	61.90	58.28	81.42
	6	7.02	7.58	7.33	99.49	58.28	82.86
	7	9.33	7.56	7.45	99.99	54.88	86.51
	8	9.38	7.57	10.36	99.99	58.28	97.27
	9	9.47	9.49	10.54	99.99	99.56	98.29

Note: colored results in the table 21 referred to the best removal properties of each metal (Cu with bleu, Cd with Red and Zn with green).

From the results showed in the Table 21, it is clear that the gradual adjustment in the initial pH (pH_i) affects the final pH value (pH_f), it increases too. The results of these experiments confirm the results presented in Sect. II.2.1, the lime and the caustic soda were the suitable precipitants compared with soda ash for the removal of individual metals (Cu(II), Cd(II), and Zn(II)), with a little preference of caustic soda than lime (Table 21 and Figure 22).

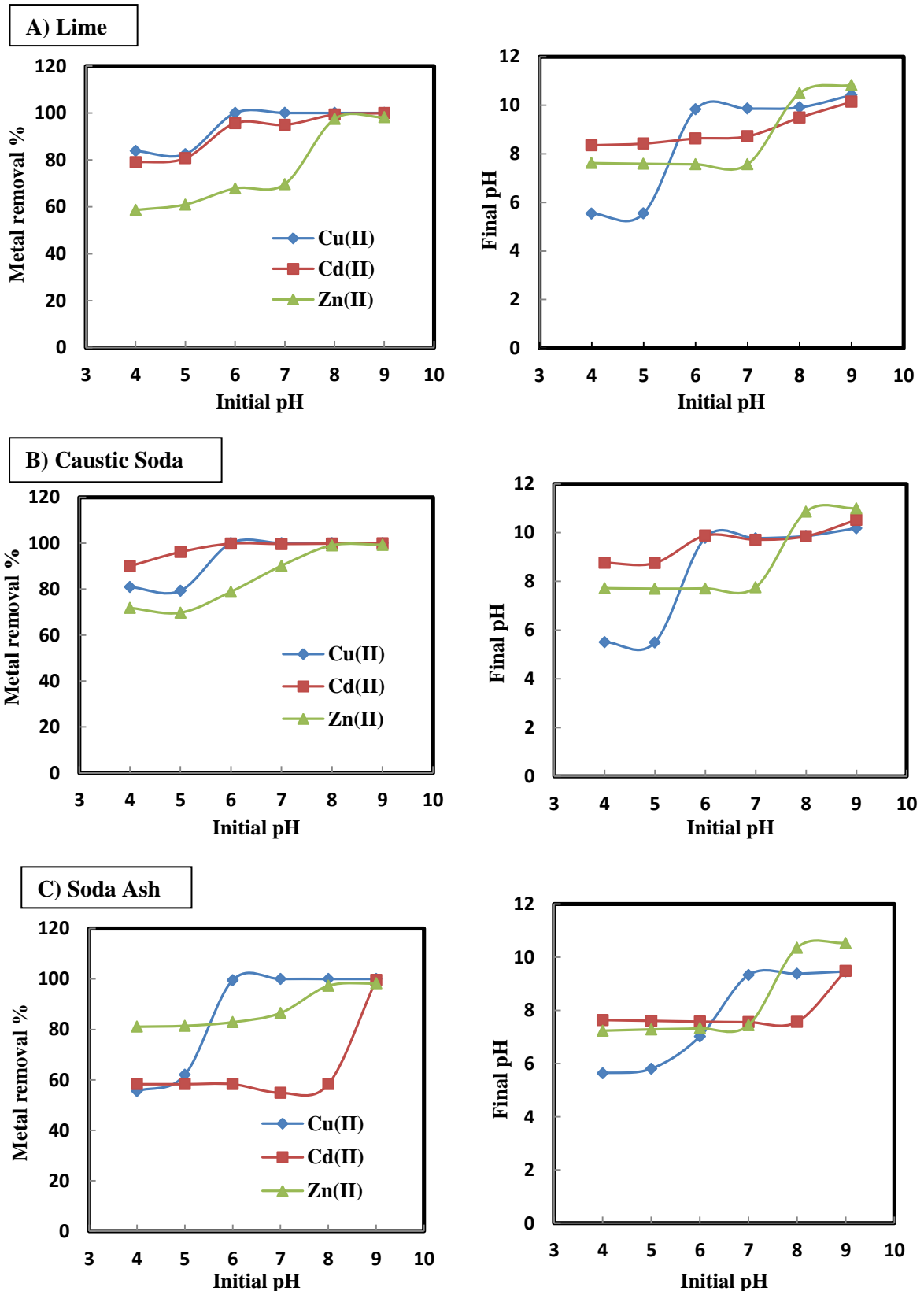


Figure 22 Effect of initial pH of synthetic solution on the removal of individual Cu(II), Cd(II), and Zn(II), using different precipitating agents (A,B and C). ($\text{Cu(II)}_0 = \text{Cd(II)}_0 = \text{Zn(II)}_0 = 100 \text{ mg/L}$; A = B = C = 80 mg/L).

The removal efficiency of Cu(II) is quite similar using the three precipitants (Figure 22). Adjusting the initial pH to 6 was sufficient to achieve the maximum removal (99.99%), in the meantime the final pH reached 9.80 when using Ca(OH)_2 and NaOH. However, for Na_2CO_3 , the maximum removal efficiency was performed at an initial pH = 7 and the final pH reached 9.33.

The removal of Cd(II) is almost similar using Ca(OH)_2 and NaOH, (Figure 22), the pH range of precipitation of Cd(II) is higher than that of Cu(II), that is why the maximum removal of Cd(II), $R_{\text{Cd}} \% > 99.90 \%$, was achieved at an alkaline pH ($\text{pH}_i = 9$; $\text{pH}_f = 10.14$ and 10.52 for Ca(OH)_2 and NaOH, respectively). However, for Na_2CO_3 , adjusting the initial pH to 9 was not sufficient to achieve the maximum Cd removal, as the remaining Cd concentration exceeded the MCL ($0.44 > 0.2 \text{ mg/L}$) and the $\text{pH}_f = 9.49 < 10$, it means that it is below the optimum pH for Cd precipitation.

Adjusting the pH to 9 was required to achieve the maximum removal of Zn(II). The maximum removal efficiencies were: 98.18 %, 98.29 % and 99.31%, for Ca(OH)_2 , Na_2CO_3 and NaOH successively. Whereas the minimum residual of Zn(II) was 1.82, 1.71, and 0.69 mg/L for the same precipitants. These residual concentrations are less than 3 mg/L and are therefore in accordance with the Algerian MCL standards. The pH_f was more than 10.50 and less than 11 for the three precipitants. At these conditions, the caustic soda is the suitable precipitant for Zn(II) removal.

It is important to note that adjusting the pH to above 10, can improve Cd(II) and Zn(II) removal in the presence of soda ash, as the final pH increases slowly.

The pH is the most important parameter affecting the removal of metals, also the nature of precipitant has a vital role in the removal efficiency (BrbootI et al., 2011 ; Chen et al., 2018 ; Charerntanyarak, 1999). As indicated in Section II.2.1, NaOH was the appropriate agent for the removal of individual metals (Cu(II), Cd(II), and Zn(II)).

Since the hydrolysis behavior of metal ions is known to influence precipitation processes (Oyaro et al., 2007), the solution speciation of Cu(II), Cd(II), and Zn(II) ions was modeled using the program Visual MINTEQ (Version 3.1) at 24 °C. Figure 23 and Table 22 show the presence of metals (copper, cadmium, and zinc) species according to pH variation. The increasing precipitation efficiency with an increase in pH in the range of 6 to 9 (Figures. 20, 22) was likely caused by the formation of hydroxide precipitation (Cu(OH)_2 , Cd(OH)_2 ,

and $Zn(OH)_2$) and hydroxide complexes of Cu(II), Cd(II), and Zn(II) such as $CuOH^+$, $Cu_2(OH)_2^{2+}$, $Cu(OH)_3^-$, $CdOH^+$, $Cd(OH)_3^-$, $ZnOH^+$, $Zn(OH)_3^-$, and $Zn(OH)_4^{2-}$.

Table 22 Cu, Cd, and Zn dominant species as function of pH (according to Fig. 22) using Visual MINTEQ (Version 3.1) at 24 °C ($Cu(II)_0 = Cd(II)_0 = Zn(II)_0 = 100$ mg/L)

pH	Dominant species	Observation
6 – 8	<ul style="list-style-type: none"> Cu^{2+}, $Cu_2(OH)_2^{2+}$ and $CuOH^+$ Cd^{2+} Zn^{2+} and $ZnOH^+$ 	<ul style="list-style-type: none"> Decrease of Cu^{2+}, in the meantime $Cu_2(OH)_2^{2+}$ and $CuOH^+$ were formed. Cd^{2+} was stable. Decrease of Zn^{2+} (from 100% to 90%) and $ZnOH^+$ were formed.
8 – 10	<ul style="list-style-type: none"> $Cu(OH)_2$ and $CuOH^+$ $Cd(OH)_2$ and $CdOH^+$ $Zn(OH)_2$ 	<ul style="list-style-type: none"> Precipitation of Copper was started by the formation of $Cu(OH)_2$, in the meantime $CuOH^+$ was constant and (Cu^{2+}, $Cu_2(OH)_2^{2+}$) disappeared. Decrease of Cd^{2+}, in that time $Cd(OH)_2$ and $CdOH^+$ were formed. Increase of $Zn(OH)_2$, it reached the maximum level at pH=10, in the meantime Zn^{2+} and $ZnOH^+$ were disappeared.
10 – 12	<ul style="list-style-type: none"> $Cu(OH)_3^-$ $Cd(OH)_2$ $Zn(OH)_2$ and $Zn(OH)_3^-$ 	<ul style="list-style-type: none"> Dissolution of $Cu(OH)_2$ and $CuOH^+$, in the meantime $Cu(OH)_3^-$ was formed. Increase of $Cd(OH)_2$ reaching the maximum level at pH=11.6, in that time $CdOH^+$ decreased after that it disappear at pH= 12. Dissolution of $Zn(OH)_2$, in the meantime $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ were formed.
> 12	<ul style="list-style-type: none"> $Cu(OH)_4^{2-}$ and $Cu(OH)_3^-$ $Cd(OH)_3^-$ and $Cd(OH)_4^{2-}$ $Zn(OH)_4^{2-}$ and $Zn(OH)_3^-$ 	<ul style="list-style-type: none"> Formation of $Cu(OH)_4^{2-}$, while $Cu(OH)_3^-$ was decreasing. Dissolution of $Cd(OH)_2$, while on the other hand the formation of $Cd(OH)_3^-$ and $Cd(OH)_4^{2-}$ Disappear of $Zn(OH)_2$ and $Zn(OH)_3^-$, and the formation of $Zn(OH)_4^{2-}$.

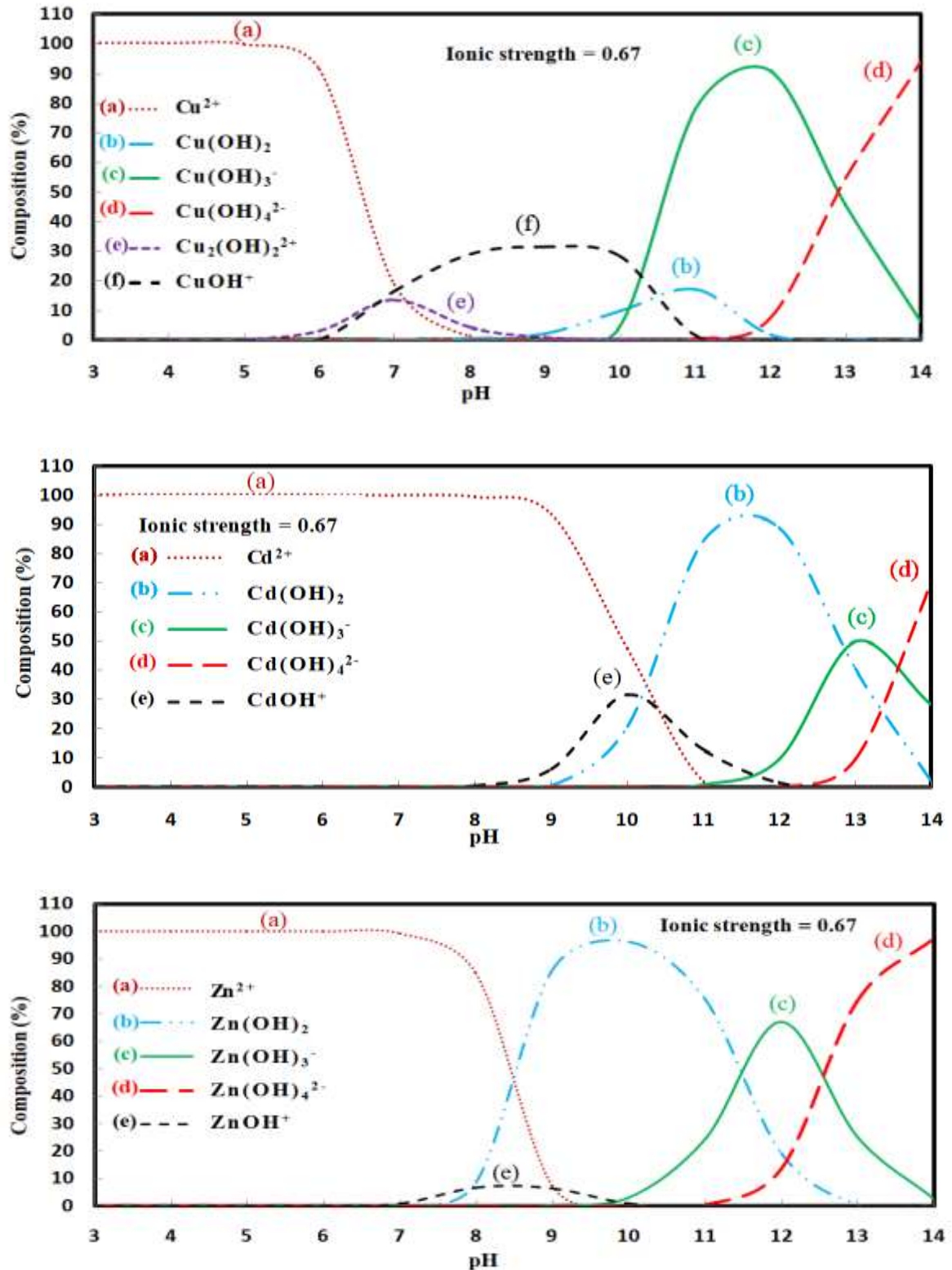


Figure 23 Speciation diagram of Cu, Cd, and Zn in an aqueous solutions system, by Visual MINTEQ (Version 3.1) at 24 °C ($\text{Cu}(\text{II})_0 = \text{Cd}(\text{II})_0 = \text{Zn}(\text{II})_0 = 100 \text{ mg/L}$).

II.3 Heavy metals combination (Cu, Cd, and Zn) removal

II.3.1 Effect of precipitating agent dose

The same Jar test conditions as those used previously have repeated (Section II.2.1), but in this case by combining the three metals: Copper, Cadmium, and Zinc in the synthetic solution and using a similar concentration of 100 mg/L of each metal at 24°C and $\text{pH}_i = 4.68 \pm 0.1$. To optimize the dosage of the precipitating agent (Ca(OH)_2 , NaOH, or Na_2CO_3), the effect of varying each precipitating agent from 10 to 1000 mg/L was tested.

The results of the final pH, the remaining metal concentration and the removal efficiency of the metal for the precipitant dosages (80, 100, 200, 300, and 1000 mg/L) are presented in Table 23 and Figure 24.

Table 23 Precipitation behavior of combined Cu(II), Cd(II), and Zn(II) by varying precipitating agent doses. ($\text{Cu(II)}_0 = \text{Cd(II)}_0 = \text{Zn(II)}_0 = 100 \text{ mg/L}$)

Precipitating agent	Dose (mg/L)	Final pH	Cu Removal (%)	Cd Removal (%)	Zn Removal (%)
Ca(OH)_2	80	6.03	95.58	93.95	9.61
	100	6.14	95.96	94.06	27.44
	200	6.58	98.01	94.73	52.36
	400	10.73	99.88	99.80	96.29
	600	11.45	99.82	99.988	87.98
	1000	11.93	99.39	99.995	65.04
NaOH	80	6.76	97.55	94.25	14.20
	100	6.88	98.79	94.63	27.77
	200	9.92	99.43	99.27	92.22
	400	11.01	99.78	99.96	95.09
	600	11.57	99.82	99.992	86.44
	1000	11.91	99.48	99.97	65.54
Na_2CO_3	80	6.45	93.97	94.77	33.86
	100	6.15	96.79	96.75	59.63
	200	7.22	98.97	99.49	93.34
	400	9.85	99.50	99.96	99.27
	600	10.28	99.69	99.98	97.11
	1000	10.60	99.34	84.36	45.79

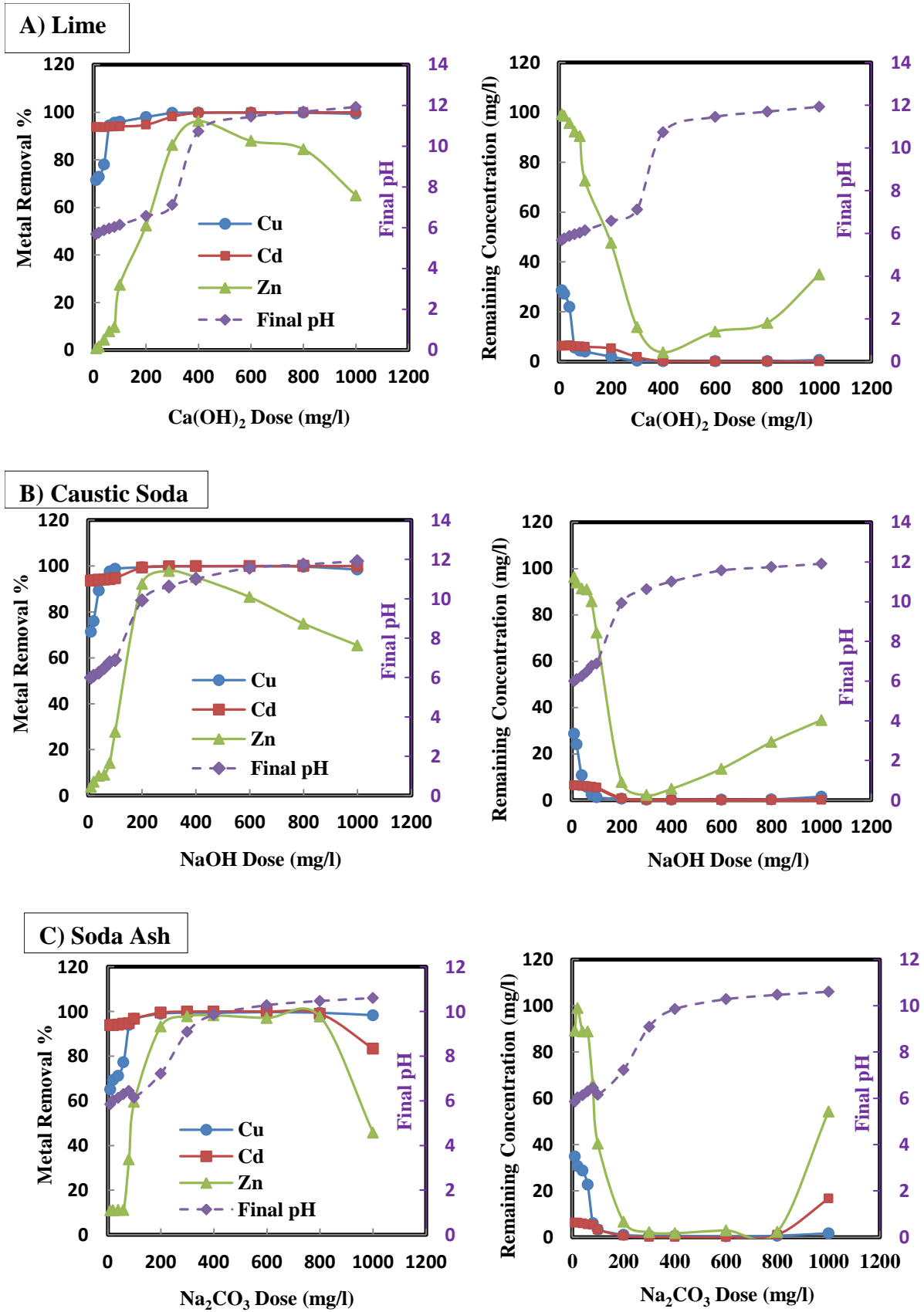


Figure 24 Effect of precipitating agents dose (A , B and C) on the removal of combined metals (Cu(II)₀ = Cd(II)₀= Zn(II)₀ = 100 mg/L each one).

The optimum dose “OD” is the dose that gives the best removal of the three metals together.

After analyzing the results of [Table 23](#) and [Figure 24](#), the results will be discussed as follow:

✓ **Precipitating agent [≤ 100 mg/L]**

At $6 < \text{pH}_f < 7$, an important removal efficiency have reached, not less than 94%, of Cu(II) and Cd(II) using the three precipitants. However, for Zn(II) the removal efficiency is very low not more than 60 %, and this confirms that such metal has his specific pH range for precipitation beyond this range the precipitation decreases. This result confirms the findings of [BrbootI et al., \(2011\)](#) and [Ain Zainuddin et al., \(2019\)](#).

✓ **Precipitating agent [100 - 200 mg/L]**

By increasing the dose of Ca(OH)_2 to 200 mg/L the pH_f is below 7, this pH value is not enough to remove Zn. In contrast, the final pH of Na_2CO_3 and NaOH exceed 7 , (7.22 and 9.92 successively), which improve a good Zn removal efficiency ($R_{\text{Zn}/\text{Na}_2\text{CO}_3} = 93.43$; $R_{\text{Zn}/\text{NaOH}} = 92.22$).

✓ **Precipitating agent [= 400 mg/L]**

For lime, It is clear that 400 mg/L of Ca(OH)_2 at $\text{pH}=10.73$, is the optimum dose, because it gave the maximum removal of Zn(II), $R_{\text{Zn}/\text{Ca(OH)}_2} \% = 96.29 \%$, and a very good removal of Cu(II) and Cd(II), 99.88 % and 99.80 % , respectively. This is supported by very low residual Cu(II) and Cd(II) concentrations, respecting the MCL set by the Algerian standards. But the remaining concentration of Zn(II) exceeded the MCL.

Cu: $0.12 \text{ mg/L} < 0.5 \text{ mg/L} \longrightarrow \text{RM}_{\text{Cu}/\text{Ca(OH)}_2} < \text{MCL}_{\text{Cu}} \longrightarrow \text{MCL respected}$

Cd: $0.2 \text{ mg/L} = 0.2 \text{ mg/L} \longrightarrow \text{RM}_{\text{Cd}/\text{Ca(OH)}_2} = \text{MCL}_{\text{Cd}} \longrightarrow \text{MCL respected}$

Zn: $3.71 \text{ mg/L} > 3 \text{ mg/L} \longrightarrow \text{RM}_{\text{Zn}/\text{Ca(OH)}_2} > \text{MCL}_{\text{Zn}} \longrightarrow \text{MCL not respected}$

For caustic soda, 400 mg/L of NaOH at $\text{pH}=11.01$ is also the optimum dose for the removal of the combined metals. The maximum removal of Zn(II) were reached, $R_{\text{Zn}/\text{NaOH}} = 95.09\%$, and a good removal of Cu(II) and Cd(II), 99.78% and 99.96%, respectively. For the RM_{Zn} concentration slightly exceeded the MCL.

Cu: $0.22 \text{ mg/L} < 0.5 \text{ mg/L} \longrightarrow \text{RM}_{\text{Cu}/\text{NaOH}} < \text{MCL}_{\text{Cu}} \longrightarrow \text{MCL respected}$

Cd: $0.04 \frac{\text{mg}}{\text{L}} < 0.2 \text{ mg/L} \longrightarrow \text{RM}_{\text{Cd}/\text{NaOH}} = \text{MCL}_{\text{Cd}} \longrightarrow \text{MCL respected}$

Zn: $4.91 \text{ mg/L} > 3 \text{ mg/L} \longrightarrow \text{RM}_{\text{Zn}/\text{NaOH}} > \text{MCL}_{\text{Zn}} \longrightarrow \text{MCL not respected}$

For soda Ash, as the previous precipitating agents, 400 mg/L is the optimum dose for the removal of the three combined metals, the results show a good removal efficiency, 99.50%, 99.96% and 99.27% for the three metals Cu(II), Cd(II), and Zn(II) respectively. All metals meet the Maximal allowable metal concentration.

Cu: $0.5 \text{ mg/L} = 0.5 \text{ mg/L} \longrightarrow \text{RM}_{\text{Cu}/\text{Na}_2\text{CO}_3} = \text{MCL}_{\text{Cu}} \longrightarrow \text{MCL respected}$

Cd: $0.04 \text{ mg/L} < 0.2 \text{ mg/L} \longrightarrow \text{RM}_{\text{Cd}/\text{Na}_2\text{CO}_3} < \text{MCL}_{\text{Cd}} \longrightarrow \text{MCL respected}$

Zn: $0.73 \text{ mg/L} < 3 \text{ mg/L} \longrightarrow \text{RM}_{\text{Zn}/\text{Na}_2\text{CO}_3} < \text{MCL}_{\text{Zn}} \longrightarrow \text{MCL respected}$

✓ **Precipitating agent [> 400 mg/L]**

By using more than 400 mg/L of precipitants at a final pH exceeded 10.5 , the removal of Zn decreased. This decrease was due to the dissolution of Zinc hydroxide, and the formation of soluble metal hydroxide complexes ($\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$), that can increase metal's solubility (see next [Table 25/ Figure 26](#)). The same idea was explained by [Chen et al., \(2018\)](#).

From the previous results, it is clear that soda ash is more effective than lime and caustic soda in removing the combined metal ions (Cu, Cd, and Zn), the following results confirm this conclusion.

- **Removal efficiency comparison (R%) at 400 mg/L of precipitants**

Cu: $99.88\% \geq 99.78\% > 99.48\% \longrightarrow \text{R}_{\text{Cu}/\text{Ca}(\text{OH})_2} \% \geq \text{R}_{\text{Cu}/\text{NaOH}} \% > \text{R}_{\text{Cu}/\text{Na}_2\text{CO}_3} \%$

Cd: $99.96\% = 99.96\% > 99.80\% \longrightarrow \text{R}_{\text{Cd}/\text{Na}_2\text{CO}_3} \% = \text{R}_{\text{Cd}/\text{NaOH}} \% > \text{R}_{\text{Cd}/\text{Ca}(\text{OH})_2} \%$

Zn: $99.27\% \geq 96.29\% > 95.09\% \longrightarrow \text{R}_{\text{Zn}/\text{Na}_2\text{CO}_3} \% \geq \text{R}_{\text{Zn}/\text{Ca}(\text{OH})_2} \% > \text{R}_{\text{Zn}/\text{NaOH}} \%$

- **Remaining metal comparison (RM_{Metal}) at 400 mg/L of precipitants**

Cu: $0.12 < 0.22 < 0.52 \frac{\text{mg}}{\text{L}} \approx 0.5 \frac{\text{mg}}{\text{L}} \longrightarrow \text{RM}_{\text{Cu}/\text{Ca}(\text{OH})_2} < \text{RM}_{\text{Cu}/\text{NaOH}} < \text{RM}_{\text{Cu}/\text{Na}_2\text{CO}_3} \approx \text{MCL}_{\text{Cu}}$

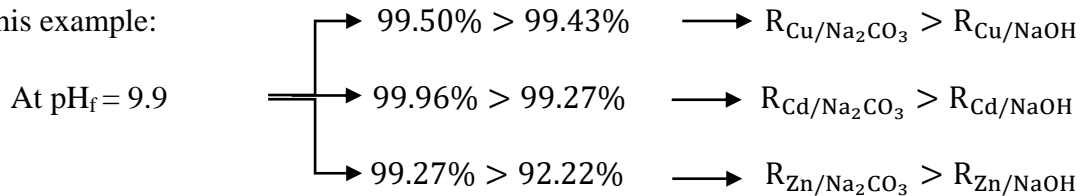
Cd: $0.04 = 0.04 < 0.2 \frac{\text{mg}}{\text{L}} = 0.2 \frac{\text{mg}}{\text{L}} \longrightarrow \text{RM}_{\text{Cd}/\text{Na}_2\text{CO}_3} = \text{RM}_{\text{Cd}/\text{NaOH}} < \text{RM}_{\text{Cd}/\text{Ca}(\text{OH})_2} = \text{MCL}_{\text{Cd}}$

Zn: $0.73 < 3 < 3.71 < 4.91 \frac{\text{mg}}{\text{L}} \longrightarrow \text{RM}_{\text{Zn}/\text{Na}_2\text{CO}_3} < \text{MCL}_{\text{Zn}} < \text{RM}_{\text{Zn}/\text{Ca}(\text{OH})_2} < \text{RM}_{\text{Zn}/\text{NaOH}}$

Na_2CO_3 is the only precipitant that respects the admissible values of the 3 metals Cu(II), Cd(II), and Zn(II). One of the important reasons for choosing soda ash as the best precipitating agent for the removal of combined metals is the good removal efficiency of

Zn(II), which can be related to the narrow pH range for Zn precipitation, also the final pH rise slowly in carbonate precipitation, in contrast to hydroxide precipitation, where the pH increases rapidly, particularly in the alkaline pH range, resulting in the rapid re-solubilization of the metal/hydroxide complex ($M(OH)_2$).

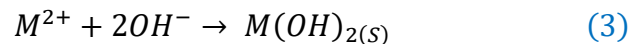
The type of precipitant is very important as the importance of pH, to improve that we use this example:



So even the pH was the same the removal was not the same.

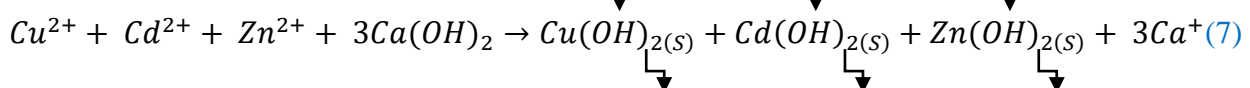
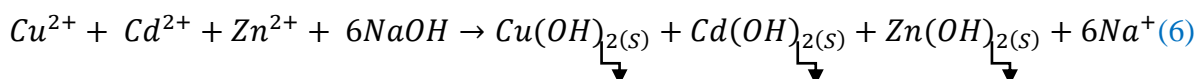
II.3.2 Mechanisms of precipitation

The basic mechanism of heavy metal removal by chemical precipitation using hydroxides (such as $Ca(OH)_2$ and $NaOH$) is presented in Eq. (3) (Wang et al., 2016), where M^{2+} represent the dissolved metal ions (Cu(II), Cd(II), and Zn(II)) and OH^- represent the precipitating agent ($Ca(OH)_2$ and $NaOH$), respectively, while $M(OH)_2$ is the insoluble metal hydroxide.

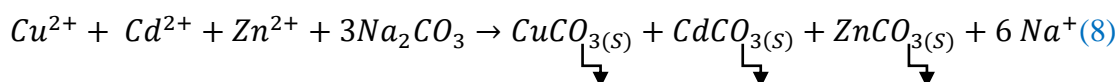


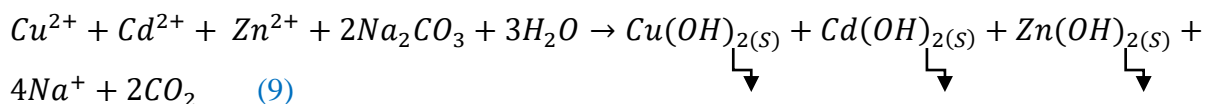
The mechanism is the same as seeing previously in Section II.2.2, but in this case heavy metals were combined together. Adjustment of pH to the basic conditions (pH 8 –11) is the important parameter that improves heavy metal removal by chemical precipitation (Brbootl et al., 2011).

For hydroxide precipitating agents ($Ca(OH)_2$ and $NaOH$), reaction of precipitation is shown by Eqs. (6) and (7):



For carbonate precipitating agents (Na_2CO_3), the reaction of precipitation is shown by Eqs. (8) or (9):





According to Chen et al., (2018), Eq. (8) may not occur, and the precipitation mechanism could be described by Eq. (9).

II.3.3 Effect of initial pH

By varying the initial pH (3 – 9) and by using 80 mg/L of the same precipitating agent, the removal of the combined metals (Cu, Cd, and Zn at $[M^{2+}] = 100$ mg/L for each ion) was investigated (Table 24 and Figure 25).

Table 24 Precipitation behavior of combined Cu(II), Cd(II), and Zn(II) by pH adjustment.

(Cu(II)₀ = Cd(II)₀ = Zn(II)₀ = 100 mg/L and 80mg/L of precipitating agent)

Precipitating agent	pH _i	Final pH	Cu Removal (%)	Cd Removal (%)	Zn Removal (%)
Ca(OH) ₂	3	6.28	69.11	93.46	5.99
	4	6.39	77.87	93.77	6.51
	6	6.52	93.13	94.07	7.00
	7	7.11	98.32	94.73	33.74
	8	10.14	99.61	99.39	95.17
	9	10.74	99.69	99.99	97.07
NaOH	3	6.58	78.14	94.35	7.16
	4	6.7	85.88	94.66	8.82
	6	6.96	96.26	94.51	11.40
	7	7.46	99.48	95.99	72.40
	8	10.52	99.52	99.36	94.30
	9	10.92	98.86	99.94	90.55
Na ₂ CO ₃	3	6.4	67.34	94.77	11.93
	4	6.51	71.74	95.06	10.85
	6	6.66	81.13	95.19	13.21
	7	7.41	97.71	96.56	32.48
	8	9.8	99.82	99.48	99.39
	9	10.09	99.83	99.97	99.10

Note: Colors are corresponding to the best removal in each part. Green to 1st part, yellow to 2nd part and blue to the 3rd part.

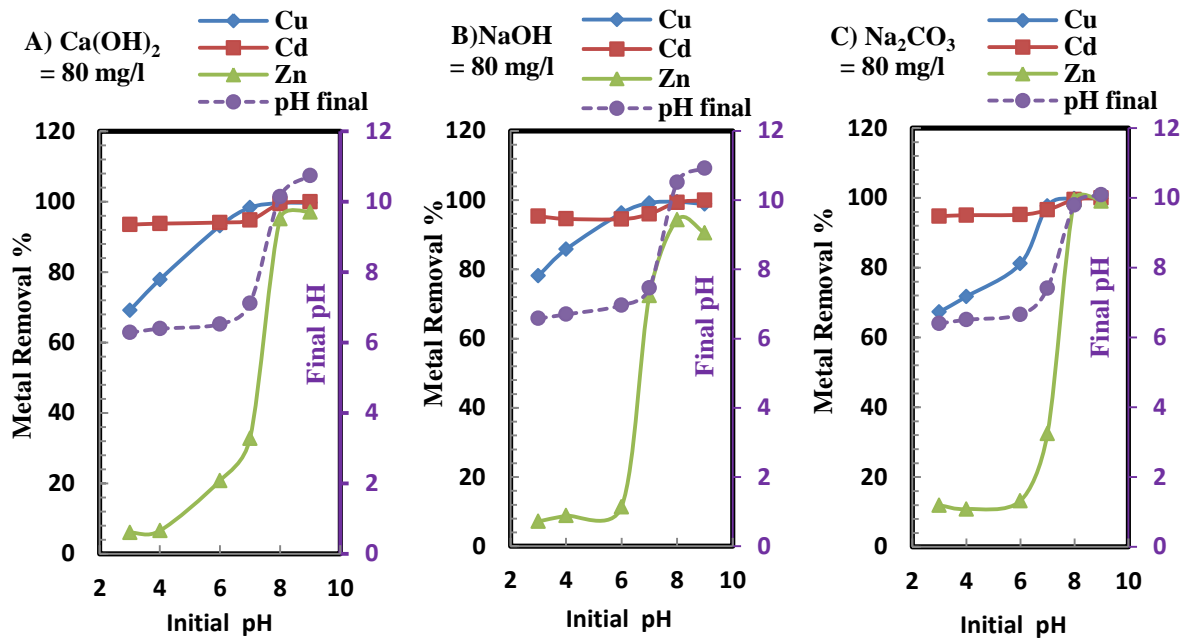


Figure 25 Effect of initial pH of synthetic solution on the removal of combined Cu(II), Cd(II) and Zn(II), using different precipitating agents (A, B and C). ($\text{Cu(II)}_0 = \text{Cd(II)}_0 = \text{Zn(II)}_0 = 100 \text{ mg/L}$; $A = B = C = 80 \text{ mg/L}$).

The results presented in Table 24 and Figure 25, can be discussed according to three initial pH ranges:

- ✓ $3 \leq \text{pH}_i \leq 6$: In this range the removal of metals increased by increasing the pH. The pH_f rises rapidly and reaches 6 from the first adjustment $\text{pH}_i = 3$. As a result we achieved a good Cu(II) and Cd(II) removal. The pH then gradually increased to a maximum of 6.96 using NaOH.

The use of NaOH provides the best removal results, 96.26% and 94.51 % of Cu(II) and Cd(II) successively. For Ca(OH)_2 , the removal was similar to NaOH. In the case of Na_2CO_3 the removal of Cu(II) and Cd(II) was lower than that of hydroxides, by 81% and 95% successively. However, the removal of Zn(II) was very low, less than 11%.

- ✓ $\text{pH}_i = 7$: The removal of all metals increased, still NaOH gives the best removal results compared to other precipitant, 99.48%, 95.99% and 72.40% for Cu(II), Cd(II), and Zn(II), respectively.
- ✓ $7 \leq \text{pH}_i \leq 9$: This is the main range of the three heavy metals precipitation. The final pH increased and exceeded 10, this pH range leads to more than 99% of metal removal. In order to choose the suitable precipitant, we have to take in consideration the MCL (maximal allowed values).

When the initial pH is equal to 9, the final pH reaches 10, this pH value is considered to be the ideal pH for precipitating all metals (Cu(II), Cd(II), and Zn(II)), and from the results it is clear that Na₂CO₃ is the appropriate precipitant for the following reasons (Table 24):

- **Removal efficiency comparison (R%) at pH_i = 9**

Cu: 99.83 % > 99.69 % > 98.86% → R_{Cu/Na₂CO₃} % > R_{Cu/Ca(OH)₂} % > R_{Cu/NaOH} %

Cd: 99.99 % > 99.97 % > 99.94 % → R_{Cd/Ca(OH)₂} % > R_{Cd/Na₂CO₃} % > R_{Cd/NaOH} %

Zn: 99.10 % > 97.07 % > 90.55 % → R_{Zn/Na₂CO₃} % > R_{Zn/Ca(OH)₂} % > R_{Zn/NaOH} %

- **Remaining metal comparison (RM) at pH_i = 9**

Cu: 0.17 < 0.31 < 0.48 < 0.5 $\frac{mg}{L}$ → RM_{Cu/Na₂CO₃} < RM_{Cu/Ca(OH)₂} < RM_{Cu/NaOH} < MCL_{Cu}

Cd: 0.01 < 0.03 < 0.2 < 0.64 $\frac{mg}{L}$ → RM_{Cd/Ca(OH)₂} < RM_{Cd/Na₂CO₃} < MCL_{Cd} < RM_{Cd/NaOH}

Zn: 0.90 < 2.93 < 3 < 5.7 $\frac{mg}{L}$ → RM_{Zn/Na₂CO₃} < RM_{Zn/NaOH} < MCL_{Zn} < RM_{Zn/Ca(OH)₂}

By using Na₂CO₃, all the remaining metal values were compatible with the MCL. In contrast, when Ca(OH)₂, and NaOH were used, it is very hard to reach the admissible value of Cd and Zn.

The final pH in the presence of Na₂CO₃ increased slowly compared to Ca(OH)₂ and NaOH by using the same initial pH, but the properties of soda ash give the ability to this agent to remove metals even in small pH compared with other hydroxide agents (Chen et al., 2018). Take example of pH_i= 8:

Ca(OH)₂ → pH_f = 10.14 → R_{Cu} = 99.61% , R_{Cd} = 99.39% and R_{Zn} = 95.17%

NaOH → pH_f = 10.52 → R_{Cu} = 99.52% , R_{Cd} = 99.36% and R_{Zn} = 94.30%

Na₂CO₃ → pH_f = 9.8 → R_{Cu} = 99.82% , R_{Cd} = 99.48% and R_{Zn} = 99.39%

With soda ash, although the pH_f was lower than that of lime and caustic soda samples, the removal was the best compared to them. Thus, the type of precipitating agent is also important and should be taken into account when removing combined heavy metals.

By using Visual MINTEQ program (Version 3.1), the results of metals (Cu, Cd, and Zn) speciation were compared (Figure 23 / Table 22 and Figure 26 / Table 25), it seems there is no huge difference between their removal individually and in combination.

Table 25 Cu, Cd, and Zn dominant species according to pH variation (according to Fig. 24) using Visual MINTEQ (Version 3.1) at 24 °C ($\text{Cu(II)}_0 = \text{Cd(II)}_0 = \text{Zn(II)}_0 = 100 \text{ mg/L}$)

pH	Dominant species	Observation
6 – 8	<ul style="list-style-type: none"> • $\text{Cu}^{2+}, \text{Cu}_2(\text{OH})_2^{2+}, \text{Cu}_3(\text{OH})_4^{2+}$ and CuOH^+ • Cd^{2+} • Zn^{2+} and ZnOH^+ 	<ul style="list-style-type: none"> • Decrease of Cu^{2+}, in the meantime $\text{Cu}_2(\text{OH})_2^{2+}$, $\text{Cu}_3(\text{OH})_4^{2+}$ and CuOH^+ were formed. • Cd^{2+} was stable. • Decrease of Zn^{2+} (from 98% to 80%) and ZnOH^+ were formed.
8 – 10	<ul style="list-style-type: none"> • $\text{Cu}_3(\text{OH})_4^{2+}$ and $\text{Cu}(\text{OH})_2$ • CdOH^+ and $\text{Cd}(\text{OH})_2$ • $\text{Zn}(\text{OH})_2$ 	<ul style="list-style-type: none"> • Disappear of CuOH^+ and $\text{Cu}_2(\text{OH})_2^{2+}$. In the other hand precipitation of Cu started by the formation of $\text{Cu}(\text{OH})_2$, and $\text{Cu}_3(\text{OH})_4^{2+}$ kept constant. • Decrease of Cd^{2+}, in that time CdOH^+ and $\text{Cd}(\text{OH})_2$ were formed. • Formation of $\text{Zn}(\text{OH})_2$, it reached the maximum level at pH=10, in the meantime Zn^{2+} and ZnOH^+ were disappeared.
10 – 12	<ul style="list-style-type: none"> • $\text{Cu}(\text{OH})_3^-$, $\text{Cu}(\text{OH})_2$ and $\text{Cu}(\text{OH})_4^{2-}$ • $\text{Cd}(\text{OH})_2$ • $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_2$ 	<ul style="list-style-type: none"> • $\text{Cu}(\text{OH})_2$ reached the maximum value at pH_f=11, in the meantime $\text{Cu}_3(\text{OH})_4^{2+}$ disappeared. Also $\text{Cu}(\text{OH})_3^-$ and $\text{Cu}(\text{OH})_4^{2-}$ were formed. • Increase of $\text{Cd}(\text{OH})_2$ reaching the maximum level at pH=11.6, and disappear of Cd^{2+} and CdOH^+. • Dissolution of $\text{Zn}(\text{OH})_2$ and the formation of $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$
> 12	<ul style="list-style-type: none"> • $\text{Cu}(\text{OH})_4^{2-}$ and $\text{Cu}(\text{OH})_3^-$ • $\text{Cd}(\text{OH})_3^-$ and $\text{Cd}(\text{OH})_4^{2-}$ • $\text{Zn}(\text{OH})_4^{2-}$ and $\text{Zn}(\text{OH})_3^-$ 	<ul style="list-style-type: none"> • Decrease of $\text{Cu}(\text{OH})_3^-$ tile disappear. However, $\text{Cu}(\text{OH})_4^{2-}$ keep increasing. • Dissolution of $\text{Cd}(\text{OH})_2$, on the other hand the formation of $\text{Cd}(\text{OH})_3^-$ and $\text{Cd}(\text{OH})_4^{2-}$. • Disappear of $\text{Zn}(\text{OH})_2$, $\text{Zn}(\text{OH})_3^-$, and $\text{Zn}(\text{OH})_4^{2-}$ keep increasing.

The differences according to Visual MINTEQ program (Version 3.1) diagrams:

- Occurrence of a new compound ($\text{Cu}_3(\text{OH})_4^{2+}$) in the metal combination, with a significant concentration. While, this compound is absent in the individual Cu diagram.
- CuOH^+ composition is very small in metal combination compared to individual Cu, maybe this is due to the occurrence of ($\text{Cu}_3(\text{OH})_4^{2+}$).
- All Cadmium compounds composition in metal combination are almost the half of its value in the cadmium alone, (Cd^{2+} , CdOH^+ , $\text{Cd}(\text{OH})_2$, $\text{Cd}(\text{OH})_3^-$, and $\text{Cd}(\text{OH})_4^{2-}$).

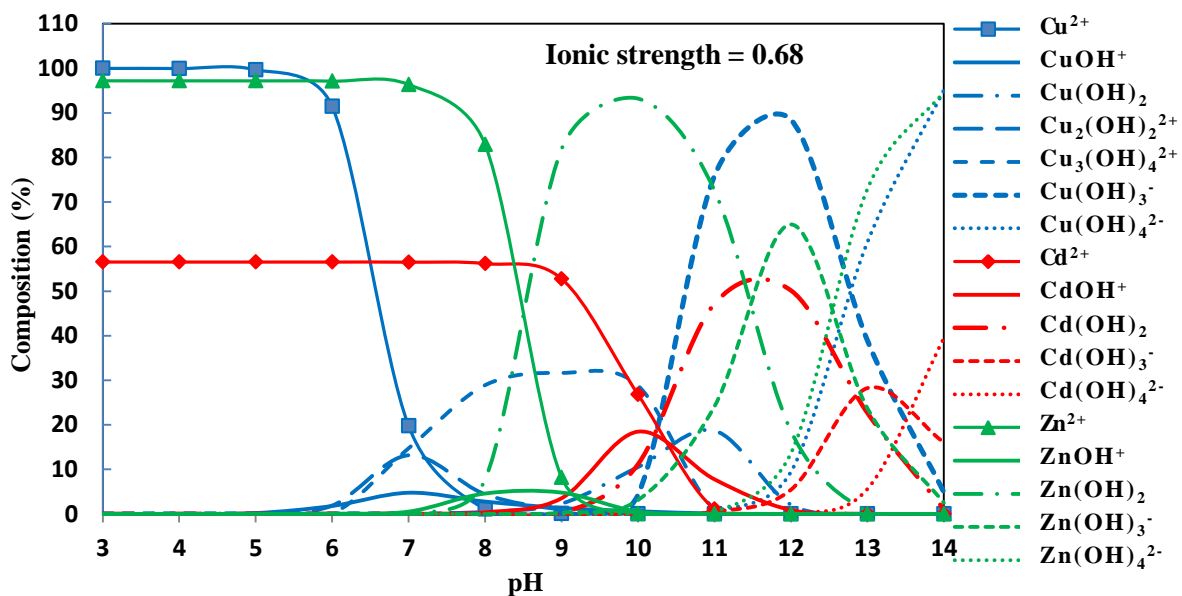


Figure 26 Speciation diagram of combined metals (Cu, Cd, and Zn) in an aqueous solutions system, by Visual MINTEQ (Version 3.1) at 24 °C ($\text{Cu}(\text{II})_0 = \text{Cd}(\text{II})_0 = \text{Zn}(\text{II})_0 = 100 \text{ mg/L}$).

II.3.4 Sludge System Analysis

Sludge was recovered and dried, while its volume (V) and precipitate mass (PM) were measured, after the treatment of combined metal in synthetic solution with $\text{Ca}(\text{OH})_2$, NaOH, and Na_2CO_3 . A measurement of the sludge volume and precipitate mass (PM) produced after one hour of settling time using 400 mg/L of the precipitating agent is shown in Figure 27. The best concentration for removing the combined metals is 400 mg/L. This concentration was chosen because the remaining levels of copper ($< 0.5 \text{ mg/L}$), cadmium ($< 0.2 \text{ mg/L}$), and zinc ($< 3 \text{ mg/L}$) were all within the Algerian standard for industrial wastewater as published in the

Official Journal of the Algerian Republic (JORA, 2006). Furthermore, the pH values of all the solutions containing precipitating agents (10.73 for $\text{Ca}(\text{OH})_2$, 11.01 for NaOH , and 9.85 for Na_2CO_3) were sufficient to achieve the lowest possible solubility of precipitation of carbonates and hydroxides. The sludge generated during the experiment was recovered after one hour of settling, indicating that settling time required is one of the most important factors in the treatment procedures since settling kinetic influences the treatment efficiency and performance (Brbootf et al., 2011). Chen et al., (2018) reported that lime and soda ash precipitation showed a fast-settling time of 60 minutes for zinc and copper aqueous solutions.

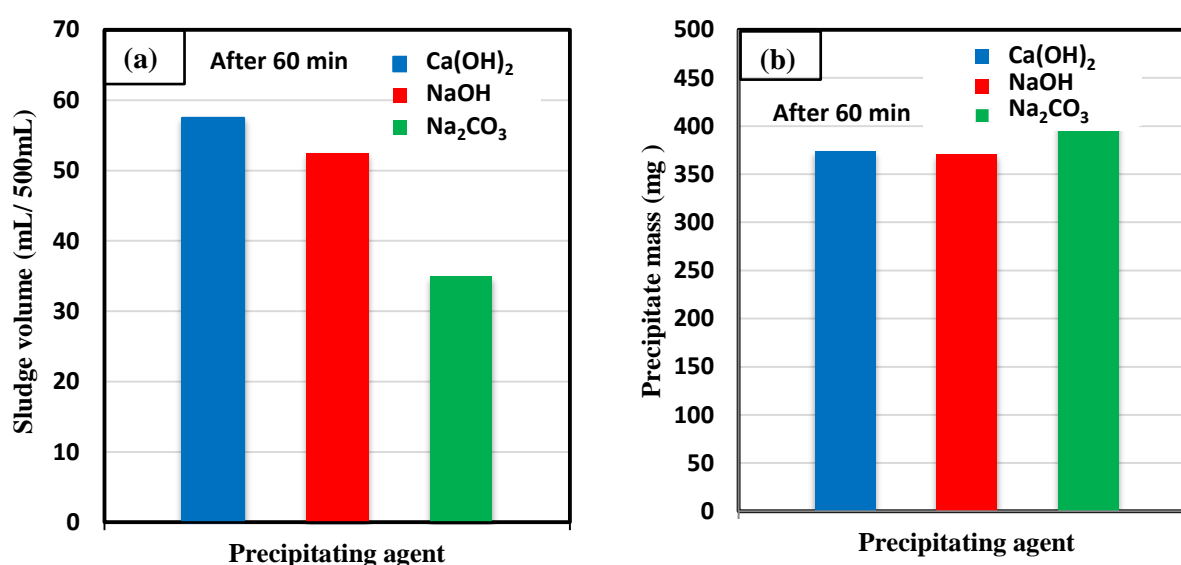


Figure 27 Sludge volume (a) and PM (b) generated by the use of 400 mg/L of precipitating agents after one hour of settling ($\text{Cu}(\text{II})_0 = \text{Cd}(\text{II})_0 = \text{Zn}(\text{II})_0 = 100 \text{ mg/L}$).

As shown in Figure 27(a), the volume of sludge produced by $\text{Ca}(\text{OH})_2$ was the largest and that produced by NaOH was also significant. While, the Na_2CO_3 sludge volume was less than that of the hydroxide precipitation, which resulted to:

$$V_{\text{Ca}(\text{OH})_2} > V_{\text{NaOH}} > V_{\text{Na}_2\text{CO}_3}$$

This result can be explained by the gelatinous nature of the sludge created from NaOH and $\text{Ca}(\text{OH})_2$, as well as the fact that the carbonate precipitates formed have a higher crystallinity than hydroxides, allowing for easier and faster recovery by decantation. As a result, the sludge's volume is reduced. Furthermore, Esmaeili and Vazirinejad, (2005) and Brbootf et al., (2011) made this claim, and Wang et al., (2005) verified.

As shown in [Figure 27\(b\)](#), the PM using Na_2CO_3 was the largest with a slight difference compared to PM for NaOH and $\text{Ca}(\text{OH})_2$. That means:

$$PM_{\text{Na}_2\text{CO}_3} > PM_{\text{Ca}(\text{OH})_2} > PM_{\text{NaOH}}$$

II.4 Difference between individual and combined metal removal

From the previous experiments ([Sect II-2](#) and [II-3](#)) the difference between individual and combined metals (Cu(II), Cd(II), and Zn(II)) removal was summarized as follow:

- ✓ The removal of Copper and Cadmium ions are more effective in individual removal compared with metal combination, more than 99.99% of removal with very low remaining metal permissible by the Algerian standards.
- ✓ The removal of Zinc ions individually is less effective compared with metal combination,
- ✓ The suitable precipitating agent is not the same, caustic soda for individual metals and soda ash for combined metals.
- ✓ Using 200 mg/L of NaOH was enough to reach the maximum removal of the individual metals. However, 400 mg/L of Na_2CO_3 is required to reach the maximum removal of the same metals in combination.
- ✓ In metal combination, the solution was charged in 3 different heavy metals, 100 mg/l of each one, that is why the pH increased slowly in the first doses of precipitating agents, but after the precipitation of Cu at pH=6 , the pH_f increased rapidly and the precipitation of other metals will be more easier.
- ✓ The removal of metals in combination is more complicated than the removal of individual metals, because a good removal efficiency for each metal occurs at different pH values, so it is not easy to have a good removal for all metals simultaneously ([Ain Zainuddin et al., 2019](#) ; [Wang et al., 2016](#)).

II.5 Removal of combined heavy metals (Cu , Cd, and Zn) by using CaO_{Eggshells} (Calcined eggshells)

II.5.1 Calcined eggshells structure and chemical composition

EDX and SEM results give more details about the CaO_{Eggshells} composition, which is prepared to be used as precipitating agent for chemical precipitation trials (Figure 28, 29 and Table 26).

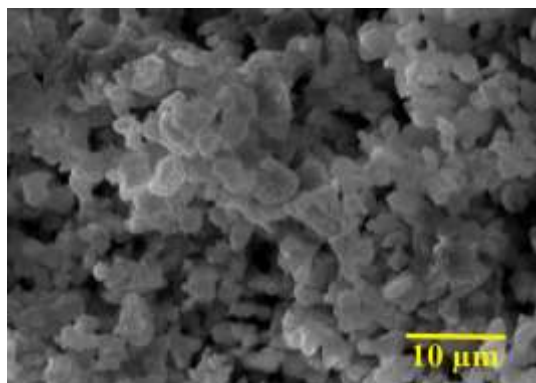


Figure 28 Scanning Electron Microscope (SEM) image of eggshells after calcination (7h of burning at a temperature of 800°C in the Muffle furnace).

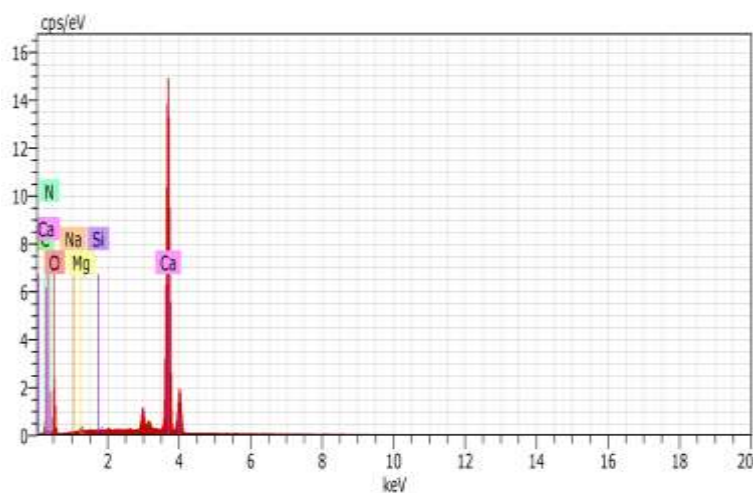


Figure 29 EDX analyses of calcined eggshells (CaO_{Eggshells} chemical composition)

Table 26 EDX analysis of calcined eggshells (CaO_{eggshells} chemical composition)

EDX—Elemental analysis content (Wt.%)						
Element	Ca	O	C	N	Mg	Na
Percentage (%)	53.45	40.47	3.86	1.77	0.38	0.07

SEM image (Figure 30) shows the micro-structure of the calcined eggshells, where the particles are small in size and are compact in structure.

Table 26 and Figure 29 resume the EDX analysis of eggshell after calcination; analysis of results shows the main composition of calcined eggshells, which are calcium (53.45%) and oxygen (40.47%) as predominant elements. However, other elements are present at low levels: 3.86% carbon, 1.77% nitrate, 0.38% magnesium and 0.07% sodium.

II.5.2 Effect of precipitating agent dose

A study of the metal removal capacity (Cu(II), Cd(II), and Zn(II)), at 100 mg/L of each metal in the synthetic solution was carried out at 24°C and $\text{pH}_0 = 4.68 \pm 0.1$. Different doses of $\text{CaO}_{\text{eggshells}}$ (10 to 1000 mg/L) were tested. A comparison between the performance of conventional lime and $\text{CaO}_{\text{Eggshells}}$ was discussed.

The results of the final pH, the remaining metal concentration and the removal efficiency of the metal using $\text{Ca}(\text{OH})_2$ and $\text{CaO}_{\text{Eggshells}}$ doses (80, 100, 200, 400, 600 and 400 mg/L) are presented in Figure 30 and Table 27.

From analyzing the results shown in Table 27 and Figure 30, it seems that there is no a huge difference between the two agents in the removal of combined metals (Cu(II), Cd(II), and Zn(II)).

Table 27 Precipitation behavior of combined Cu(II), Cd(II), and Zn(II) by varying precipitating agent doses. ($\text{Cu}(\text{II})_0 = \text{Cd}(\text{II})_0 = \text{Zn}(\text{II})_0 = 100 \text{ mg/L}$)

Precipitating agent	Dose (mg/L)	Final pH	Cu Removal (%)	Cd Removal (%)	Zn Removal (%)
$\text{CaO}_{\text{Eggshells}}$	80	5.93	63.80	4.60	0.5
	100	6.07	64.60	7.40	1.10
	200	8.59	98.74	40.20	91.06
	400	11.53	99.69	97.30	97.00
	600	11.87	99.60	99.67	92.88
	1000	11.93	98.59	99.89	85.90
$\text{Ca}(\text{OH})_2$	80	6.03	95.58	93.95	9.61
	100	6.14	95.96	94.06	27.44
	200	6.58	98.01	94.73	52.36
	400	10.73	99.88	99.75	96.29
	600	11.45	99.82	99.98	87.98
	1000	11.93	99.39	99.99	65.04

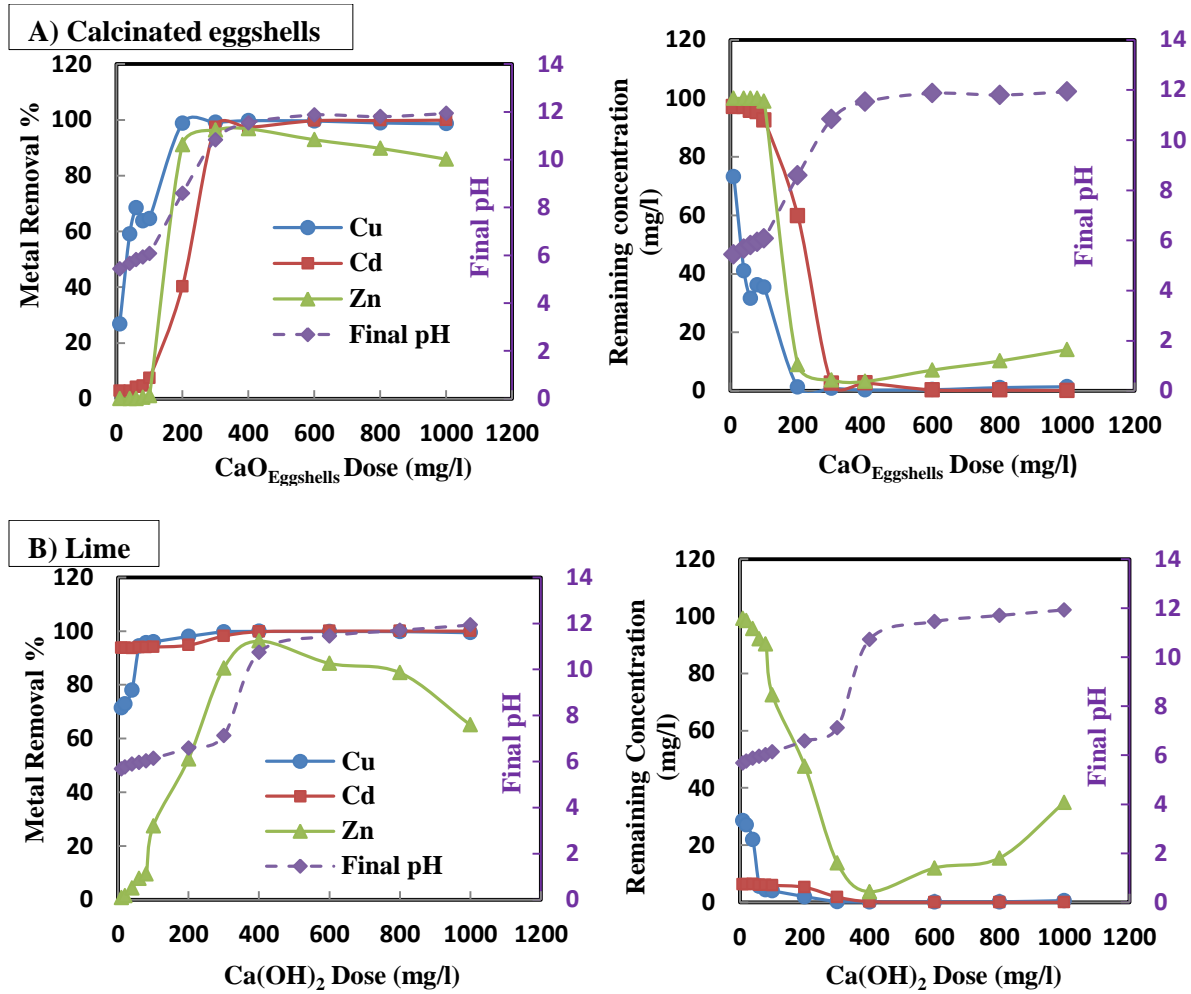


Figure 30 Effect of varying $CaO_{Eggshells}$ and $Ca(OH)_2$ doses in the removal of 100 mg/L of combined metals (Cu(II), Cd(II), and Zn(II)).

A. For $CaO_{eggshells}$

It is difficult to choose the optimum dose (OD) and optimum (OpH) for removing the three metals simultaneously; two choices will be discussed taking into account the maximum contaminant level (MCL) (Table 27 and Figure 30) :

✓ OD and OpH (400 mg/L ; 11.53), good removal for the all metals have performed, 99.69%, 97.30% and 96.80% for Cu(II), Cd(II), and Zn(II) respectively. But the MCL set by the Algerian standards has respected only with Cu(II) and Zn(II), not with Cd(II).

Cu: $0.31 \text{ mg/L} < 0.5 \text{ mg/L} \rightarrow RM_{Cu/CaO_{Eggshells}} < MCL_{Cu} \rightarrow$ MCL respected

Zn: $3 \text{ mg/L} = 3 \text{ mg/L} \rightarrow RM_{Zn/CaO_{Eggshells}} = MCL_{Zn} \rightarrow$ MCL respected

Cd: $2.7 \text{ mg/L} > 0.2 \text{ mg/L} \rightarrow RM_{Cd/CaO_{Eggshells}} > MCL_{Cd} \rightarrow$ MCL not respected

✓ OD and OpH (600 mg/L ; 11.87), for this dose the final pH (pH_f) increased and the removal of Cd(II) also increased, it reached 99.67 %, but remains superior a bit than the MCL_{Cd} value. Whereas, the removal of the other metals Cu(II) and Zn(II) decreased to 99.60% and 92.88% respectively. At a very high pH value, more than 11, the RM_{Zn} increased and exceeded the MCL_{Zn} due to the resolubilization of Zn(OH)₂.

Cu: $0.4 \text{ mg/L} < 0.5 \text{ mg/L} \longrightarrow \text{RM}_{\text{Cu}/\text{CaO}_{\text{Eggshells}}} < \text{MCL}_{\text{Cu}} \longrightarrow \text{MCL respected}$

Zn: $7.12 \text{ mg/L} > 3 \text{ mg/L} \longrightarrow \text{RM}_{\text{Zn}/\text{CaO}_{\text{Eggshells}}} > \text{MCL}_{\text{Zn}} \longrightarrow \text{MCL not respected}$

Cd: $0.33 \text{ mg/L} > 0.2 \text{ mg/L} \longrightarrow \text{RM}_{\text{Cd}/\text{CaO}_{\text{Eggshells}}} > \text{MCL}_{\text{Cd}} \longrightarrow \text{MCL not respected}$

From the previous results, the optimum couple: (OD = 400 mg/L; OpH = 11.53) was selected for the removal of combined heavy metals, in this choice the permissible values (MCL) for Cu(II) and Zn(II) are respected, whereas Cd(II) requires more increase in pH to achieve better removal efficiency.

So CaO_{Eggshells} is a good choice to remove combined heavy metals (Cu, Cd, and Zn) from synthetic solution.

B. For Ca(OH)₂

From the results shown in Table 27, the optimum couple (OD = 400 mg/L ; OpH = 10.73) is selected for removing combined heavy metals. The removal efficiency of Cu(II), Cd(II), and Zn(II) was significant, 99.88%, 99.75% and 96.29%, respectively. With the exception of copper and cadmium, the removal of zinc was not sufficient, as this metal slightly exceeds the MCL set by Algerian standards.

Cu: $0.12 \text{ mg/L} < 0.5 \text{ mg/L} \longrightarrow \text{RM}_{\text{Cu}/\text{Ca}(\text{OH})_2} < \text{MCL}_{\text{Cu}} \longrightarrow \text{MCL respected}$

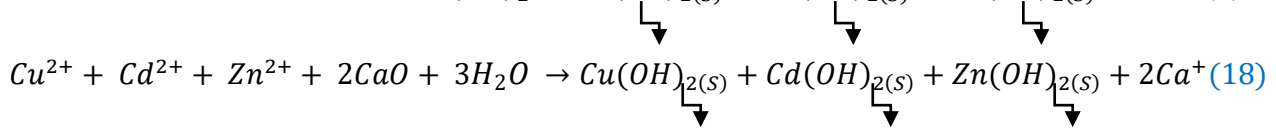
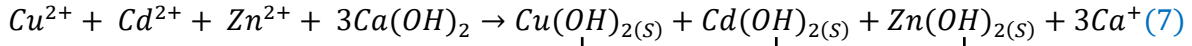
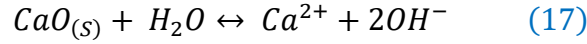
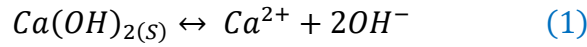
Zn: $3.71 \text{ mg/L} > 3 \text{ mg/L} \longrightarrow \text{RM}_{\text{Zn}/\text{Ca}(\text{OH})_2} > \text{MCL}_{\text{Zn}} \longrightarrow \text{MCL not respected}$

Cd: $0.2 \text{ mg/L} = 0.2 \text{ mg/L} \longrightarrow \text{RM}_{\text{Cd}/\text{Ca}(\text{OH})_2} = \text{MCL}_{\text{Cd}} \longrightarrow \text{MCL respected}$

II.5.3 Mechanisms of precipitation

The mechanism is the same as seeing previously, removing combined heavy metals (Cu(II), Cd(II), and Zn(II)) by using conventional lime (Ca(OH)₂) and calcined eggshells (CaO_{Eggshells}). In order to release this removal we adjust the pH to the basic conditions (pH 8 – 11) by adding Ca(OH)₂ and CaO_{Eggshells}.

The acid base neutralization reaction using Ca(OH)_2 and $\text{CaO}_{\text{Eggshells}}$ and the hydroxide precipitation reaction are below (Eqs. 1, 17 and 7, 19).



II.5.4 Effect of initial pH

Tests were carried out by varying the initial pH (3–9) of the solutions and using 80 mg/L $\text{CaO}_{\text{Eggshells}}$. A comparison between the results obtained using $\text{CaO}_{\text{Eggshells}}$ and Ca(OH)_2 was discussed (results presented previously in Section II.3.3) (Table 28 and Figure 31).

Table 28 Precipitation behavior of combined Cu(II), Cd(II), and Zn(II) After pH adjustment.

($\text{Cu(II)}_0 = \text{Cd(II)}_0 = \text{Zn(II)}_0 = 100 \text{ mg/L}$ and 80mg/L of precipitating agent)

Precipitating agent	pH _i	Final pH	Cu Removal (%)	Cd Removal (%)	Zn Removal (%)
$\text{CaO}_{\text{Eggshells}}$	3	5.76	10.90	10.20	0.20
	4	5.91	94.02	10.60	4.20
	6	6.48	98.97	18.80	10.60
	7	6.77	99.04	38.80	74.70
	8	9.93	99.12	98.82	99.12
	9	10.28	99.79	99.89	99.47
Ca(OH)_2	3	6.28	69.11	93.46	5.99
	4	6.39	77.87	93.77	6.51
	6	6.52	93.13	94.07	7.00
	7	7.11	98.32	94.73	33.74
	8	10.14	99.61	99.39	95.17
	9	10.74	99.69	99.99	97.07

A. For $\text{CaO}_{\text{Eggshells}}$

- $\text{pH}_i \leq 6$, the final pH increases rapidly, it reaches 6.48 for $\text{pH}_i = 3$. This pH value favors the precipitation of Cu, $R_{\text{Cu}}\% = 98.97\%$ and $\text{RM}_{\text{Cu}/\text{CaO}_{\text{Eggshells}}} = 1.03 \text{ mg/L}$. however, this pH value is not enough for the precipitation of Cd and Zn.
- $6 \leq \text{pH}_i \leq 8$, the final pH continues increasing, reaching 9.93 at $\text{pH}_i = 8$. This pH value is good for the precipitation of all metals. The removal efficiency is 99.12%, 98.82% and 99.12% for Cu(II), Cd(II), and Zn(II) respectively.

While, the removal of Cu(II) and Cd(II) is not sufficient because the RM concentrations do not meet the MCL standards.

Cu: $0.88 \text{ mg/L} > 0.5 \text{ mg/L} \rightarrow \text{RM}_{\text{Cu/CaO}_{\text{Eggshells}}} > \text{MCL}_{\text{Cu}} \rightarrow \text{MCL not respected}$

Cd: $1.18 \text{ mg/L} > 0.2 \text{ mg/L} \rightarrow \text{RM}_{\text{Cd/CaO}_{\text{Eggshells}}} \leq \text{MCL}_{\text{Cd}} \rightarrow \text{MCL not respected}$

Zn: $0.88 \text{ mg/L} < 3 \text{ mg/L} \rightarrow \text{RM}_{\text{Zn/CaO}_{\text{Eggshells}}} > \text{MCL}_{\text{Zn}} \rightarrow \text{MCL respected}$

- $\text{pH}_i = 9$, the final pH reaches 10.28. This pH value is the best for the precipitation of all metals. The removal efficiency are: 99.79%, 99.89% , and 99.47% for Cu(II), Cd(II) and Zn(II), respectively. All RM concentrations are below the MCL.

Cu: $0.21 \text{ mg/L} < 0.5 \text{ mg/L} \rightarrow \text{RM}_{\text{Cu/CaO}_{\text{Eggshells}}} > \text{MCL}_{\text{Cu}} \rightarrow \text{MCL respected}$

Cd: $0.11 \text{ mg/L} < 0.2 \text{ mg/L} \rightarrow \text{RM}_{\text{Cd/CaO}_{\text{Eggshells}}} \leq \text{MCL}_{\text{Cd}} \rightarrow \text{MCL respected}$

Zn: $0.53 \text{ mg/L} < 3 \text{ mg/L} \rightarrow \text{RM}_{\text{Zn/CaO}_{\text{Eggshells}}} > \text{MCL}_{\text{Zn}} \rightarrow \text{MCL respected}$

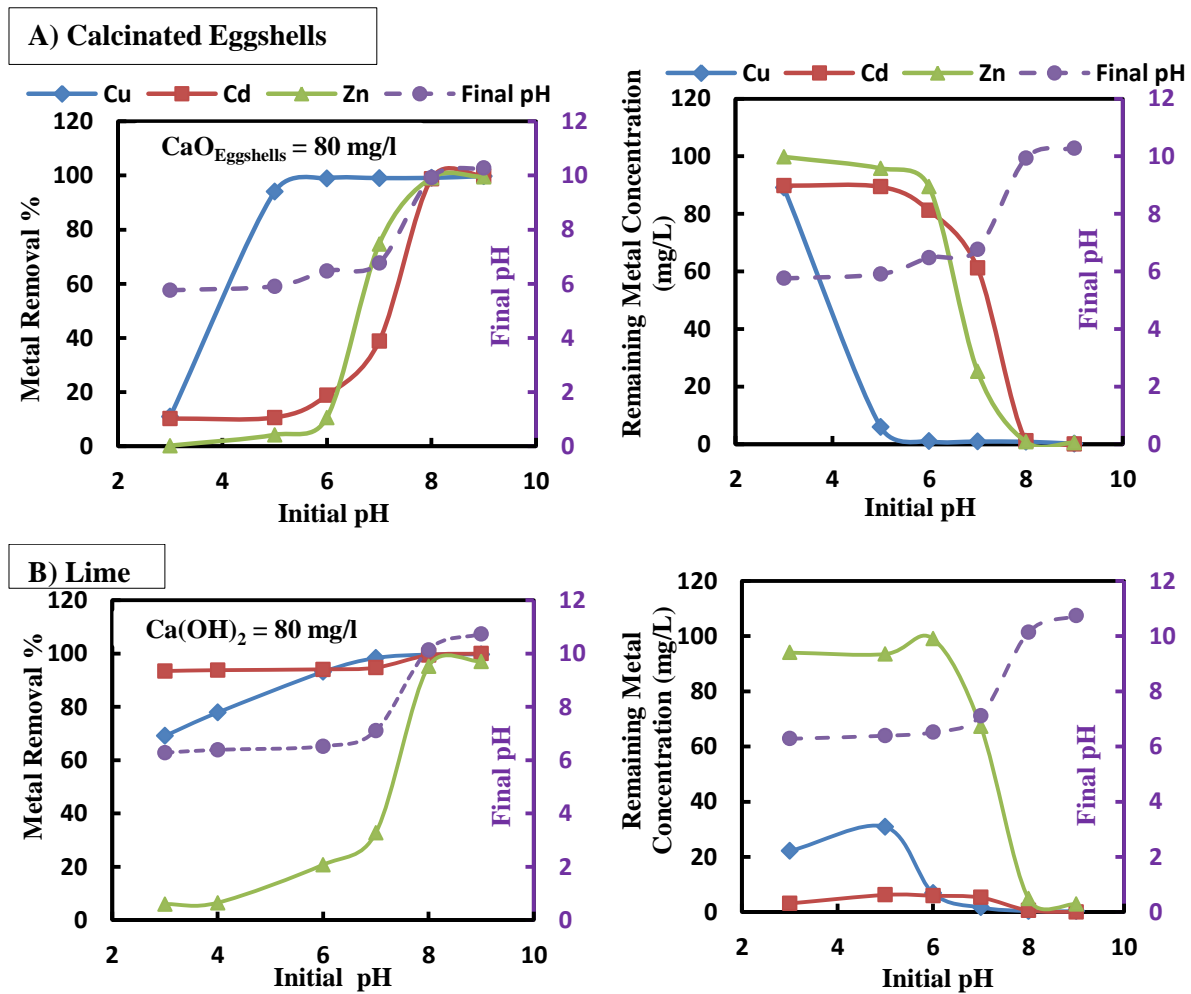


Figure 31 Effect of initial pH of synthetic solution on the removal of combined Cu(II), Cd(II) and Zn(II), using $\text{CaO}_{\text{Eggshells}}$ and $\text{Ca}(\text{OH})_2$ (A and B). ($\text{Cu}(\text{II})_0 = \text{Cd}(\text{II})_0 = \text{Zn}(\text{II})_0 = 100 \text{ mg/L}$; $A = B = 80 \text{ mg/L}$).

B. For Ca(OH)₂

As discussed previously in [Section II.3.3](#), using lime when $\text{pH}_i \leq 6$, the removal of Cu(II) and Cd(II) was good, and in order to achieve a very good removal of all metals, the pH was adjusted to 9 and the final pH reached 10.74, this pH value was sufficient to achieve good removal efficiency of all metals and respects the Algerian standards.

III.5.5 Sludge System Analysis

Sludge recovered after the treatment of combined metal in synthetic solution by CaO_{Eggshells} and Ca(OH)₂ were characterized as to volume (V), precipitate mass (PM). [Figure 32](#) shows an estimation of the volume of sludge and the precipitate mass (PM) produced by using 400 mg/L and 600 mg/L of precipitating agents (Conventional lime and CaO_{Eggshells}), after different settling times (30, 60 and 90 min). These doses were selected because: 400 mg/L is the optimum dose for the removal of the combined metals (Cu(II), Cd(II) and Zn(II)), also 600 mg/L release a good metals removal.

[Figure 32 \(a, b and c\)](#) show the volume of sludge produced by using two different doses (400 and 600 mg/L) of conventional Ca(OH)₂ and calcined eggshells (CaO_{Eggshells}) for removing combined metals (Cu, Cd, and Zn ions), at different settling time (30, 60, and 90 min).

According ([Figure 31\(a\)](#)), the sludge volume produced after 30 min by CaO_{Eggshells} was higher than that produced by Ca(OH)₂ using the both doses (400 and 600 mg/L).

$$V_{30\text{min}/\text{CaO}_{\text{Eggshells}}} > V_{30\text{min}/\text{Ca}(\text{OH})_2}$$

However, by increasing the settling time to 60 min ([Figure 32\(b\)](#)), sludge volume decreased and stabilized at 90 min of settling ([Figure 32\(c\)](#)). As a result, the sludge volume produced by Ca(OH)₂ was higher than the one produced by CaO_{Eggshells}.

$$V_{60\text{min}/\text{Ca}(\text{OH})_2} > V_{60\text{min}/\text{CaO}_{\text{Eggshells}}} \quad \text{and} \quad V_{90\text{min}/\text{Ca}(\text{OH})_2} > V_{90\text{min}/\text{CaO}_{\text{Eggshells}}}$$

These results can be explained by the fact that the precipitates formed using Ca(OH)₂ and CaO_{Eggshells} (hydroxide precipitating agents) were gelatinous (the same conclusion made by [\(BrbootI et al. 2011\)](#)), so that the sludge volume was high for both precipitating agents and less gelatinous for CaO_{Eggshells}.

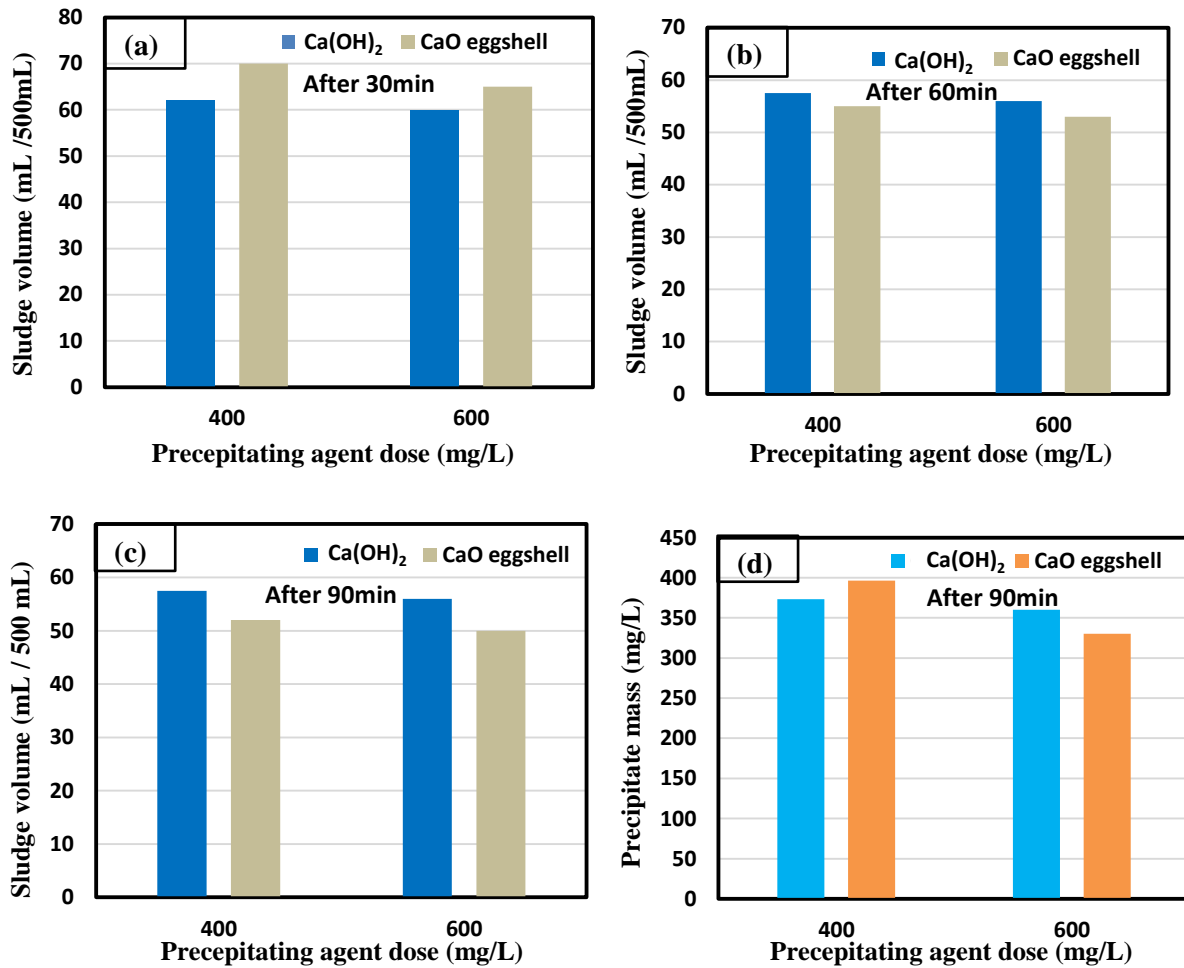


Figure 32 Sludge volume (a , b and c) and PM (d) generated by the use of 400 mg/L and 600 mg/L of Ca(OH)_2 and $\text{CaO}_{\text{Eggshells}}$ for the removal ($\text{Cu(II)}_0 = \text{Cd(II)}_0 = \text{Zn(II)}_0 = 100 \text{ mg/L}$), after different settling times (30 , 60 and 90 min).

As shown in [Figure 32\(d\)](#), the PM, after 90 min of settling, decreased by increasing the precipitating agent, Ca(OH)_2 and $\text{CaO}_{\text{Eggshells}}$ doses.

- For $\text{Ca(OH)}_2 \rightarrow 373.4 \text{ mg/L} > 360 \text{ mg/L} \rightarrow PM_{400 \text{ mg/L}} > PM_{600 \text{ mg/L}}$
- For $\text{CaO}_{\text{Eggshells}} \rightarrow 369.2 \text{ mg/L} > 330 \text{ mg/L} \rightarrow PM_{400 \text{ mg/L}} > PM_{600 \text{ mg/L}}$

When using 400 mg/L of precipitating agents, the $PM_{\text{Eggshells}}$ was slightly higher than $PM_{\text{Ca(OH)}_2}$. However, the decrease of PM, after using 600 mg/l of precipitants, is related to the decrease in the removal efficiency of Cu(II) and Zn(II) (return to [Table 27](#) and [Figure 30](#)).

- For 400 mg/L of precipitants: $PM_{\text{CaO}_{\text{Eggshells}}} > PM_{\text{Ca(OH)}_2}$
- For 600 mg/L of precipitants: $PM_{\text{Ca(OH)}_2} > PM_{\text{CaO}_{\text{Eggshells}}}$

SEM images (Figure 33(a,b)) show that the resulting precipitates from the reaction of precipitation are small in size and are compact in structure. The analysis of particle size distribution, using Image J program and origin 2018 tools, has showed that the average particle size (Mean Value “ M_{value} ”) of the precipitates was found approximately 1.37 μm in the $\text{Ca}(\text{OH})_2$ system and 1.93 μm in the $\text{CaO}_{\text{Eggshells}}$ system (Figure 33(c)), so the average particle size of lime system is smaller than calcined eggshell system. This result confirms the difference in the PM of the sludge formed by precipitating agents (Figure 33(d)).

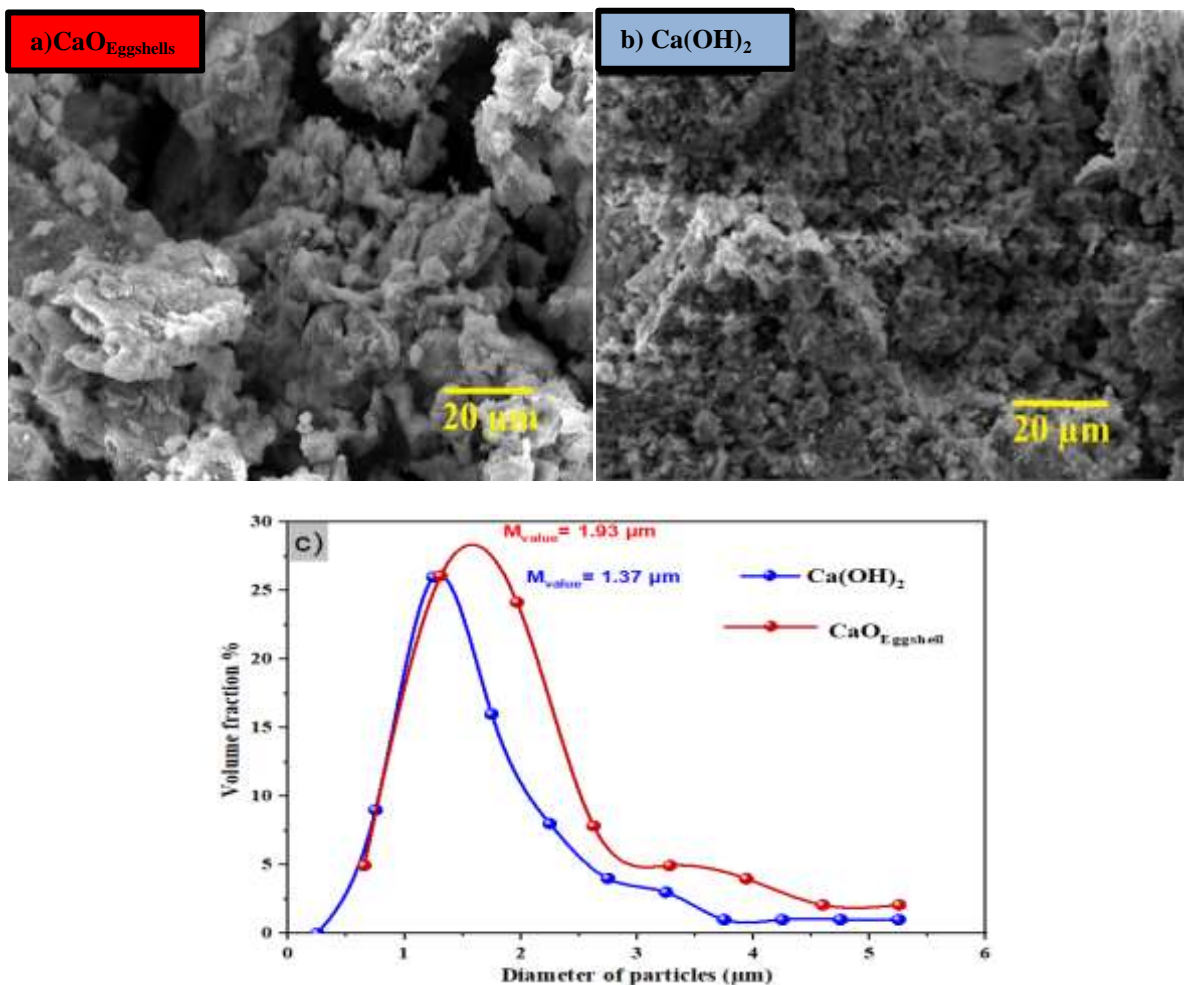


Figure 33 Scanning electron microscopy (SEM) images of sludge produced by precipitation of combined heavy metals in synthetic solution by using (a) $\text{CaO}_{\text{Eggshells}}$ and (b) $\text{Ca}(\text{OH})_2$. (c) Particle size distribution ($\text{Cu}(\text{II})_0 = 100 \text{ mg/L}$; $\text{Cd}(\text{II})_0 = 100 \text{ mg/L}$; $\text{Zn}(\text{II})_0 = 100 \text{ mg/L}$, dosage of precipitating agent = 400 mg/L, settling time = 90 min).

To confirm the presence of metal ions in the sludge recovered after treatment, SEM-EDS analysis was carried out on a sample of the sludge after using $\text{CaO}_{\text{Eggshells}}$ (Figure 34).

According to this color map, the presence of all three elements: Cu (in purple), Zn (in yellow) and Cd (in orange) is clearly evident.

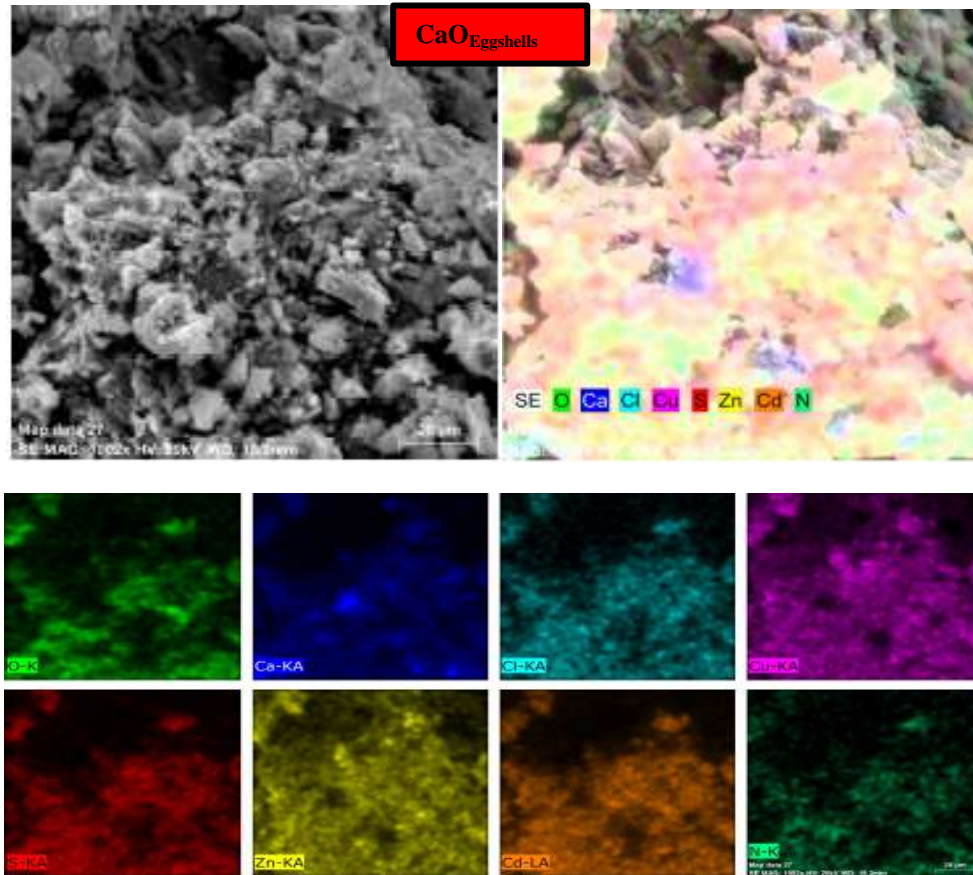


Figure 34 : SEM-EDS- elemental chemical mapping of the sludge recovered after chemical precipitation of the three combined heavy metals in synthetic solution ($\text{Cu(II)}_0 = 100 \text{ mg/L}$; $\text{Cd(II)}_0 = 100 \text{ mg/L}$; $\text{Zn(II)}_0 = 100 \text{ mg/L}$, dosage of $\text{CaO}_{\text{Eggshells}} = 400 \text{ mg/L}$, settling time = 90 min).

Figure 35 (a,b) represent a comparison between the XRD spectra of $\text{CaO}_{\text{Eggshells}}$, and the sludge sample recovered after treatment with $\text{CaO}_{\text{Eggshells}}$ highlights the remarkable crystalline proportions of copper, zinc, and cadmium in the recovered sludge.

By analyzing the 1st pie chart, which represents the mineral composition of $\text{CaO}_{\text{Eggshells}}$ powder Figure 35 (b), the main composition was portlandite (Ca(OH)_2) (76.8%). However, the other components are small, 9.1 % each one of vaterite and calcite and just 5 % of calcium oxide.

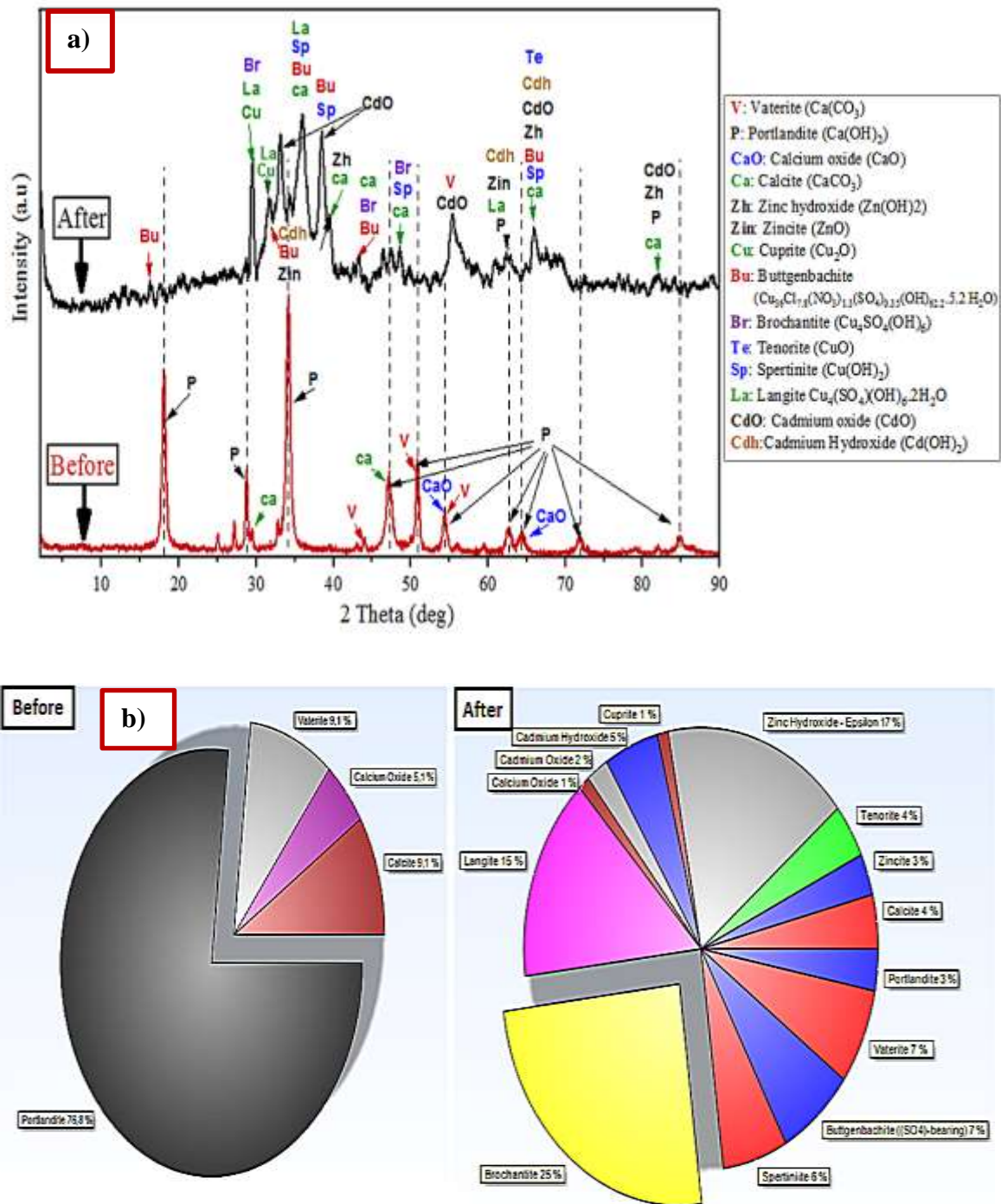


Figure 35 a) Comparison between the crystalline compounds present by analysis of XRD spectra. b) Quantification of crystalline compounds present in CaO_{Eggshells} and the sludge sample recovered after treatment with CaO_{Eggshells}.

The 2nd Pie chart **Figure 35 (b)**, resumes the mineral composition of the recovered sludge after treatment using CaO_{Eggshells}, the main copper crystal compounds in precipitates were 25 % of Brochantite (Cu₄SO₄(OH)₆), 15 % of Langite Cu₄(SO₄)(OH)₆·2H₂O, 7% of

Buttgenbachite ((SO₄)-bearing) Cu₃₆Cl_{7.8}(NO₃)_{1.3}(SO₄)_{0.35}(OH)_{62.2}·5.2 H₂O), 6 % of Spertinite (Cu(OH)₂), 4 % of Tenorite and just 1% of cuprite.

The quantitative composition of Zinc compounds were 17 % of Zinc hydroxide (Zn(OH)₂) and 3% of Zincite (ZnO).

The Cadmium compounds occurring in the recovered sludge were 5 % of Cadmium hydroxide (Cd(OH)₂) and 2% of Cadmium oxide (CdO).

On the basis of the previous quantitative values, copper compounds represent the majority of the sludge composition, and Brochantite is the highest mineral component. According to [Kinnunen et al., 2018](#), Brochantite has the highest composition due to the presence of sulphate in the composition of Brochantite, and lime is known to be a suitable precipitating agent for sulphate removal. These results were in accordance with the results shown in ([Table 27 and Figure 30](#)), they confirmed that the eggshells have a good efficiency of removing Cu(II) and Zn(II) more than Cd(II).

II.5.6 Comparison between lime and calcined eggshells in removing combined heavy metals (Cu, Cd, and Zn)

From the results presented and discussed previously, the difference between the two similar agents (Ca(OH)₂ and CaO_{Eggshells}) is summarized in the following points:

- The pH_f increases faster using Ca(OH)₂ than CaO_{Eggshells}, which could affect the efficiency of metal removal ([Table 28 and Figure 31](#)).
- The both precipitating agents provide very good removal of all metals Cu(II), Cd(II), and Zn(II).
- CaO_{Eggshells} is the appropriate precipitating agent for Zn(II) removal, pH_f = 9.93 was sufficient to remove 99.12% of Zn(II) and have only 0.88 mg/L of RM, which is in accordance with Algerian standards ([Table 27 and Figure 30](#)).
- The pH_f = 10.28 of the solution (Heavy metals + CaO_{Eggshells}) is sufficient to achieve good removal of all metals. However, using Ca(OH)₂, this pH value is not sufficient to achieve the same removal, so CaO_{Eggshells} performs better ([Table 27 and Figure 30](#)).
- CaO_{Eggshells} is not the best choice for Cd(II) removal, if MCL is considered.
- Ca(OH)₂ is not the best choice for Zn(II) removal, if MCL is considered.

The use of calcined eggshells as an alternative to lime is a very good choice. According to the results discussed, CaO_{Eggshells} performs well in the removal of combined metals (Cu(II),

Cd(II), and Zn(II)) by chemical precipitation and in some aspects, are better than lime, particularly for the removal of Zn(II), which poses various problems, the first being the re-solubilization of the precipitate (Zn(OH)_2), and the second that its pH range for precipitation is very narrow. For these reasons, $\text{CaO}_{\text{Eggshells}}$ are more effective in removing Zn(II), as its pH increases slowly, unlike conventional lime, which facilitates Zn precipitation and avoids re-solubilization of the precipitate. On the other hand, eggshells are a waste product and CaO extraction is inexpensive, making them a good choice for heavy metal removal.

II.5.7 Conclusion

In this chapter, the removal of heavy metals (Cu(II), Cd(II), and Zn(II)) from synthetic solution “distilled water” was studied in simple and complex media, using the same precipitants (Ca(OH)_2 , NaOH, Na_2CO_3 , and $\text{CaO}_{\text{Eggshells}}$). The simple one represents the removal of each metal individually. However, the complex media studied the removal of the three metals together.

From analyzing the results of this chapter, here are the important conclusions:

- ✓ The three precipitating agents were very effective for removing heavy metals (Cu(II), Cd(II), and Zn(II)) individually .
- ✓ Caustic soda was the best choice compared to lime and soda ash in the removal of the individual metals.
- ✓ The maximum precipitation of Zn occurred in the pH range [10 _11], beyond this range the hydroxide-metal complex re-solubilizes.
- ✓ A good efficiency of metal removal requires an important amount of precipitating agent, if not a precipitant deficiency occurs, which affect the precipitation process.
- ✓ Soda ash was more effective than lime and caustic soda in removing the combined metal ions (Cu, Cd, and Zn).
- ✓ Soda ash has an advantage of removing metals at smaller pH compared to hydroxide agents.
- ✓ Removal of metals in combination is more complicated than removal of individual metals, because good removal efficiency for each metal occurs at different pH values, so it is difficult to get a good removal for all metals at the same time.
- ✓ The re-use of waste eggshells is a great idea especially for removing heavy metals.

- ✓ The calcined eggshell is a good choice for the removal of Cu and Zn. However, it is not the best one for removing Cd. It has a good performance in removing Zn(II), and it solves the problem of metal re-solubilization.
- ✓ The average particle size of lime system is smaller than calcined eggshell system. This result confirms the difference in the PM.

CHAPTER III

REMOVAL OF HEAVY

METALS FROM INDUSTRIAL

WASTEWATER

III.1 Introduction

The study of the chemical precipitation of heavy metals in synthetic solution has allowed us to identify the parameters influencing the effectiveness of the treatment. In order to extrapolate these results to really polluted effluents, in this chapter the results of tests carried out on two industrial effluents will be presented and discussed. The first contained exceeding standards levels of Cu(II) and Zn(II) ions and the second contained high levels of Cu(II) and Ni(II). The characterization of the sludge recovered after the decantation stage will be also discussed.

III.2 Removal of heavy metals (Cu and Zn) from *ENICAB* wastewater

III.2.1 Characterization of industrial wastewater

Table 29 lists the chemical and physical properties of the industrial wastewater. The pH of this wastewater is almost acid (pH ~ 6.08), and it was turbid at an average of 95 NTU. This wastewater was extremely mineralized since the conductivity was greater than 1000 $\mu\text{S}/\text{cm}$. High concentrations of sulfates, calcium, magnesium, and chloride were found in this wastewater. Zinc and copper had average concentrations of 10.21 and 18.10 mg/L, respectively. The amounts of both metals were significantly higher than the Algerian limit for liquid industrial discharges, as mentioned in Table 29 of the Algerian Republic's Official Journal (JORA, 2006).

Table 29 Physical and chemical characteristics of the *ENICAB* wastewater

Parameter	Mean value	Maximum allowable for industrial liquid discharges (JORA, 2006)
Temperature (C°)	24	< 30
pH	6.08	6.5–8.5
Conductivity ($\mu\text{S}/\text{cm}$)	4470	–
Turbidity (NTU)	95	–
TH (Hardness) (meq/L)	52	–
Calcium (mg/L)	124	–
Magnesium (mg/L)	549.6	–
Chlorides (mg/L)	784	–
Sulfates (mg/L)	754	–
TAC (Alkalinity) (meq/L)	3.94	–
Ammonia (mg/L)	1.4	–
Copper (mg/L)	18.10	0.5
Zinc (mg/L)	10.21	3

III.2.2 Effect of precipitating agent dose

Jar tests with varying concentrations of $\text{Ca}(\text{OH})_2$, NaOH , and Na_2CO_3 precipitants were carried out at 24 °C.

The optimum dosage for the purification of industrial wastewater is determined by increasing the concentration of each agent from 10 to 400 mg/L. This also identifies the precipitant, that is most effective in removing $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ from the wastewater, which are present at concentrations of 18.10 mg/L and 10.21 mg/L, respectively (Figure 36). Table 30 shows the final pH, the remaining metal concentration, and the metal removal efficiency for the doses of precipitating agents (80, 100, 200, 300, and 400 mg/L).

Table 30 Effect of precipitating agent dose on the removal of $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ from *ENICAB* wastewater

Precipitant	Dose (mg/L)	Final pH	Cu Removal (%)	Zn Removal (%)
$\text{Ca}(\text{OH})_2$	80	6.41	84.88	73.54
	100	6.44	89.70	75.80
	200	8.73	99.92	98.02
	300	9.96	99.99	99.13
	400	10.73	99.99	69.82
NaOH	80	6.83	95.99	80.51
	100	7.14	98.46	83.29
	200	9.15	99.99	97.28
	300	9.96	99.99	99.75
	400	10.74	99.99	97.59
Na_2CO_3	80	7.88	98.93	83.71
	100	7.99	99.11	87.98
	200	8.85	99.87	95.18
	300	9.21	99.94	99.28
	400	9.62	99.98	99.05

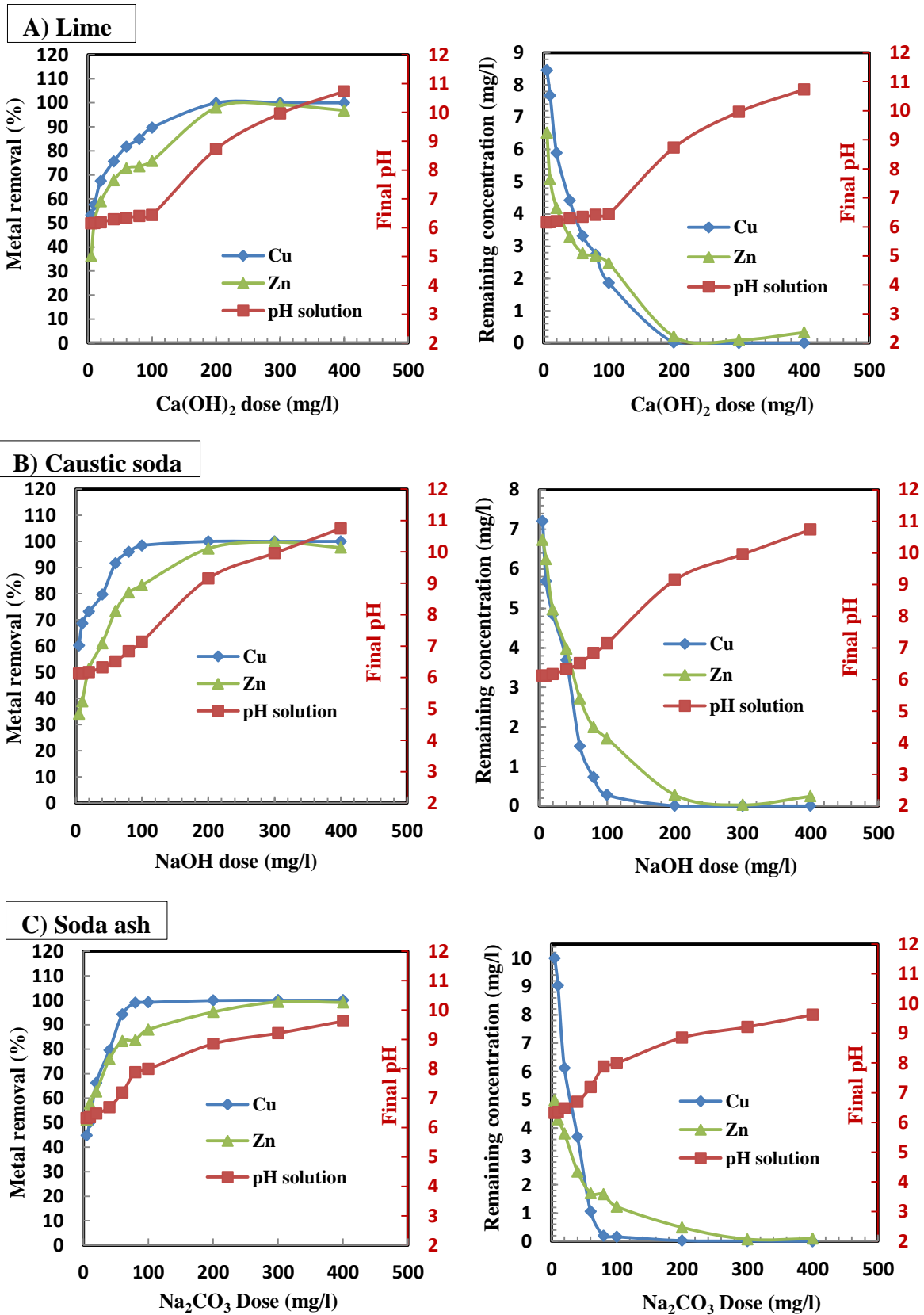


Figure 36 Influence of different precipitating agent doses (A) lime, (B) caustic soda, (C) soda ash on the final pH variation and on the removal of Cu(II) and Zn(II) and (Cu(II)₀ = 18.10 mg/L Zn(II)₀ = 10.21 mg/L, pH₀ = 6.08).

The hydrated soda ash was the most suitable precipitant among the three precipitating agents, for slightly alkaline pH conditions ($6 < \text{final pH} < 8$; dose less than 100 mg/L), as the final pH range of Na_2CO_3 is consistently higher than that of $\text{Ca}(\text{OH})_2$ and NaOH at low concentrations, leading to more effective removal.

The residual metal content (RM) of $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ at 100 mg/L of hydrated soda ash were 0.160 mg/L and 1.227 mg/L, respectively. It was noted that these RM concentrations were in compliance with the MCL specified by the Algerian regulations (JORA, 2006), (Figure 36, Table 30).

❖ For a better understanding, the optimum results are given below:

For Cu(II): $99.11\% > 98.46\% > 89.70\% \rightarrow R\%_{\text{Cu}/\text{Na}_2\text{CO}_3} > R\%_{\text{Cu}/\text{NaOH}} > R\%_{\text{Cu}/\text{Ca}(\text{OH})_2}$

$$0.16 \frac{\text{mg}}{\text{L}} < 0.28 \frac{\text{mg}}{\text{L}} < 0.5 \frac{\text{mg}}{\text{L}} < 1.87 \frac{\text{mg}}{\text{L}} \rightarrow \text{RM}_{\text{Cu}/\text{Na}_2\text{CO}_3} < \text{RM}_{\text{Cu}/\text{NaOH}} < \text{MCL}_{\text{Cu}} < \text{RM}_{\text{Cu}/\text{Ca}(\text{OH})_2}$$

For Zn(II): $87.98\% > 83.29\% > 75.80\% \rightarrow R\%_{\text{Zn}/\text{Na}_2\text{CO}_3} > R\%_{\text{Zn}/\text{NaOH}} > R\%_{\text{Zn}/\text{Ca}(\text{OH})_2}$

$$1.23 \frac{\text{mg}}{\text{L}} < 1.71 \frac{\text{mg}}{\text{L}} < 2.47 \frac{\text{mg}}{\text{L}} < 3 \frac{\text{mg}}{\text{L}} \rightarrow \text{RM}_{\text{Zn}/\text{Na}_2\text{CO}_3} < \text{RM}_{\text{Zn}/\text{NaOH}} < \text{RM}_{\text{Zn}/\text{Ca}(\text{OH})_2} < \text{MCL}_{\text{Zn}}$$

Nevertheless, the most effective precipitant at a high pH level ($8 < \text{Final pH} < 10$) was caustic soda, with maximum efficiency (R%) of 99.99% for $\text{Cu}(\text{II})$ and 99.75% for $\text{Zn}(\text{II})$ at an ideal dose and pH, ($\text{OD}_{\text{NaOH}} = 300 \text{ mg/L}$; $\text{OpH}_{\text{NaOH}} = 9.21$). The RM concentrations were 0.0002 mg/L of Cu and 0.025 mg/L for Zn, they are very low than the MCL (Figure 36, Table 30).

❖ For a better understanding, the optimum results are given below:

For Cu(II): $99.99\% \geq 99.99\% > 99.94\% \rightarrow R\%_{\text{Cu}/\text{NaOH}} \geq R\%_{\text{Cu}/\text{Ca}(\text{OH})_2} > R\%_{\text{Cu}/\text{Na}_2\text{CO}_3}$

$$0.0002 \frac{\text{mg}}{\text{L}} \leq 0.0003 \frac{\text{mg}}{\text{L}} < 0.01 \frac{\text{mg}}{\text{L}} < 0.5 \frac{\text{mg}}{\text{L}} \rightarrow \text{RM}_{\text{Cu}/\text{NaOH}} \leq \text{RM}_{\text{Cu}/\text{Ca}(\text{OH})_2} < \text{RM}_{\text{Cu}/\text{Na}_2\text{CO}_3} < \text{MCL}_{\text{Cu}}$$

For Zn(II): $99.75\% > 99.28\% > 99.13\% \rightarrow R\%_{\text{Zn}/\text{NaOH}} > R\%_{\text{Zn}/\text{Na}_2\text{CO}_3} > R\%_{\text{Zn}/\text{Ca}(\text{OH})_2}$

$$0.03 \frac{\text{mg}}{\text{L}} < 0.07 \frac{\text{mg}}{\text{L}} < 0.09 \frac{\text{mg}}{\text{L}} < 3 \frac{\text{mg}}{\text{L}} \rightarrow \text{RM}_{\text{Zn}/\text{NaOH}} < \text{RM}_{\text{Zn}/\text{Na}_2\text{CO}_3} < \text{RM}_{\text{Zn}/\text{Ca}(\text{OH})_2} < \text{MCL}_{\text{Zn}}$$

The remaining zinc increased from 0.089 mg/L, 0.025 mg/L, and 0.074 mg/L to 0.325 mg/L, 0.246 mg/L, and 0.096 mg/L, respectively, at a dose of 400 mg/L for hydroxide precipitation ($\text{Ca}(\text{OH})_2$ and NaOH), ($\text{pH}_f > 10$) and in the case of Na_2CO_3 ($\text{pH}_f = 9.62$). These results are illustrated in Figure 36 and Table 30. While, this is not the case for copper, the increases were caused by the dissolution of amphoteric hydroxide of zinc produced (Chen et al., 2018 ; Wang et al., 2016).

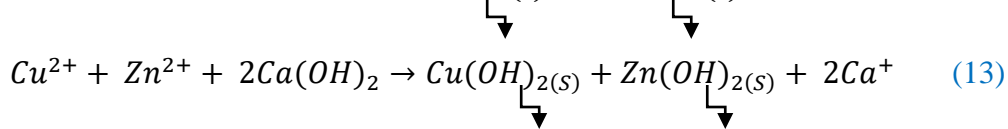
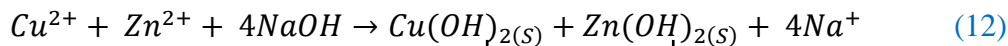
As stated by [BrbootI et al., \(2011\)](#) and [Ain Zainuddin et al., \(2019\)](#), the precipitation of each metal is limited to a specific pH range and beyond this range the metals re-solubilizes.

Additionally, it is clear that copper has slightly better removal efficiency than zinc for each precipitating agent. The elemental analysis by the EDX reported in [Table 31](#) confirmed this. It is evident that in all recovered sludge, the proportion of copper is greater than that of zinc.

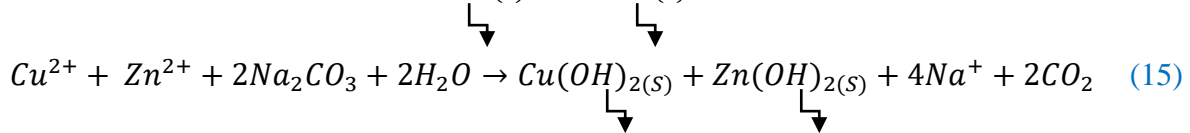
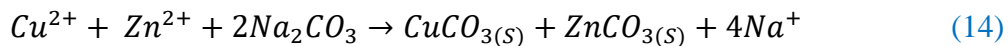
III.2.3 Mechanisms of precipitation

Adjustment of pH to the basic conditions (pH 9 – 11), is the major parameter that significantly improves heavy metal removal by chemical precipitation ([Barakat, 2011](#)). The mechanism is the same as seeing before in Chapter II ([Section II.2.2](#), [II.3.2](#) and [II.5.2](#)). In this case, the treated water initially contained two heavy metals simultaneously.

For hydroxide precipitating agents ($\text{Ca}(\text{OH})_2$ and NaOH), reaction of precipitation are presented by [Eqs. \(12\)](#) and [\(13\)](#):



Using Na_2CO_3 , the reaction of precipitation of divalent metal ions is given by [Eqs. \(14\)](#) and [\(15\)](#):



Based on the results of X-ray diffraction of the sludge deposited, using *X'Pert HighScore Plus* tools ([Figure 37](#), [Table 31](#)), ZnCO_3 and CuCO_3 have not identified. This occurrence was supported by [Chen et al., \(2018\)](#). According to these researchers, the precipitation mechanism might be defined by [Eq. \(15\)](#), and [Eq. \(14\)](#) might not occur. [Ya et al., \(2009\)](#) made a similar remark. These researchers verified that copper can be removed by adsorption on CaCO_3 in the presence of Na_2CO_3 , but that $\text{Cu}(\text{II})$, OH^- , and CO_3^{2-} would react more frequently and that $\text{Cu}(\text{OH})_2$ (94.5%) would form more noticeably than CuCO_3 (5%).

The X-ray diffraction results of the sludge product, which are presented in [Table 31](#) and [Figure 37](#), indicate the existence of a significant number of more phases.

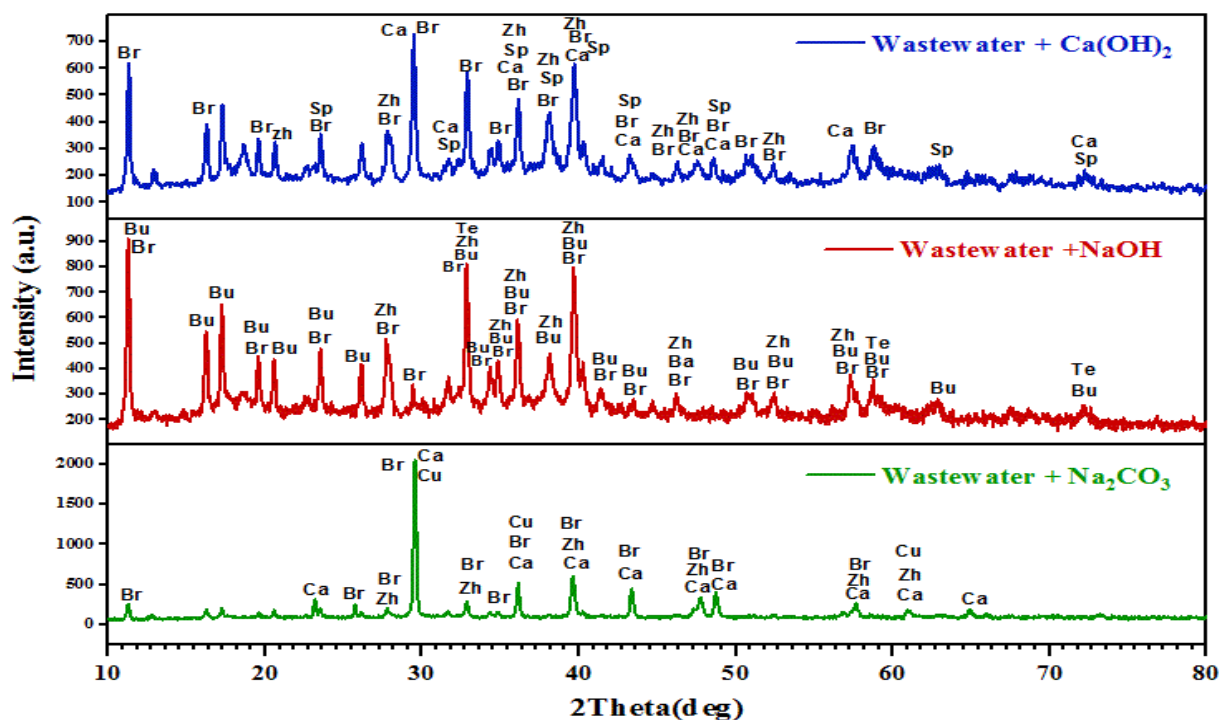


Figure 37 Diffractograms for sludges produced using precipitating agents for the treatment of ENICAB wastewater (Br: Brochantite, Ca: calcite; Zh: Zinc hydroxide, Cu: Cuprite, Bu: Buttgenbachite, Te: Tenorite, Sp: Speritine).

Table 31 XRD and EDX analysis for sludge produced using different precipitating agents for the treatment of ENICAB wastewater

Patern	Elemental analysis content of patterns-HighScore Plus (%)			Element	EDX—Elemental analysis content (%)		
	Ca(OH) ₂	NaOH	Na ₂ CO ₃		Ca(OH) ₂	NaOH	Na ₂ CO ₃
Brochantite Cu ₄ SO ₄ (OH) ₆	38.4	33	17.2	C	37.68	4.06	23.30
Zinc hydroxide Zn(OH) ₂	17.2	16	7.1	O	33.62	34.33	44.26
Calcite CaCO ₃	12.1	2	14.1	Mg	7.76	12.27	0.63
Speritine Cu(OH) ₂	11.1	9	3	Ca	4.89	2.55	15.10
Buttgenbachite ((SO ₄)-bearing)	10.1	15	4	Cl	2.27	5.07	2.26
Cu ₃₆ Cl _{7,8} (NO ₃) _{1.3} (SO ₄) _{0.35} (OH) _{62.2} ·5.2 H ₂ O)				S	0.49	1.54	1.57
Langite Cu ₄ (SO ₄)(OH) ₆ ·2H ₂ O	9.1	11	7.1	Cu	13.06	40.05	12.77
Zincite ZnO	2	2	1				
Tenorite CuO	–	12	1	Zn	0.23	0.13	0.11
Cuprite Cu ₂ O	–	–	45.5				

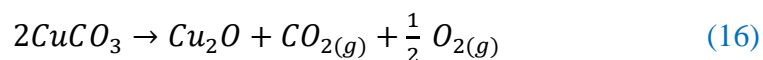
A. For Copper Removal

- In the case of lime precipitation, the main copper crystal compounds in precipitates were 38.4% of Brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$), 11.1% of Spertinite ($\text{Cu}(\text{OH})_2$), 10.1% of Buttgenbachite ((SO_4)-bearing) $\text{Cu}_{36}\text{Cl}_{7.8}(\text{NO}_3)_{1.3}(\text{SO}_4)_{0.35}(\text{OH})_{62.2.5.2} \text{H}_2\text{O}$ and 9.1% of Langite $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2\text{H}_2\text{O}$.

- With lime, 38 percent of Brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$) appears to be significant because lime is a well-suited precipitating agent for the removal of sulfates (Kinnunen et al., 2018). Wastewater initially includes 754 mg/L of sulfate, as Table 31 showed. With such a percentage, Brochantite (which is stable in a pH range of 8 to 9) may form in the presence of copper and sulfates when lime is used.

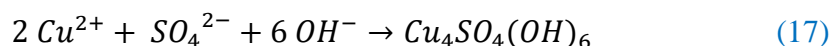
- Regarding the precipitation of caustic soda, the following elements were identified: 33% brochantite, 15% buttgenbachite (containing SO_4), and 12% tenorite (CuO). Furthermore, it contains 11% Langite and 9% Spertinite.

- By applying soda ash, the following elements were identified: 45.5% of Cuprite (Cu_2O), 17.2% of Brochantite, 7.1% of Langite and small concentrations (< 4 %) of Buttgenbachite ((SO_4)-bearing), Spertinite and Tenorite. It appears that 45.5% cuprite (Cu_2O) is high, since the CuCO_3 formed in the presence of Na_2CO_3 , as stated by Eq. (14), it could be converted into a stable compound (Cu_2O) during the drying process of the sludge that was generated under the following conditions: 80 °C for 12 hours. According to Brown et al., (1984), CuCO_3 is unstable after thermal treatment, and it will be transformed to Cu_2O as shown in the following reaction Eq. (16):

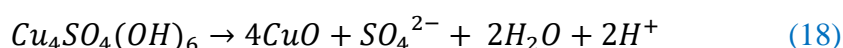


Muller, (2010) affirms that copper ions ($\text{Cu}(\text{II})$) can form associations with the species in the medium, when they are present in an electrolyte. The compounds that are generated after cuprite (Cu_2O) are mostly determined by the medium's concentrations of nitrate, carbonate, sulfate, and chloride. The presence of ammonium, chlorides, and sulfates ions in the wastewater can be used to explain the formation of Buttgenbachite ((SO_4)-bearing). Brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$) is produced when sulfate ions in solution combine with $\text{Cu}(\text{II})$ cations.

Thus, the compound formed precipitates at the oxide/electrolyte interface following the reaction (Eq. 17) (Muller, 2010):



Brochantite exhibits stability within the pH range of 3.6 to 6.2, when dissolved in a solution comprising 2 – 10 mol/L of sulfate. According to Eq. (18), Brochantite can change into Tenorite (CuO) through a dissolution/reaction event, when the pH near the electrode increases (Fitzgerald et al., 1998). Tenorite (CuO) formation was also due to spontaneous dehydration of Cu(OH)₂ (Chen et al., 2018). A low SO₄²⁻ content favors the formation of Langite Cu₄(SO₄)(OH)₆.2H₂O, also a precursor of Brochantite (Strandberg et al., 1997).



B. For Zinc Removal

The sludge generated through the application of each precipitating agent was quantitatively analyzed, and found to contain zinc hydroxide (Zn(OH)₂) at a percentage of 17.2% with lime, 16% with NaOH, and 7.1% with Na₂CO₃. Moreover, when all precipitating agents are used, zinc oxide (ZnO) is present in amounts less than 2%. Zincite is formed when zinc hydroxide is dehydrated during the precipitation process, as explained by Chen et al., (2018).

The effectiveness of removing copper and zinc ions using Ca(OH)₂, NaOH, and Na₂CO₃ is compared to certain results from earlier research on Cu(II) and Zn(II) precipitation in wastewater and synthetic solutions (Table 16). Indeed, numerous variables influence the efficiency of this particular treatment approach, including the initial pH of the aqueous solutions, the final pH of metals precipitation and the specific type and dosage of the precipitant. The results clearly show that applying enough precipitating agent dose to achieve an alkaline pH greater than 8 is essential for achieving residual Cu(II) and Zn(II) levels that meet industrial discharge regulations.

III.2.4 Effect of initial pH of wastewater

In order to determine the impact of wastewater initial pH on the removal efficiency of Cu(II) and Zn(II), an experiment was carried out in which 80 mg/L of the same precipitants was used by varying initial pH from 3 to 9 (Figure 38). The pH was adjusted using solutions of 0.1 N HCl and 0.1 N NaOH. As shown in Figure 38, when the initial pH of the wastewater increases, the removal efficiency of copper or zinc improves within the pH range investigated (3–9).

pH appears to have a significant role in the chemical precipitation process. According to [BrbootI et al. \(2011\)](#), the solubility of the metal typically falls as pH rises (hydroxide concentration increases) until the formation of soluble hydroxide complexes becomes considerable, and then the total solubility starts to increase with pH. The minimal solubility of copper hydroxide (0.03 mg/L) and zinc hydroxide (0.13 mg/L) is generally found at pH = 9.5, within the pH range of 7.5–11.5 [BrbootI et al., \(2011\)](#) also affirmed this claim.

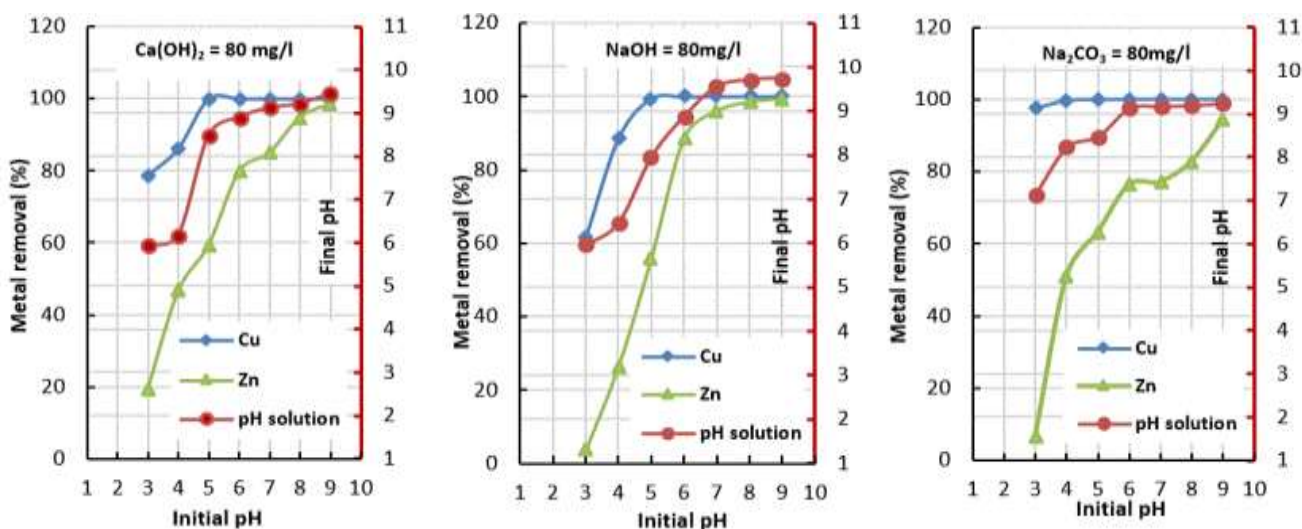


Figure 38 Effect of initial pH of wastewater on the removal of Cu(II) and Zn(II), using different precipitating agent ($\text{Cu(II)}_0 = 18.10 \text{ mg/L}$, $\text{Zn(II)}_0 = 10.21 \text{ mg/L}$).

[Figure 38](#) illustrates that the optimum efficiency of Cu(II) was achieved at $\text{pH}_f = 8.9$, when using NaOH and at $\text{pH}_f = 8.5$ when using Ca(OH)_2 , dependent on the final pH value. It occurred for Zn(II) at a higher ultimate pH of $\text{pH} = 9.45$ for Ca(OH)_2 and $\text{pH} = 9.75$ for NaOH. Selective precipitation would be necessary if multiple metals were present at the same time.

It was observed that the pH range of metal precipitation in the prior work (Chapter II), on the removal of copper and zinc separately from synthetic solution using lime and caustic soda was different from the results obtained in this application. Cu(II) and Zn(II) were maximally removed at pH values of 9.83 and 11, respectively. According to [Lorthois et al., \(1990\)](#), in application, it would be predicted that the combination of various heavy metals would cause a change in each metal's precipitation range to lower values.

For Na_2CO_3 , adjusting the initial pH to 4 was sufficient to provide an excellent Cu(II) removal (99.71%) at a final pH of 8.23. However, It was not possible to obtain the maximum

removal of Zn(II) (94% removal) with a pH adjustment of 9. As demonstrated in [Section II.3.3 of Chapter II](#), even if the final pH is less than 9.8, it is still well outside of the restricted range of maximal precipitation since each metal has a range of precipitation, outside this range the maximum removal cannot be achieved. In addition, the simultaneous presence of different metals would require selective precipitation.

The solution speciation of Cu(II) and Zn(II) ions was modelled using the computer software Visual MINTEQ (Version 3.1) at 24 °C, because it is known that the hydrolysis behavior of metal ions influences precipitation processes ([Wang et al., 2005](#)).

[Figure 39](#) and [Table 32](#) show the presence of metals (copper and zinc) species, according to pH variation. The formation of hydroxide-Metal precipitates ($\text{Cu}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$) and hydroxide complexes of Cu(II) and Zn(II) such as CuOH^+ , $\text{Cu}_2(\text{OH})_2^{2+}$, $\text{Cu}_3(\text{OH})_4^{2+}$ and ZnOH^+ is achieved in the pH range between 8 and 10, which is the optimum pH for the both metals removal. So the dominance of that species confirms the success of the chemical precipitation process.

Table 32 Cu and Zn dominant species according to pH variation ([Fig. 38](#)) using Visual MINTEQ (Version 3.1) at 24 °C ($\text{Cu}(\text{II})_0 = 18.10 \text{ mg/L}$, $\text{Zn}(\text{II})_0 = 10.21 \text{ mg/L}$)

pH	Dominant species	Observation
6 – 8	<ul style="list-style-type: none"> Cu^{2+}, $\text{Cu}_2(\text{OH})_2^{2+}$, CuOH^+ and $\text{Cu}_3(\text{OH})_4^{2+}$ Zn^{2+} and ZnOH^+ 	<ul style="list-style-type: none"> Decrease of Cu^{2+} and formation of $\text{Cu}_2(\text{OH})_2^{2+}$, CuOH^+ and $\text{Cu}_3(\text{OH})_4^{2+}$ Decrease of Zn^{2+} and ZnOH^+ were formed.
8 – 10	<ul style="list-style-type: none"> $\text{Cu}(\text{OH})_2$, $\text{Cu}(\text{OH})_3^-$ and $\text{Cu}_3(\text{OH})_4^{2+}$. $\text{Zn}(\text{OH})_2$ 	<ul style="list-style-type: none"> Formation of $\text{Cu}(\text{OH})_2$, $\text{Cu}(\text{OH})_3^-$ and $\text{Cu}_3(\text{OH})_4^{2+}$ by disappear of Cu^{2+}, $\text{Cu}_2(\text{OH})_2^{2+}$ and CuOH^+. Increase of $\text{Zn}(\text{OH})_2$, arriving the maximum level at pH=10, in the meantime Zn^{2+} and ZnOH^+ were disappeared gradually.
> 10	<ul style="list-style-type: none"> $\text{Cu}(\text{OH})_4^{2-}$, $\text{Cu}(\text{OH})_3^-$ and $\text{Cu}(\text{OH})_2$ $\text{Zn}(\text{OH})_4^{2-}$, $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_2$ 	<ul style="list-style-type: none"> Dissolution of $\text{Cu}(\text{OH})_2$ and the formation of $\text{Cu}(\text{OH})_3^-$ and $\text{Cu}(\text{OH})_4^{2-}$. Dissolution of $\text{Zn}(\text{OH})_2$ and the formation of $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$.

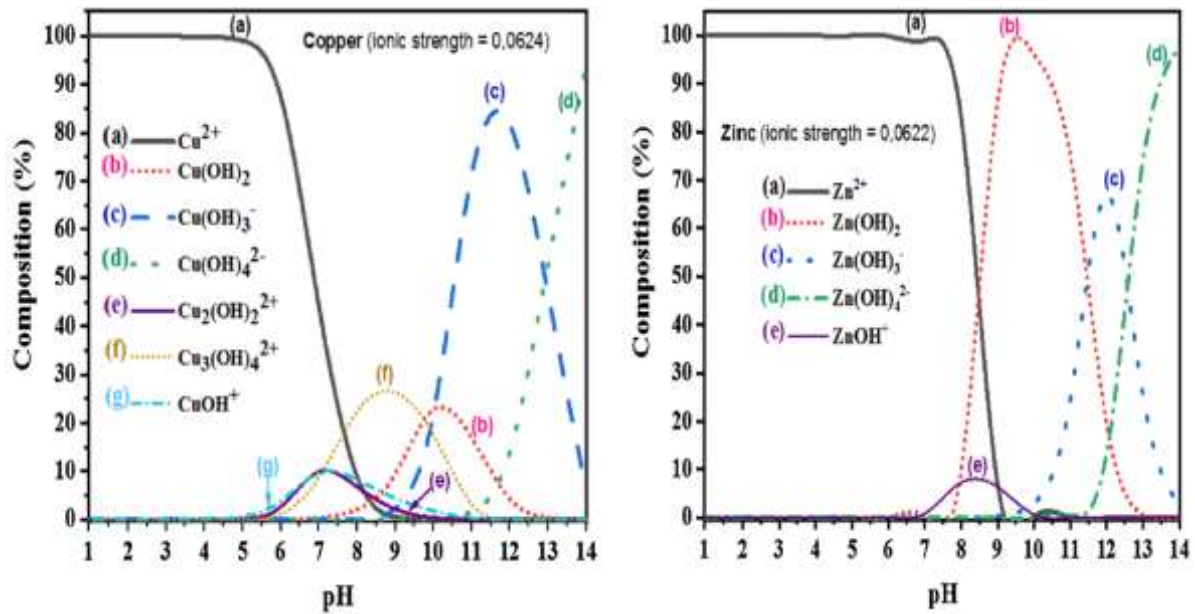


Figure 39 Speciation diagram of Cu and Zn in an aqueous solutions system at 24 °C ($\text{Cu(II)}_0 = 18.10$ mg/L, $\text{Zn(II)}_0 = 10.21$ mg/L).

III.2.5 Sludge System Analysis

After wastewater treatment by Ca(OH)_2 , NaOH , and Na_2CO_3 , sludge was recovered and dried and its volume (V), precipitate mass (PM) and average particle size were measured using the same methodology as in Chapter II (Section II.3.4). Figure 40 shows an estimation of the volume of sludge and the precipitate mass (PM) produced when using 200 mg/L of the precipitating agent after 1 h of settling time. The dose of 200 mg/L was selected on the basis that the residual of copper (< 0.5 mg/L) and zinc (< 3 mg/L) content was within the Algerian standard for liquid industrial discharges indicated in the Official Journal of the Algerian Republic (JORA, 2006). Moreover, the pH of solutions using all precipitating agents (8.73 for Ca(OH)_2 , 9.15 for NaOH and 8.85 for Na_2CO_3) was enough to reach minimum solubility of carbonates and hydroxides precipitation. The sludge generated during the experiment was recovered after one hour of settling, indicating that settling time is one of the important aspects of the treatment procedures since settling kinetics controls the treatment efficiency and performance (BrbootI et al. 2011). Chen et al., (2018) reported that lime and soda ash precipitation showed a fast-settling time (60 min) for zinc or copper aqueous solutions.

As shown in Figure 40(a), the volume of sludge produced by Ca(OH)_2 was significant but it stills less than the sludge produced by NaOH . In contrast to the hydroxide precipitation, the volume of sludge produced by Na_2CO_3 was small.

$$V_{NaOH} > V_{Ca(OH)_2} > V_{Na_2CO_3}$$

The sludge volume formed by soda ash was lower than that formed by hydroxide precipitating agents, because the carbonate precipitates formed have a better crystallinity than the hydroxides, so their recovery by decantation is easier and faster. This comment was also made by BrbootI et al., (2011) and Esmaeili and Vazirinejad, (2005) and related by Wang et al.,(2005).

As shown in Figure 40(b), the PM using Na_2CO_3 was larger with a slight difference compared to NaOH, while the PM using $Ca(OH)_2$ was small compared to the other precipitating agents.

$$PM_{Na_2CO_3} > PM_{NaOH} > PM_{Ca(OH)_2}$$

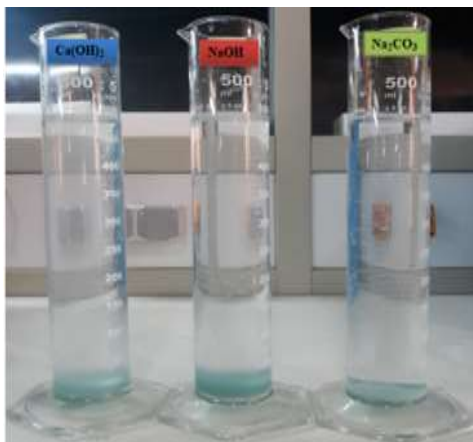
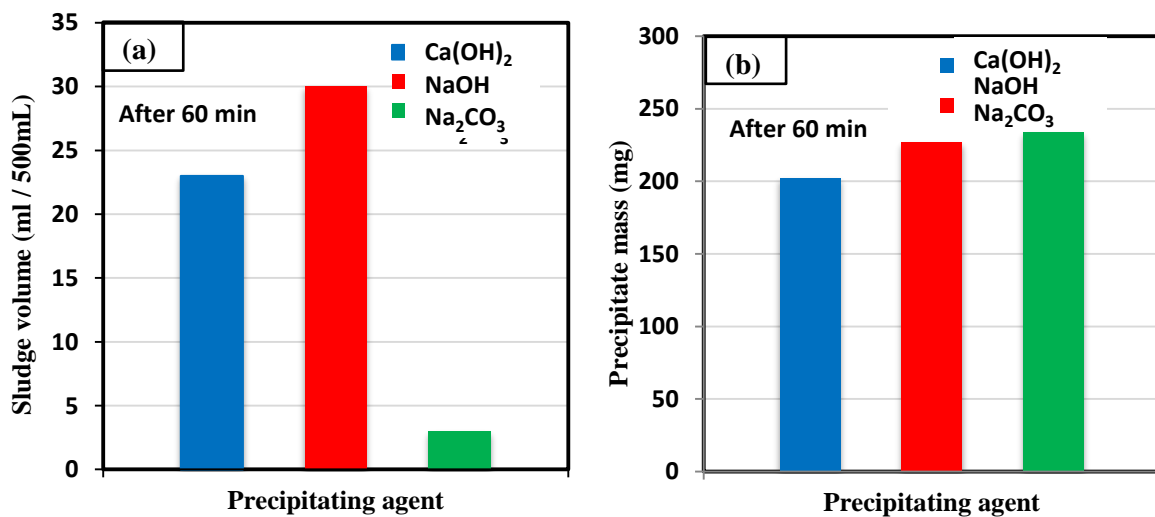


Figure 40 Sludge volume (a) and Precipitate mass (b) generated by the use of 200 mg/L of precipitating agents after one hour of settling ($Cu(II)_0 = 18.10$ mg/L ; $Zn(II)_0 = 10.21$ mg/L).

In the case of wastewater, as shown on the results presented in Table 29, the total hardness is high (52 meq/L) as is the content of magnesium (549.6 mg/L), calcium (124 mg/L), chlorides (784 mg/L) and sulfates (754 mg/L).

These parameters indicate that the total water hardness is high, as well as permanent hardness. In addition to the copper and zinc precipitation scenario, removal of hardness by the precipitation of CaCO_3 and MgCO_3 is added. The PM generated after lime treatment is low, this is for the reason that the precipitate formed is not consistent enough since lime is able to remove the temporary hardness (Lee and Scholz, 2006).

In addition, if the permanent hardness is high (the case of our wastewater), soda ash and caustic soda will be more efficient than lime. The contribution of these reactions made the PM follows the order below:

$$PM_{\text{Na}_2\text{CO}_3} > PM_{\text{NaOH}} > PM_{\text{Ca(OH)}_2}$$

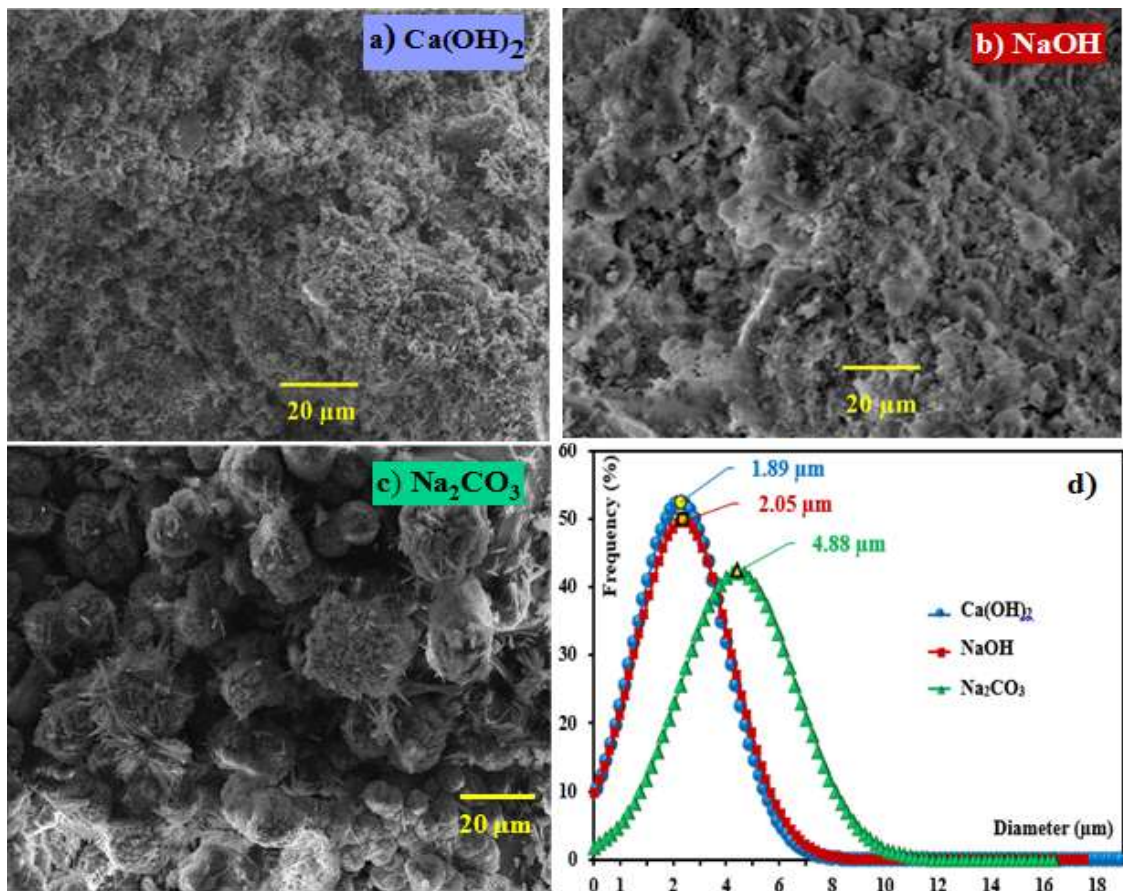


Figure 41 Scanning electron microscopy (SEM) images of sludge produced by precipitation of wastewater (by using (a) Ca(OH)_2 , (b) NaOH and (c) Na_2CO_3) and (d) Particle size distribution ($\text{Cu(II)}_0 = 18.10 \text{ mg/L}$; $\text{Zn(II)}_0 = 10.21 \text{ mg/L}$, dosage of precipitating agent = 200 mg/L).

SEM images (Figure 41(a–c)) show that the products from the reaction of precipitation are not large in size and are compact in structure. The analysis of particle size distribution, using Image J program and Origin Pro 2018, has showed that the average particle size of the precipitate was found approximately 1.89 μm in the $\text{Ca}(\text{OH})_2$ system, 2.05 μm in the NaOH system, while that of Na_2CO_3 was 4.88 μm (Figure 40(d)). This result confirms the difference in the PM formed by precipitating agents. Lime produced a lower precipitate mass and particle size related to other precipitating agents. According to Wang et al., (2016), the high OH^- concentration in $\text{Ca}(\text{OH})_2$ and NaOH slurry thus promotes the formation of new but small hydroxide particles. Metal carbonate precipitates formed have a better crystallinity than hydroxides so that their recovery by filtration or decantation is easier (Pénéliou, 2003).

III.3 Removal of Cu(II) and Ni(II) from industrial wastewater by using $\text{CaO}_{\text{Eggshells}}$ and conventional $\text{Ca}(\text{OH})_2$

III.3.1 Origin and characteristics of industrial wastewater treated

The Galvanic wastewater has been collected from an industrial plant (electroplating plant) located in Padova (Italian city). It should be noted that in the electroplating plant, chemical and electrochemical copper plating, nickel plating processes are applied. Two different samples were taken from the storage tank collecting raw industrial wastewater generated in the plant, wastewater 1 (WW1) charged with copper (II) and Wastewater 2 (WW2) charged with Nickel (II).

The physical and chemical characteristics of the industrial wastewater are given in Table 33. The pH of these wastewaters was very acid ($\text{pH} \approx 1 - 1.5$). The presence of high levels of Potassium, chlorides and sulfates was noted in these two samples (WW1 and WW2). The mean concentration of copper and nickel was 22961 mg/L and 36666 mg/L respectively. The Total Organic Carbon (TOC) is also very high, more than 35150 mg/L in WW2 (Table 33). All the previous parameters confirm the high pollution of this wastewater, exceeded too much the MCL indicated in the Official Journal of the Algerian Republic (JORA, 2006), even the highest metal concentrations require dilution before studying the possibility of treatment, to reduce wastewater pollution to a level where treatment can be carried out without any risk.

Table 33 Physical and chemical characteristics of the *Galvanic* wastewater (WW1 + WW2)

Parameter	Mean value of WW1	Mean value of WW2	Maximum allowable for industrial liquid discharges (JORA, 2006)
Temperature (C°)	20	20	< 30
pH	1 – 1.5	1 – 1.5	6.5–8.5
Chlorides (mg/L)	182	725	–
Sulfates (mg/L)	538770	39700	–
Potassium _{Tot} (mg/L)	45151	–	–
TOC (mg/L)	825	35150	–
Copper (mg/L)	22961	–	0.5
Nickel (mg/L)	–	36666	3

Table 34 shows the new physical and chemical characteristics of the combined wastewater (WW3) after dilution (1:500 of WW1 and 1:100 of WW2). The pH of WW3 remains very acidic (pH \approx 1.7 – 2.05). The levels of Potassium_{Tot} and Sulfates were high, while Chlorides were very low after dilution, only 7.61 mg/L, Total Organic Carbon (TOC) was minimized to 351.50 mg/L. The new wastewater is still polluted and requires treatment to remove 51.55 mg/L of copper (II) and 36.66 mg/L of nickel (II), which exceed the maximum concentration limits (MCL) of Algerian standards (JORA, 2006).

Table 34 Physical and chemical characteristics of the *Galvanic* wastewater WW3 (After dilution) (1:500 of WW1 and 1:100 of WW2)

Parameter	Mean value	Maximum allowable for industrial liquid discharges [JORA, 2006]
Temperature (C°)	20	< 30
pH	1.77– 2.05	6.5–8.5
Chlorides (mg/L)	7.61	–
Sulfates (mg/L)	1474.54	–
Potassium _{Tot} (mg/L)	451.51	–
TOC (mg/L)	353.15	–
Copper (mg/L)	51.55	0.5
Nickel (mg/L)	36.66	0.5

III.3.2 Comparison between conventional lime, eggshell powder and calcined eggshell (structure and chemical composition)

Conventional lime and quicklime extracted from eggshell after calcination were chosen for removing heavy metals (Cu(II) and Ni(II)) from galvanized wastewater, the both of them have almost the same chemical formula composed by calcium and oxygen, the only difference is that conventional lime is hydrated: $CaO + H_2O \rightarrow Ca(OH)_2$

So: $Quicklime + H_2O \rightarrow Conventional\ lime$

Figure 42 shows the visual shape of $CaCO_{3Eggshells}$, $CaOEggshells$ and $Ca(OH)_2$. It's clear that all the samples have the same white color and it seems that $Ca(OH)_2$ is softer than $CaOEggshell$.



Figure 42 Visual form of $Ca(OH)_2$ and eggshell powder before and after calcination ($CaCO_{3Eggshells}$ and $CaOEggshells$).

As mentioned previously (Section I.2.2), the dominant component of eggshell is limestone " $CaCO_3$ ", which is calcined to quicklime " CaO " by removing CO_2 . In order to improve this information mentioned by many researchers (Ashok, C. et al., 2014 ; Park et al. 2007), two important analyses were applied: XRF and EDX examinations (Figure 43 and Figure 29).

➤ XRF analyses

Figure 43(a,b,c) shows X-ray fluorescence (XRF) results for conventional lime and also eggshells before and after calcination.

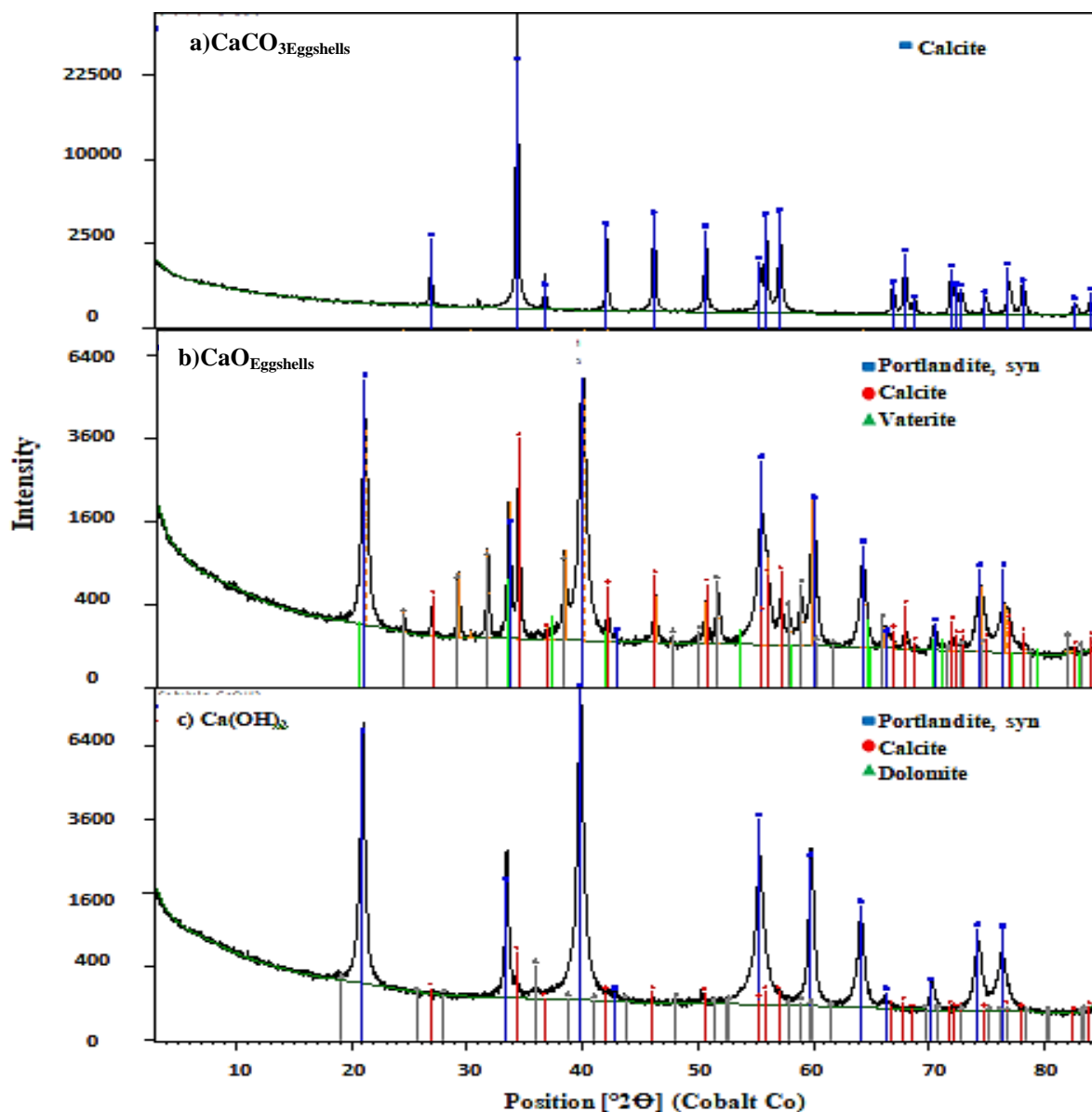


Figure 43 X-ray fluorescence (XRF) results for three different components (a) CaCO_3 Eggshells (b) CaO Eggshells , and (c) $\text{Ca}(\text{OH})_2$.

From analyzing the results shown in [Figure 43\(a,b\)](#), which represent the chemical composition of eggshell powder before and after calcinations. Before calcination ([Figure 43\(a\)](#)), the powder composed from pure calcite “ CaCO_3 ”. However, after calcination ([Figure 43\(b\)](#)), a new component appears is the Portlandite “ $\text{Ca}(\text{OH})_2$ ”, which is the predominant component. While, the pure calcite decreased and a very small amount of Vaterite appears (another type of CaCO_3), this result is consistent with the EDX analysis presented previously in [Table 26](#) and [Figure 29](#), i.e: calcinations is not completed and there is a small amount of CaCO_3 which can be ignored in the overall formula because the predominant component was

CaO. The XRF data of conventional lime $\text{Ca}(\text{OH})_2$ confirms the presence of Portlandite " $\text{Ca}(\text{OH})_2$ " and other trace elements of Calcite and Dolomite " $\text{CaMg}(\text{CO}_3)_2$ " Figure 43(c).

The XRF analysis was very important for comparing calcined eggshell " $\text{CaO}_{\text{Eggshells}}$ " and conventional lime $\text{Ca}(\text{OH})_2$, the main difference is in the percentage of CaCO_3 , which is a little bit more available in calcined eggshell.

➤ SEM analyzes

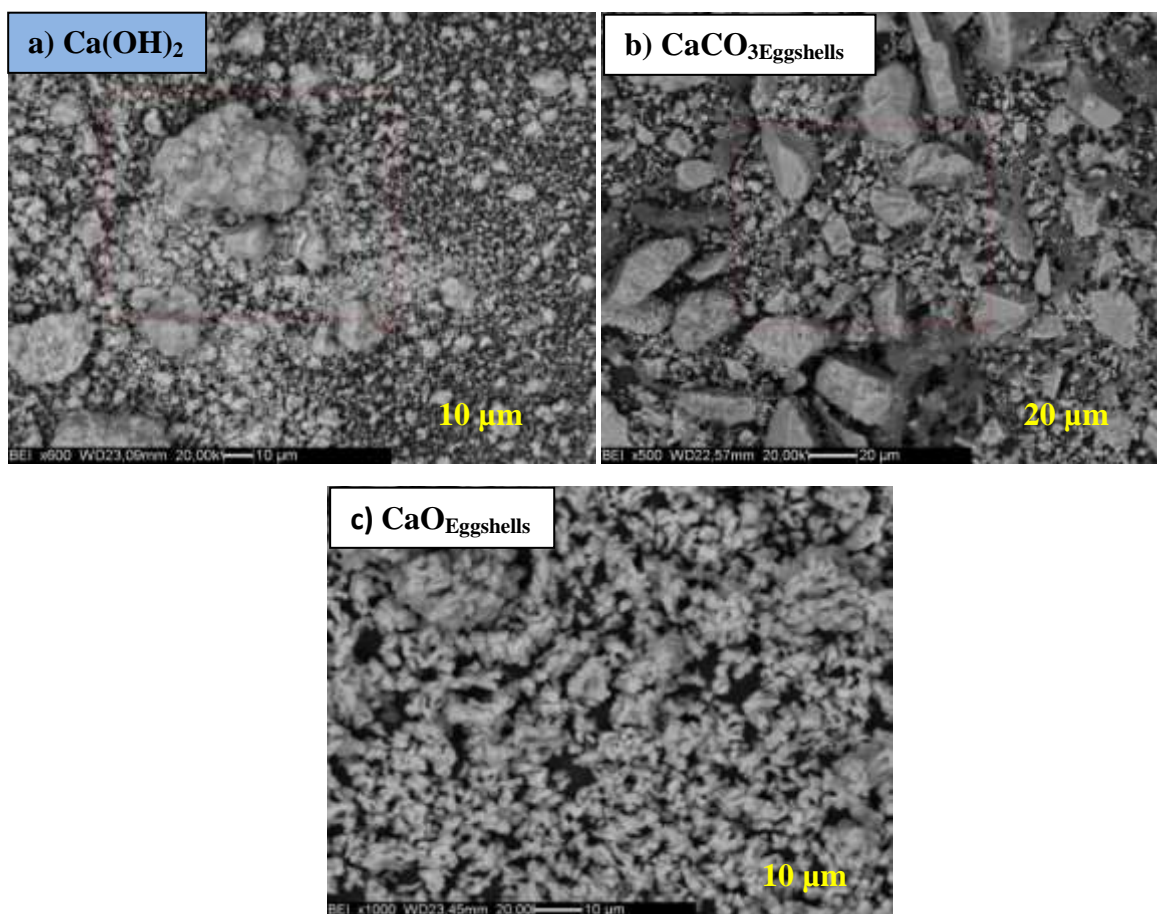


Figure 44 SEM images of three different reactifs; $\text{Ca}(\text{OH})_2$, $\text{CaCO}_3_{\text{Eggshells}}$ and $\text{CaO}_{\text{Eggshells}}$.

Figure 44 (a,b and c) illustrate the morphology, structure and particle size of conventional lime ($\text{Ca}(\text{OH})_2$), and eggshells powder before and after calcination, i.e. two different chemical components (calcium carbonates " CaCO_3 " and calcium oxide " CaO "). Based on SEM image analysis, it is clear that there is a difference in the structure and size of the particles between the precipitants studied, for example for $\text{Ca}(\text{OH})_2$ and CaCO_3 , the size of the particles is not homogeneous (very small or too large), whereas for CaO , the particles

are small but very similar in size and more coherent. It seems that there is a similarity between the particle size of Ca(OH)_2 and $\text{CaO}_{\text{Eggshells}}$, the both are small in size.

III.3.3 Effect of $\text{CaO}_{\text{Eggshells}}$ and conventional Ca(OH)_2 dose on the removal of Cu(II) and Ni(II)

Jar tests using variable amounts of each precipitating agent ($\text{CaO}_{\text{Eggshells}}$ and Ca(OH)_2) were performed at 20 °C and $\text{pH}_0 = 1.77 - 2$.

Increased doses of (100 to 1800 mg/L) of each agent are used to determine the optimum dosage for purification of the galvanic wastewater (WW3), and to indicate the appropriate precipitant for the removal of 51.55 mg/L and 36.66 mg/L of Zn(II) and Ni(II) successively (Figure 36). The results of the final pH, the remaining metal concentration and the removal efficiency of the metal for the precipitating agent dosages (600, 1000, 1200, 1400, 1600 and 1800 mg/L) are presented in Table 35.

Table 35 Effect of varying $\text{CaO}_{\text{Eggshells}}$ and Ca(OH)_2 dose in the removal of Cu(II) and Ni(II) from galvanic wastewater

Precipitating agent	Dose (mg/L)	Final pH	Cu Removal (%)	Ni Removal (%)
$\text{CaO}_{\text{Eggshells}}$	600	6.09	12.00	22.53
	1000	8.49	20.55	34.26
	1200	9.70	29.82	51.17
	1400	11.10	59.00	68.09
	1600	11.91	85.33	84.89
	1800	12.30	93.05	90.45
	Ca(OH)_2	600	6.01	6.36
1000		9.37	25.27	48.31
1200		10.90	53.73	77.14
1400		12.19	80	87.56
1600		12.40	93.95	93.83
1800		12.72	88.65	96.34

A. For calcined eggshells

Table 34 and Figure 45(a), show that Cu(II) and Ni(II) removal increases with increasing $\text{CaO}_{\text{Eggshells}}$ dosage, it reached the maximum removal : 93.05% and 90.45%

successively, at a high dosage and at a very alkaline pH ($OD = 1800\text{mg/L}$, $OpH = 12.30$). However, this removal is not enough because the RM concentrations are higher than the MCL indicated by the Algerian Standards (JORA, 2006).

Cu: $3.82\text{ mg/L} > 0.5\text{ mg/L} \rightarrow RM_{Cu/CaO_{Eggshells}} > MCL_{Cu} \rightarrow MCL\text{ not respected}$

Ni: $3.5\text{ mg/L} > 0.5\text{ mg/L} \rightarrow RM_{Ni/CaO_{Eggshells}} > MCL_{Ni} \rightarrow MCL\text{ not respected.}$

Comparing with the results of synthetic solution presented previously (Section II.5.2), using the same $CaO_{Eggshells}$ precipitating agent, the Cu removal efficiency in synthetic solution ($R_{Cu(SS)}\%$) was higher than that in wastewater ($R_{Cu(WW)}\%$), and the residual Cu (RM_{Cu}) in synthetic solution was very low compared to wastewater. In addition, the OD_{WW} of Cu removal from wastewater was more four times than the OD_{SS} of the same metal removal from the synthetic solution.

$$1800\text{ mg/L} = 4.2 \times 400\text{ mg/L} \rightarrow OD_{WW} = 4.2 \times OD_{SS}$$

$$99.69\% > 93.05\% \rightarrow R_{Cu(SS)}\% > R_{Cu(WW)}\%$$

$$0.21\frac{\text{mg}}{\text{L}} < 3.82\frac{\text{mg}}{\text{L}} \rightarrow RM_{Cu(SS)} < RM_{Cu(WW)}$$

This decrease can be related to the nature of the wastewater, which is polluted and charged with different mineral and organic elements (TOC, low concentration of other heavy metals, P_{Tot} , sulfates...), all of these elements affect the removal efficiency of the both metals Cu(II) and Ni(II).

a) Calcined Eggshells

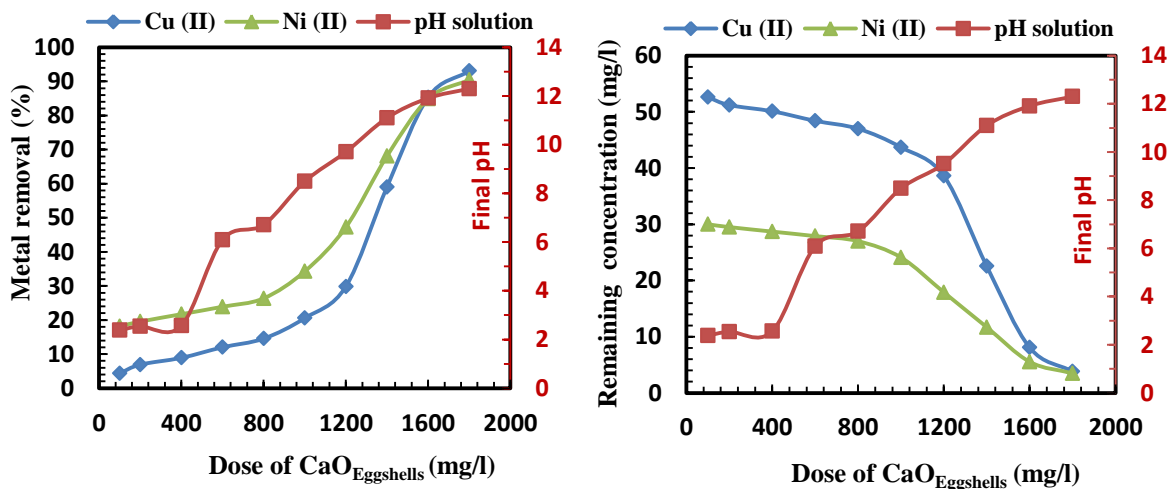


Figure 45 Effect of precipitating agent dosage (A) $CaO_{Eggshells}$ in the removal of Cu(II) and Ni(II). ($Cu(II)_0 = 55.05\text{ mg/L}$, $Ni(II)_0 = 36.66\text{ mg/L}$, $pH_0 = 1.77 - 2$).

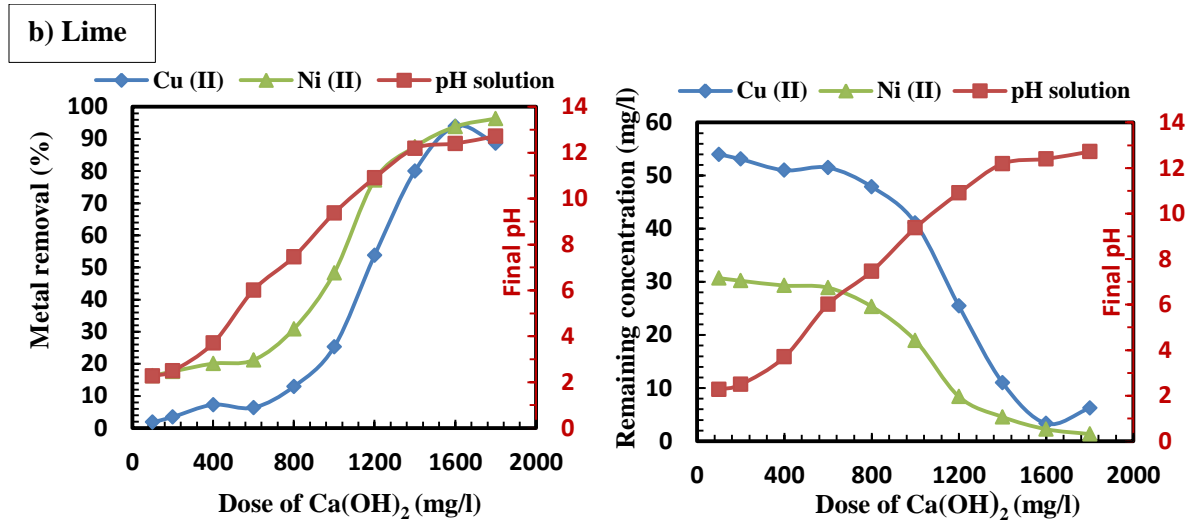


Figure 45 Effect of precipitating agent dosage (B) $\text{Ca}(\text{OH})_2$, in the removal of $\text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$. ($\text{Cu}(\text{II})_0 = 55.05 \text{ mg/L}$, $\text{Ni}(\text{II})_0 = 36.66 \text{ mg/L}$, $\text{pH}_0 = 1.77 - 2$) (continued).

B. For Lime

Analysis of the results in [Table 35](#) and [Figure 45\(b\)](#) shows that the optimum point correspond to the best removal of $\text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$ is : (OD = 1600 mg/L , OpH = 12.40), with a removal efficiency of 93.95% and 93.83% for $\text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$, respectively. The RM concentrations was 3.33 mg/L and 2.26 mg/L for $\text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$, respectively. The efficiency obtained is relatively high but it is not enough to meet the MCL standards.

Cu: $3.33 \text{ mg/L} > 0.5 \text{ mg/L} \rightarrow \text{RM}_{\text{Cu}/\text{Ca}(\text{OH})_2} > \text{MCL}_{\text{Cu}} \rightarrow \text{MCL not respected}$

Ni: $2.26 \text{ mg/L} > 0.5 \text{ mg/L} \rightarrow \text{RM}_{\text{Ni}/\text{Ca}(\text{OH})_2} > \text{MCL}_{\text{Ni}} \rightarrow \text{MCL not respected}$

Conventional lime ($\text{Ca}(\text{OH})_2$) performs better in removing $\text{Cu}(\text{II})$ from synthetic solution, individually ([Section II.2](#)) and in combination with other metals ([Section II.3](#)), also it has good efficiency in removing $\text{Cu}(\text{II})$ from ENICAB wastewater ([Section III.2](#)). A comparison of all of these results is summarized in [Table 36](#).

Table 36 Results of the previous experimental trials studying the removal of Cu(II) by using Ca(OH)₂

Nature of solution	Heavy metals in water	OpH	OD(mg/L)	R _{Cu} (%)	RM _{Cu} (mg/L)
Galvanic wastewater	Cu(II) + Ni (II)	12.40	1600	93.95	3.33
ENICAB wastewater	Cu(II) + Zn (II)	9.96	300	99.99	3×10^{-4}
Synthetic solution	Cu(II) alone	9.98	200	99.99	2.28×10^{-5}
Synthetic solution	Cu(II) + Cd(II) + Zn(II)	10.73	400	99.88	0.12

In the results presented in [Table 36](#), the optimum removal for all different treated waters has been chosen. The removal of Cu(II) using conventional lime was almost completely in synthetic solution (with Cu(II) alone), and in ENICAB wastewater (charged in two different heavy metals Cu(II) and Zn(II)) more than 99.99% of removal at $pH_f \leq 10$, by using 200 and 300 mg /L of Ca(OH)₂.

For the synthetic solution charged with three different metals Cu(II), Cd(II), and Zn(II), the removal of Cu(II) required more Ca(OH)₂ dose, which means more increase in the final pH (OD = 400 mg/L ;OpH = 10.73), as a result the removal efficiency of Cu(II) slightly decreased reaching 99.88%.

At last, the galvanic wastewater charged with two different metals Cu(II) and Ni(II), a high concentration of Ca(OH)₂ equal to 1600 mg/L was required to achieve 93.95%. This value is the maximum removal of Cu(II) at a very basic pH equal to 12.40, this decrease in the removal efficiency of Cu(II) compared to the other solutions can be related to the nature and the chemical and physical characteristics of the wastewater (return to [Table 33](#)), it means that this wastewater is too polluted and charged with other elements which affect the removal efficiency of Cu.

As a conclusion, the removal efficiency of Cu(II) or any other metal can be influenced by the following factors:

- The nature of the treated water (synthetic or wastewater).

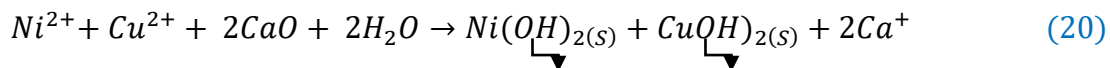
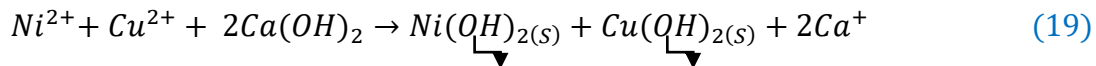
- The chemical and physical characteristics of the wastewater and the degree of pollution expressed by the presence of inorganic compounds like heavy metals and organic matter (TOC, BOD₅, COD).
- The presence of other heavy metals creates a competition between the present metals.

It seems that there is no large difference between Ca(OH)₂ and CaO_{Eggshells} for the removal of Cu(II) and Ni(II) from the galvanic wastewater, with a small advantage of Ca(OH)₂ for two reasons:

- The pH_f increases faster with Ca(OH)₂ than CaO_{Eggshells}, enhancing Cu(II) and Ni(II) removal in the presence of lime.
- 1600 mg/L of Ca(OH)₂ was enough to get the maximum metals removal. However, to reach the same removal efficiency, more than 1800 mg/L of CaO_{Eggshells} are required.

III.3.4 Mechanisms of precipitation

The mechanism of Cu(II) and Ni(II) removal from galvanic wastewater using CaO_{Eggshells}, and Ca(OH)₂ expressed by Eq. 19 and Eq. 20 respectively, as follow:



It seems that the Eqs. 19 and 20 are semilare, as a result the same precepitates in hydroxide form were obtained, Ni(OH)₂ and Cu(OH)₂.

III.3.5 Effect of Initial pH

Jar's tests applying the same procedure, by varying the initial pH (2 to 11.5) and using 600 mg/L of CaO_{Eggshells} and Ca(OH)₂, studying the removal of heavy metals Cu(II) and Ni(II) from the galvanic wastewater (WW3), tenor of 51.55 mg/L and 36.66 mg/L successively, than a comparison between CaO_{Eggshells} and Ca(OH)₂ will be performed to select the appropriate precipitant (Table 37 and Figure 46).

Table 37 Effect of pH adjustment on the removal of Cu(II) and Ni(II) by using $\text{CaO}_{\text{Eggshells}}$ and $\text{Ca}(\text{OH})_2$. ([precipitant]= 600 mg/L ; [Cu(II)] = 51.55 mg/L ; [Ni(II)] = 36.66 mg/L)

Precipitating agent	pH	Final pH	Cu Removal (%)	Ni Removal (%)
$\text{CaO}_{\text{Eggshells}}$	2	5.67	6.69	24.16
	3	7.37	6.89	24.71
	4	8.46	9.89	33.03
	5	9.2	17.36	38.49
	6	9.99	22.41	47.22
	7	11.17	41.42	71.63
	9	12.01	66.63	80.01
	11.5	12.53	86.94	90.18
	$\text{Ca}(\text{OH})_2$	2	6.12	7.86
3		8.97	19.01	42.71
4		9.75	22.70	47.76
5		10.04	26.09	52.13
6		11.24	47.33	73.38
7		11.98	69.93	80.47
9		12.36	83.82	85.88
11.5		12.74	95.36	93.75

A. For calcined eggshells ($\text{CaO}_{\text{eggshells}}$),

According to [Figure 46](#), after adjusting the initial pH (pH_i) from (2 to 11.5), using 600 mg/L of $\text{CaO}_{\text{eggshells}}$, and a calculated volume of NaOH, the final pH (pH_f) increases, so the Residual concentration of Cu(II) and Ni(II) decreases and the removal efficiency increases too.

For all pH_i adjustments, Ni(II) removal was better than Cu(II), although the best pH value of copper precipitation was lower than that of nickel (pH 10 - 10.5 for nickel, pH 8.5 - 9.5 for copper), it is suggested that this effect is linked to the metals selectivity.

The maximum removal reaching 86.94% and 90.18% of Cu(II) and Ni(II) successively at $\text{pH}_i = 11.5$ and $\text{pH}_f = 12.53$. These efficiencies are high but they are not sufficient, as the corresponding RM concentrations were not in compliance with MCL standards.

Cu: $3.6 \text{ mg/L} > 0.5 \text{ mg/L} \rightarrow \text{RM}_{\text{Cu}/\text{CaO}_{\text{Eggshells}}} > \text{MCL}_{\text{Cu}} \rightarrow \text{MCL not respected}$

Ni: $6.73 \text{ mg/L} > 0.5 \text{ mg/L} \rightarrow \text{RM}_{\text{Ni}/\text{CaO}_{\text{Eggshells}}} > \text{MCL}_{\text{Ni}} \rightarrow \text{MCL not respected}$

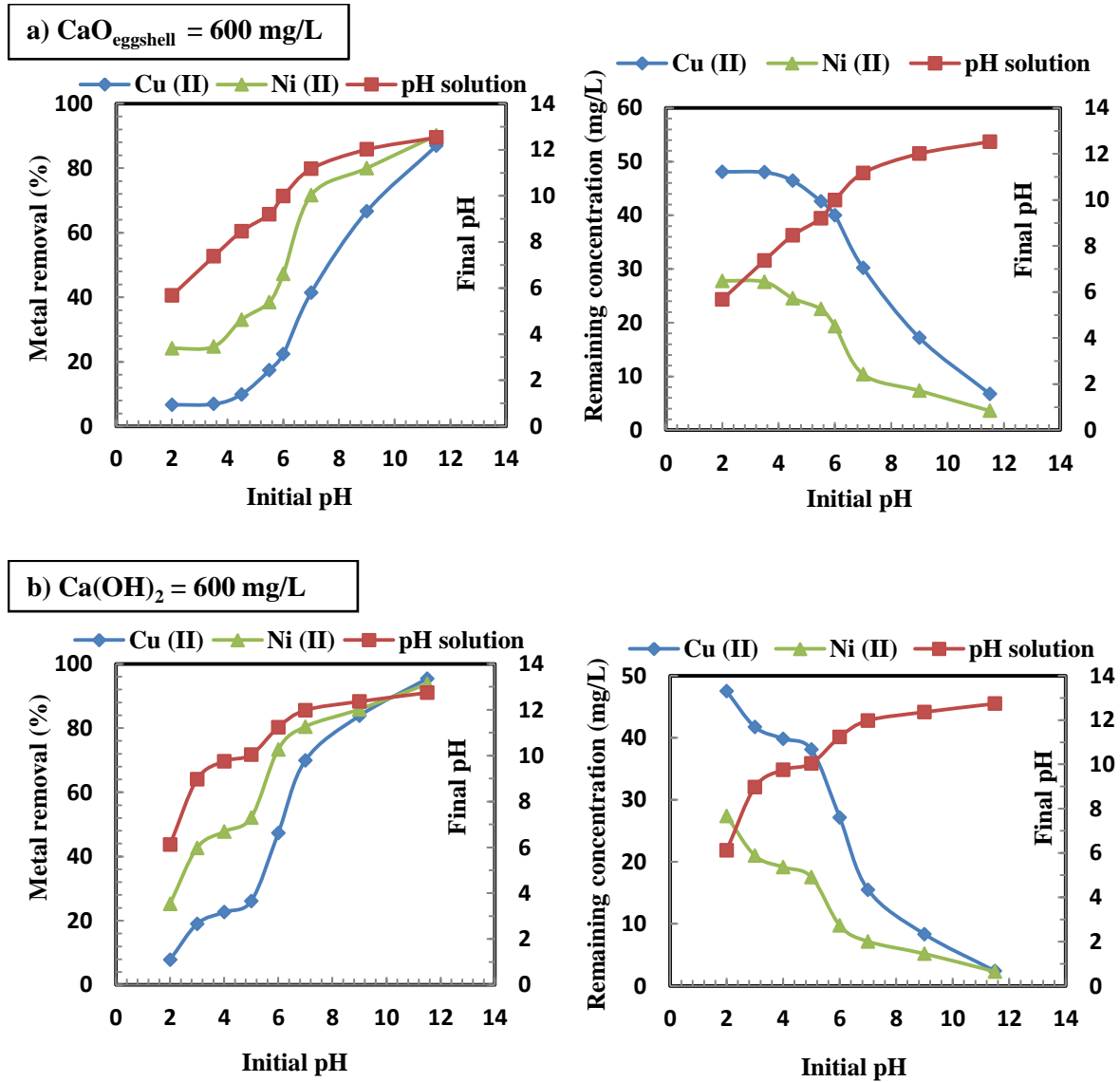


Figure 46 Effect of initial pH of galvanic wastewater on the removal of Cu(II) and Ni(II), using $\text{CaO}_{\text{Eggshells}}$ and Ca(OH)_2 ((a) and (b)). ($\text{Cu(II)}_0 = 51.55 \text{ mg/L}$, $\text{Ni(II)}_0 = 36.66 \text{ mg/L}$; $[\text{A}] = [\text{B}] = 600 \text{ mg/L}$).

B. For conventional lime (Ca(OH)_2)

This experiment was similar to $\text{CaO}_{\text{eggshells}}$ in procedure and provided slightly similar results. The difference was in the final pH, which increased rapidly when using Ca(OH)_2 , making the removal better (Table 37 and Figure 46).

The removal of both metals increased with increasing pH_i and pH_f , while the maximum removal reached 95.36% and 93.75% of Cu(II) and Ni(II) respectively, at $\text{pH}_i = 11.5$ and $\text{pH}_f = 12.74$. These removal (R%) is very high compared to the removal obtained using $\text{CaO}_{\text{eggshells}}$, but still not sufficient.

Cu: $2.93 \text{ mg/L} > 0.5 \text{ mg/L} \longrightarrow \text{RM}_{\text{Cu}/\text{Ca}(\text{OH})_2} > \text{MCL}_{\text{Cu}} \longrightarrow \text{MCL not respected}$

Ni: $2.29 \text{ mg/L} > 0.5 \text{ mg/L} \longrightarrow \text{RM}_{\text{Ni}/\text{Ca}(\text{OH})_2} > \text{MCL}_{\text{Ni}} \longrightarrow \text{MCL not respected}$

C. General observations

- For both precipitants, the pH range of Cu(II) and Ni(II) precipitation was changed, as previously indicated, pH_f [8.5 - 9.5] was enough to obtain a relatively high Cu(II) removal efficiency. And pH_f [10 - 10.5] was enough to obtain a relatively high Ni(II) removal efficiency. In this case, maximum removal efficiency occurred at very basic pH levels for both metals.
- The removal efficiency of $\text{CaO}_{\text{eggshells}}$ and $\text{Ca}(\text{OH})_2$ is similar. The only difference is relating to the dose of precipitant used. So, to achieve the same efficiency, more than 600 mg/L of $\text{CaO}_{\text{eggshells}}$ are needed to raise the final pH and reach the same final pH of conventional lime.
- The Calcined eggshells can be used as an alternative of conventional lime for hydroxide precipitation.

III.3.6 Sludge System Analysis

Sludge recovered and dried after the treatment of galvanic wastewater by $\text{CaO}_{\text{Eggshells}}$ and $\text{Ca}(\text{OH})_2$ were characterized, the Volume (V) and Precipitate Mass (PM) also measured. [Table 38](#) and [Figure 47](#) show an estimation of the volume and mass of sludge produced by using four different concentrations 600, 800, 1400, and 1800 mg/L of the precipitating agent after different settling times (60, 90, and 120 min). All the concentrations selected have a final pH slightly alkaline, ranging from 6 and reaching 12 at 1800 mg/L of precipitants. In this experiment, the settling time has been extended to give the precipitates more time to deposit, and to confirm whether one hour is sufficient for settling galvanic wastewater sludge. Recognizing that settling time required is one of the key factors in the treatment processes, since settling kinetic governs the treatment efficiency and performance ([BrbootI et al., 2011](#)).

Table 38 Sludge volume and PM generated by the use of (600 - 1800 mg/L) of $\text{CaO}_{\text{Eggshells}}$ and $\text{Ca}(\text{OH})_2$ for the removal ($\text{Cu}(\text{II})_0 = 51.55 \text{ mg/L}$ and $\text{Ni}(\text{II})_0 = 36.66 \text{ mg/L}$), after different settling times (60 - 120 min).

Precipitants concentration (mg/L)	$\text{CaO}_{\text{Eggshells}}$				$\text{Ca}(\text{OH})_2$			
	$V_{S/60\text{min}}$ (mL)	$V_{S/90\text{min}}$ (mL)	$V_{S/120\text{min}}$ (mL)	PM (mg)	$V_{S/60\text{min}}$ (mL)	$V_{S/90\text{min}}$ (mL)	$V_{S/120\text{min}}$ (mL)	PM (mg)
600	0.5	0.5	0.5	11.6	0.01	0.01	0.01	6.3
800	0.65	0.65	0.65	113	3.8	3.5	3.8	66.1
1400	6.5	6.5	6.5	331	12.5	10	9.5	224
1800	11	11	11	531	15	14	14	325

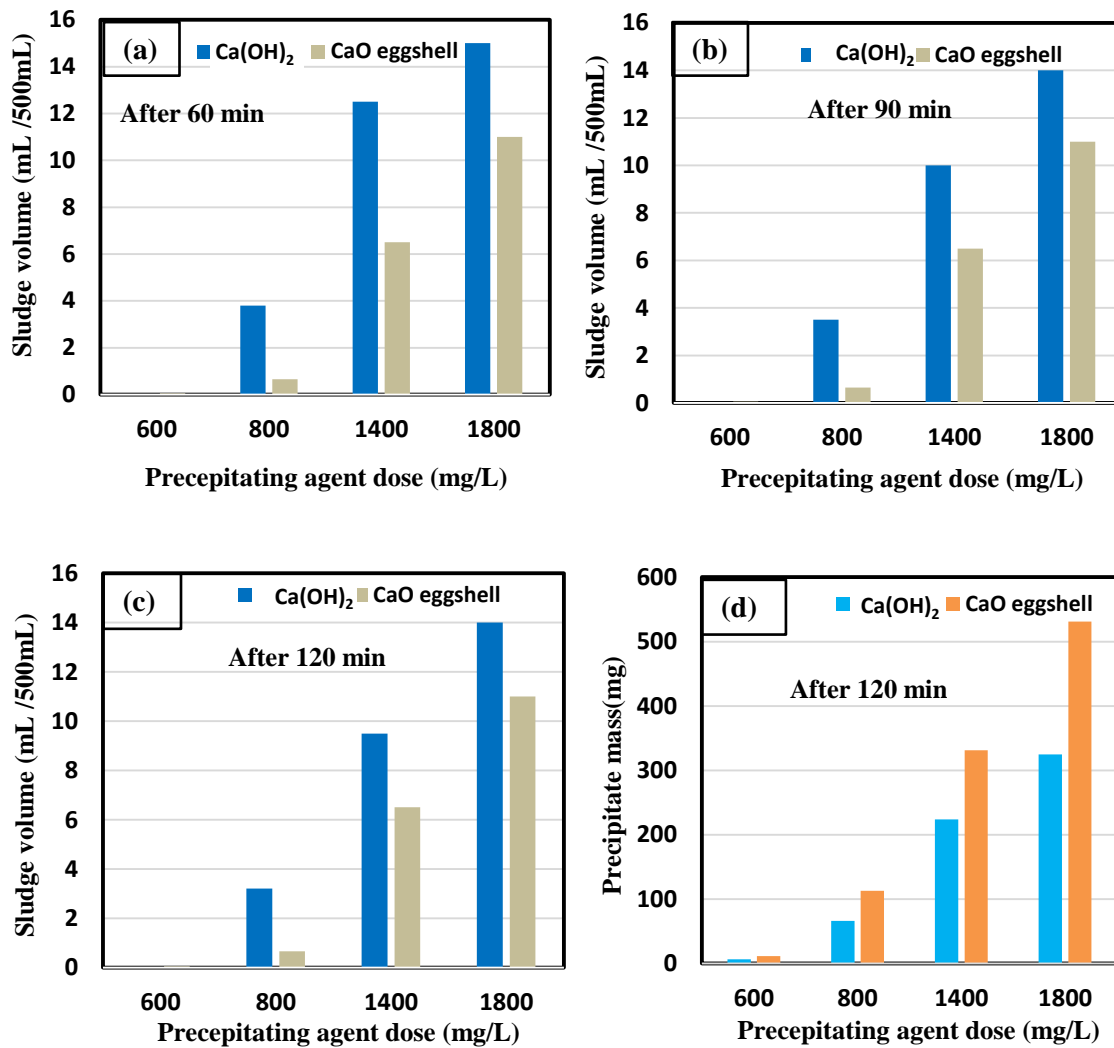


Figure 47 Sludge volume (a, b, and c) and PM (d) generated by the use of (600 - 1800 mg/L) of $\text{Ca}(\text{OH})_2$ and $\text{CaO}_{\text{Eggshells}}$ for the removal ($\text{Cu}(\text{II})_0 = 51.55 \text{ mg/L}$ and $\text{Ni}(\text{II})_0 = 36.66 \text{ mg/L}$), after different settling times (60 - 120 min).

After analysis of results presented in [Figure 47\(a-b and c\)](#), it is clear that sludge volume increases as the dose of precipitant increases. The sludge volume produced by using $\text{Ca}(\text{OH})_2$ was higher than that produced by using $\text{CaO}_{\text{Eggshells}}$ for all doses. However, the latter was more stable than that of $\text{Ca}(\text{OH})_2$, which decreased over time. It means that settling stage is faster by using $\text{CaO}_{\text{eggshells}}$.

$$V_{S/\text{Ca}(\text{OH})_2} > V_{S/\text{Eggshells}}$$

According to [Brbootl et al., \(2011\)](#), the settling time required is one of the key factors in treatment processes. For this study, 1 hour of settling time is sufficient for the precipitates produced by calcined eggshells to settle completely. In contrast, the full precipitation time for conventional lime was 2 hours. Sludge formed by using $\text{Ca}(\text{OH})_2$ were gelatinous and $\text{CaO}_{\text{Eggshells}}$ precipitates formed have a better crystallinity so that their recovery by decantation is easier and faster.

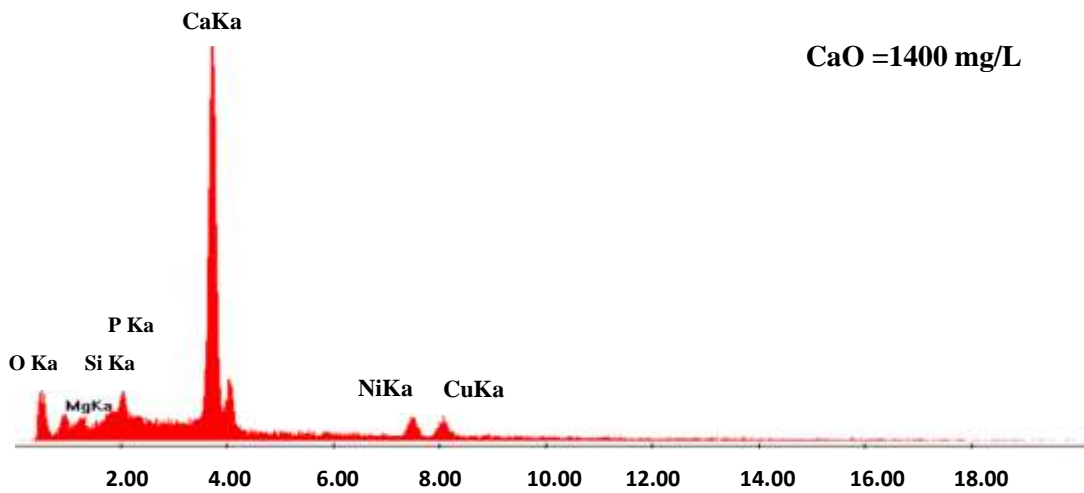
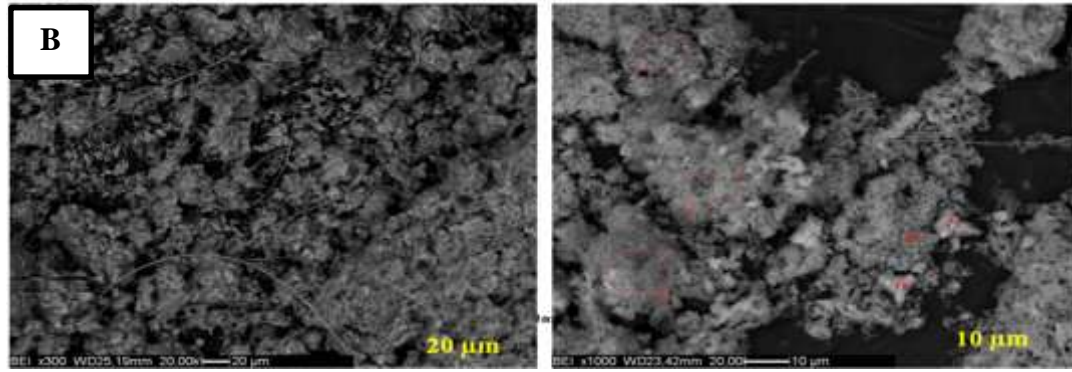
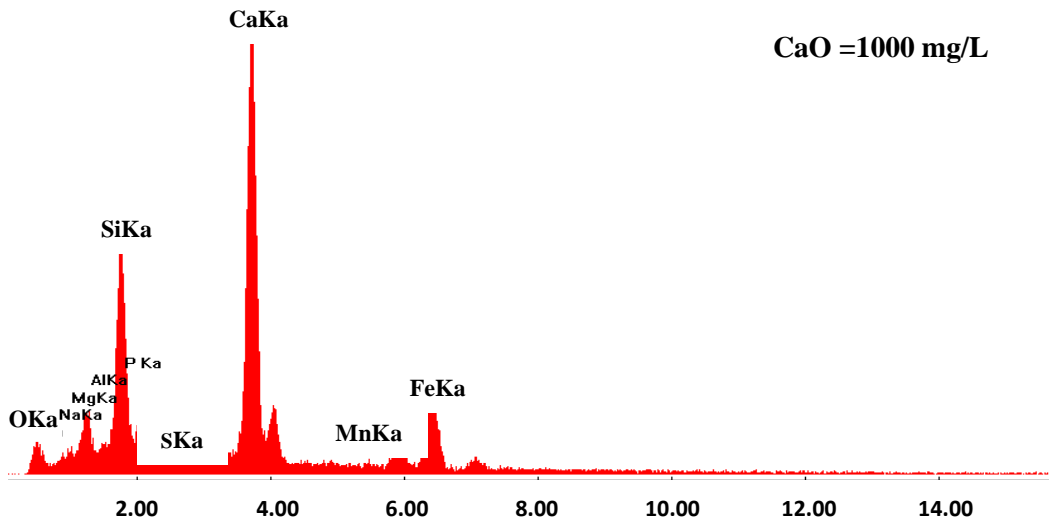
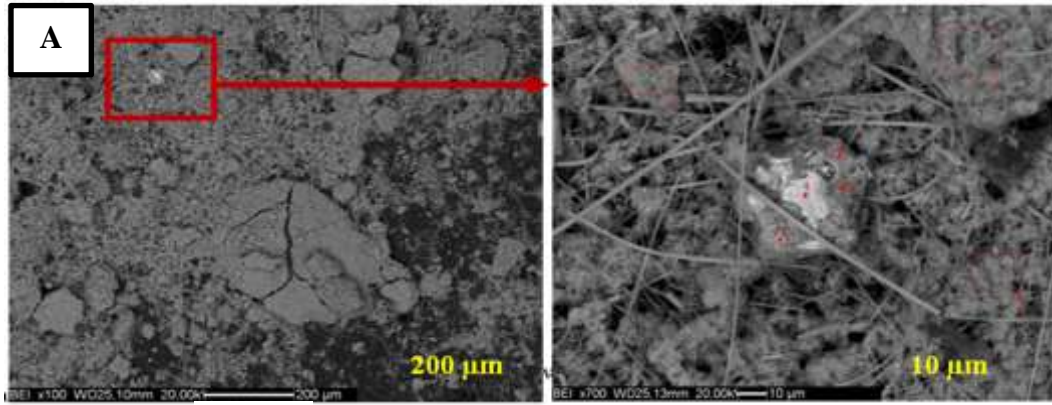
[Figure 47\(d\)](#) shows the variation of PM by increasing the dose of precipitant after 2 hours of settling, the results show that PM also increases by increasing the dose of precipitant, but here the reverse is true in relation to sludge volume, the PM obtained by $\text{CaO}_{\text{eggshells}}$ is very significant compared to the PM obtained by $\text{Ca}(\text{OH})_2$.

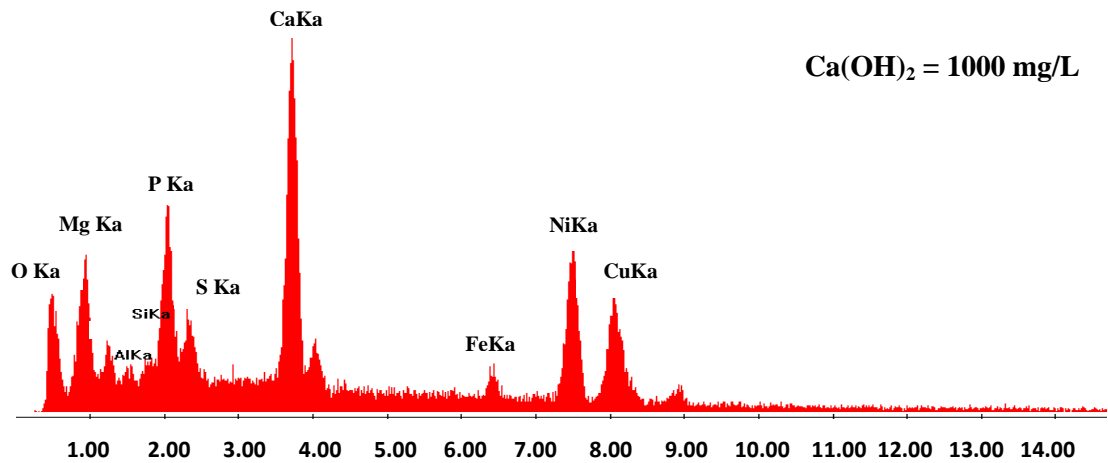
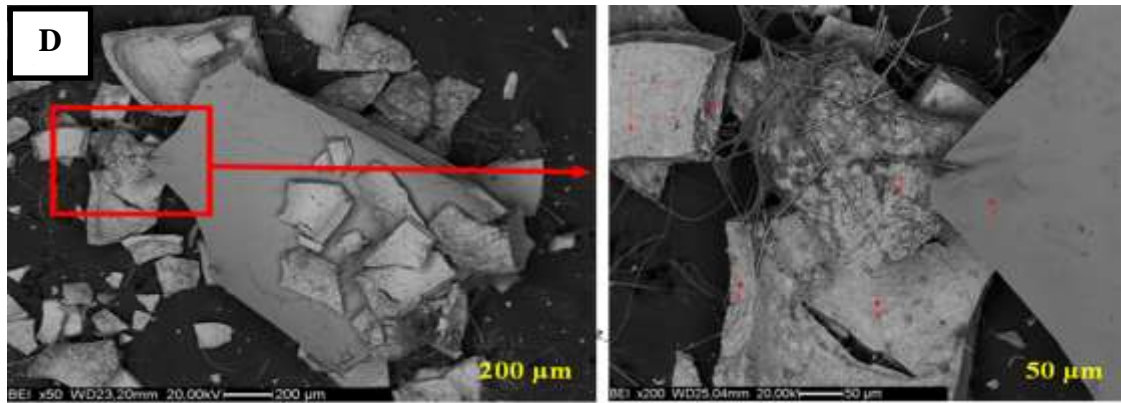
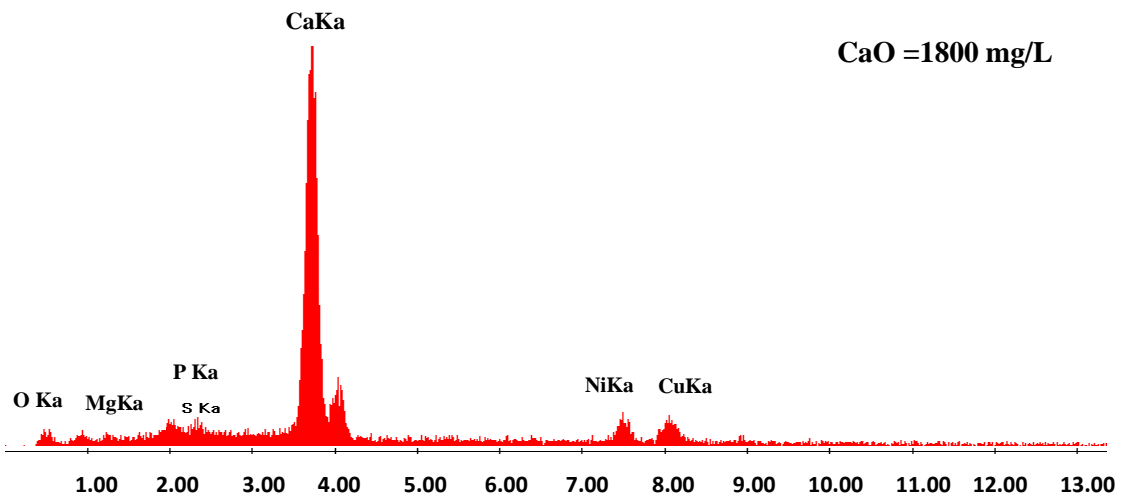
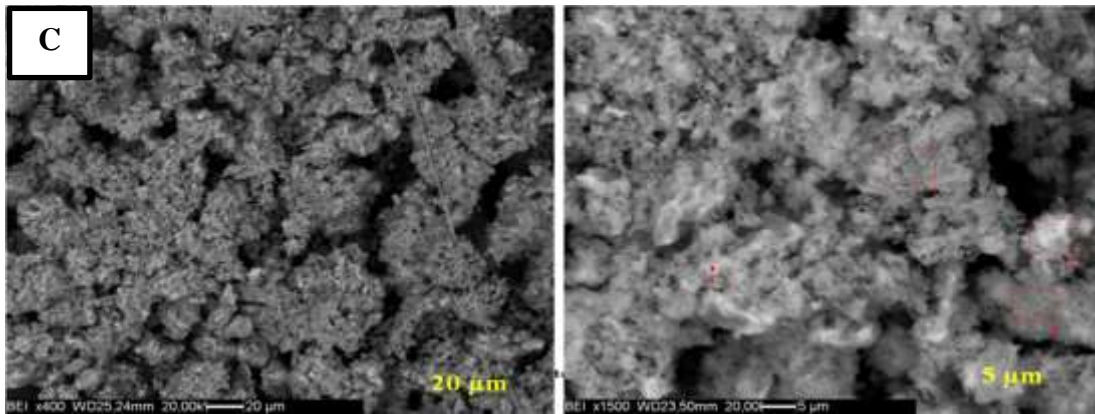
$$PM_{\text{CaO}_{\text{Eggshells}}} > PM_{\text{Ca}(\text{OH})_2}$$

EDX and SEM analyses give more details on sludge composition and structure at three different concentrations (1000, 1400, and 1800 mg/L), of precipitating agent ($\text{Ca}(\text{OH})_2$ and $\text{CaO}_{\text{eggshells}}$), it means three different pH values ([Table 39](#) and [Figure 48](#)).

Table 39 EDX results of recovered sludge at three different precipitant doses

Parameter	Precipitant	CaO _{eggshells}			Ca(OH) ₂		
		1000	1400	1800	1000	1400	1800
Dose (mg/L)		1000	1400	1800	1000	1400	1800
pH _f		8.09	11.15	12.51	9.37	12.19	12.72
Predominant elements	Ca	Ca	Ca	Si	Ca	Ca	
	Si	O	Cu	Ca	Cu	Cu	
	Fe	Cu	Ni	Ni	Ni	Ni	
	Mn	Ni		Cu	S	S	
	P	P		P	P	P	
	Al			O	O		
	Mg						
	O						
Negligible elements	Na	Si	P	Mg	Mg	Si	
	S	Mg	S	Al		O	
			O	Fe		Mg	
			Mg	S		Fe	





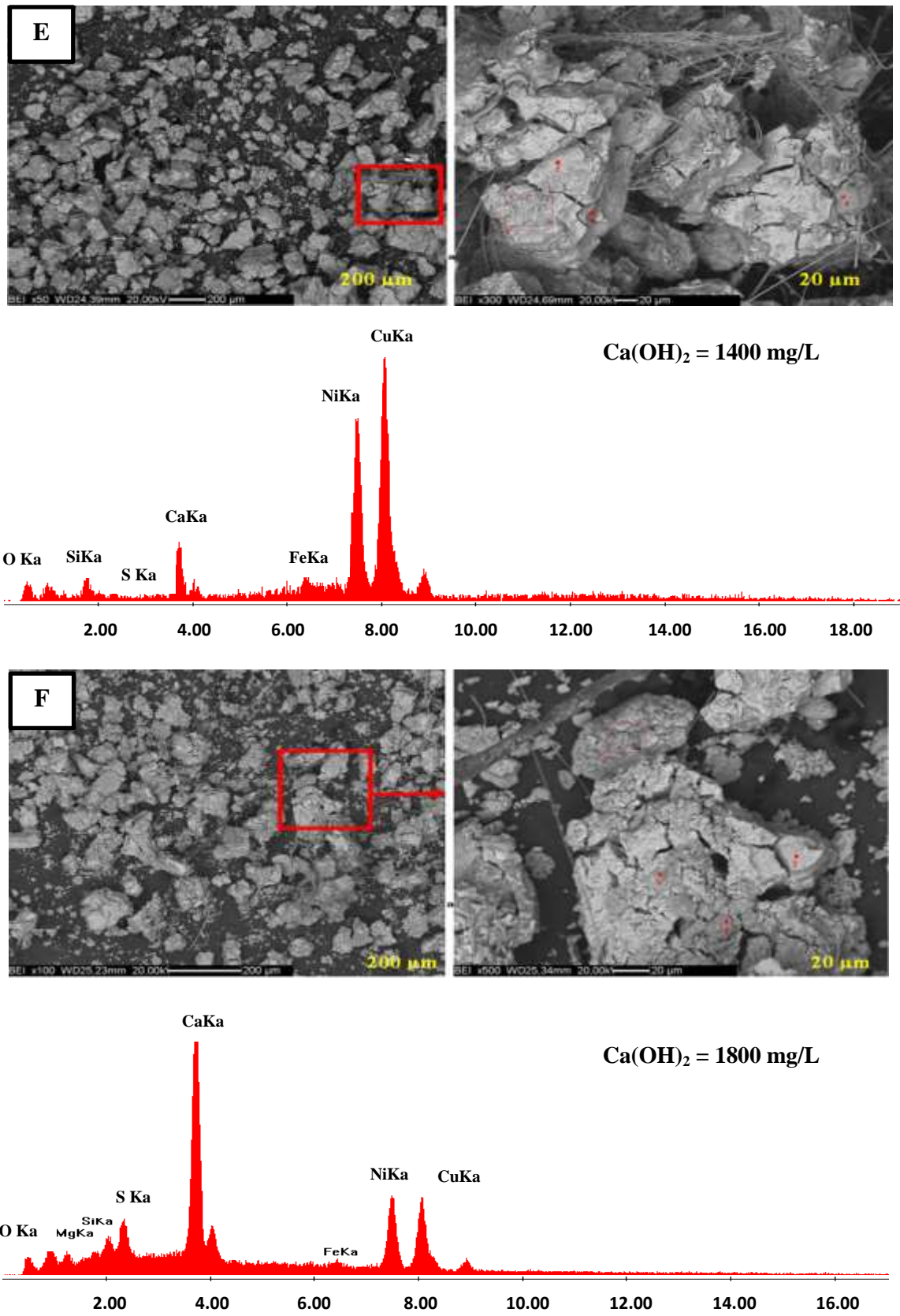


Figure 48 SEM and EDX analyzes of precipitates resulting from precipitation using different doses (1000 , 1400 and 1800 mg/L) from lime and calcined eggshell.

Figure 48 contains multi-figures (A, B, C, D, E and F), each figure present different SEM and EDX results of recovered sludge produced by using $\text{Ca}(\text{OH})_2$ and $\text{CaO}_{\text{Eggshells}}$ (extracted after eggshells calcination).

For the precipitates generated by calcined eggshells, Figures (A, B and C), it is clear that the morphology of precipitates changes by increasing $\text{CaO}_{\text{Eggshells}}$ concentration it means increase of pH (Table 39 and Figure 48). From SEM results, gelatinous form of these precipitates make the measure of particle size very difficult and the formation of particles released for more than 1000 mg/L of $\text{CaO}_{\text{Eggshells}}$. The particles appear very small and the gelatinous form makes them stick together, making them difficult to separate and measure. EDX results shown in Figure 48 and Table 39 summarize the most important elements present in solution during precipitation.

For all $\text{CaO}_{\text{Eggshells}}$ doses at $\text{pH}_f > 8$, calcium was the predominant element, of course because the hardness (TH) of this wastewater is very high, and it removed by precipitation or co-precipitation of Ca as CaCO_3 , $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$, CaHPO_4 precipitates (Figures A, B and C). This result is also mentioned by Mohammed and Shanshool, (2009).

For 1000 mg/L of $\text{CaO}_{\text{Eggshells}}$ at $\text{pH}_f = 8.07$, some predominant metals occurred (Fe, Si, Al, P, Mn), it means this range of pH is ideal for removing these metals by precipitation or co-precipitation. Chemical precipitation produce these complexes: $\text{Fe}_3(\text{PO}_4)_2$, $\text{Fe}_x(\text{OH})_y(\text{PO}_4)_3$, $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Fe}_x(\text{OH})_y(\text{PO}_4)_z$, $\text{Fe}(\text{OH})_3$, $\text{Al}_x(\text{OH})_y(\text{PO}_4)_z$, $\text{Al}(\text{OH})_3$, $\text{Mn}(\text{OH})_2$, H_3SiO_4^- (Figure A).

For 1400 mg/L of $\text{CaO}_{\text{Eggshells}}$ at $\text{pH}_f = 11.15$, beside the Ca, the apparition of a small amount of Cu and Ni, so the precipitation of these metals starts late at $\text{pH} > 11$, also P and O keep occurring. However, some other metals have disappeared like Al, Si, Mn and Fe, this is related to the re-solubilization of the precipitates (complex metal-Hydroxide), which means the pH plays an important role in the precipitate solubilization and each metal has a specific range of pH for precipitation beyond this range the precipitate will solubilize. Some of the produced species are: $\text{Cu}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$, $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$, CaHPO_4 (Figure B).

For 1800 mg/L of $\text{CaO}_{\text{Eggshells}}$ and at $\text{pH}_f = 12.51$, predominant metals are Cu and Ni (small values), it means at pH superior than 12 the precipitation of the previous mentioned metals decreases, occurred as trace metals: P, Mg and S (Figure C).

For the precipitates generated by conventional lime, Figures (D, E and F) show the SEM results which describe the morphology, shape and size of the particles, all of these properties

being affected by the variation of the $\text{Ca}(\text{OH})_2$ dose, which means that the pH value plays an important role in the predominance of elements.

SEM results (Figures D, E and F) show the difference between the morphology and the crystallinity of precipitates. In the presence of 1000 mg/L of lime the particles were few in number but big in size, the form was less gelatinous (Figure D). However, by decreasing the dose of lime to 1400 and 1800, the opposite happen, the particles were multiple in numbers but small in size.

There is a difference between the precipitates generated by using $\text{CaO}_{\text{Eggshells}}$ and $\text{Ca}(\text{OH})_2$. The difference consist in the form and the size of precipitates, by comparing Figures A, B and C with figures D, E and F, the precipitates produced in the presence of $\text{CaO}_{\text{Eggshells}}$ are very gelatinous and their particles are very small and adhere to each other, unlike the precipitates produce in the presence of $\text{Ca}(\text{OH})_2$ which are less gelatinous and the particles are larger and their size is easier to measure.

The EDX results shown in Figures D, E and F represent the elements occurring for each dose of lime. For 1000 mg/L of $\text{Ca}(\text{OH})_2$ at $\text{pH}_f = 9.37$, these elements appeared at a significant concentration: Si, Ca, Ni, Cu, P and O, by chemical precipitation, some of resulting species that may appear at $\text{pH}_f = 9.37$ are: H_3SiO_4^- , $\text{Cu}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$, CaCO_3 , $\text{Al}_x(\text{OH})_y(\text{PO}_4)_z$. The metals “Fe and Al” were small, which can be linked to the pH_f , which is higher than 9, which means that the precipitation of these metals is outside the pH range of the precipitation of Fe and Al (Figure D). By increasing the dose of lime to 1400 mg/L and 1800 mg/L at a $\text{pH}_f > 12$, the predominant elements produced are Ca at the top of the list and other metals Cu, Ni, P and S. The Cu and Ni EDX peaks increased, which means that the removal efficiency of Cu(II) and Ni(II) increased too (Figure E and F), the predominant species that may result are : $\text{Cu}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$, $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$, CaHPO_4 , CuS and NiS .

Cu(II) and Ni(II) results shown in EDX analysis was in accordance with the results presented in Sect. III.3.3 (Table 35 and Figure 45), where the removal of metals increased by increasing of precipitant dose and pH value.

III.4 Sludge treatment processes (Propositions)

According to the tests carried out, it should be noted that chemical precipitation generates precipitates which must be removed in a subsequent processing step. As previously stated in the bibliographical part ([Chapitre II section II.3.4.7](#)), there are various methods of disposing sludge (eg. landfill, ocean dumping, incineration, and land application). ([Wang et al., 2009](#)). Heavy metal sludge need to be recycled ([Kurniawan et al., 2006](#) ; [Chen et al. 2018](#), [Li et al., 2020](#)). acid leaching tests are suggested because, according to [Li et al., \(2020\)](#), acid leaching allows easy recycling of heavy metals in the resulting sludge. Metal ion leaching rates in the sample are over 99%.

III.5 Conclusion

The application of chemical precipitation in real industrial wastewaters gave more details about the possibility of removing heavy metals from a complex media.

Removing Cu(II) and Zn(II) from *ENICAB* wastewater had a significant results, more than 99% of removal using 300 mg/L of precipitating agent ($\text{Ca}(\text{OH})_2$, NaOH, and Na_2CO_3) at $\text{pH}_f = 9.96$. The sludge volume produced using NaOH was the highest; however, the biggest precipitant mass (PM) resulted by using Na_2CO_3 .

XRD analyses help us to characterize the final recovered sludge, the Brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$) was the predominant component when we used hydroxide precipitants. While, Cuprite (Cu_2O) was the predominant component for Na_2CO_3 . SEM analyses shown the crystallinity and the structure of precipitates; in addition we have used ImageJ and Origin pro programs for particle size estimation. Carbonate precipitates has a big particle size compared to hydroxide. The calcined eggshells have a similar mineral composition, crystallinity and structure compared to lime according to SEM, XRF and EDX analyses.

Removing Cu(II) and Ni(II) from *Galvanic* wastewater had a satisfied results even when MCL standards were not reached. For $\text{CaO}_{\text{Eggshells}}$, adjusting pH at 11.5 raised the final pH to very basic pH equal to 12.53, we have got 86 % of Cu(II) removal and 93% of Ni(II) removal, which was enough to get the best removal. While, at the same pH adjustment with higher $\text{pH}_f = 12.74$, we have got 93% of both Cu(II) and Ni(II) removal.

GENERAL CONCLUSION

General conclusion

This research aimed to study the removal of three hazardous heavy metals (Cu(II), Cd(II), and Zn(II)) separately and in combination. The chemical precipitation process was selected for the removal of these heavy metals from synthetic solutions and industrial wastewater. This process was applied using different agents (lime, caustic soda, soda ash, and calcined eggshells) and focusing on different parameters (pH, solubility, agent dose, metal content, and sludge characteristics).

The study was presented in two main sections: the bibliographic part and the experimental part. The first one was structured into two chapters. Chapter I presented important and useful information on the three heavy metals (Cu, Cd, and Zn). It appears that the natural occurrences and sources (in water, soil, and air), are considered very low. While the anthropogenic sources (agriculture, domestic, and industrial activities) remain the significant sources of heavy metals.

Both metals (Cu and Zn) are essential elements for human body, fauna, and flora. They played an important role in plants and animals growth; indeed, in human body Cu and Zn are necessary for physiological functions and for a variety of metabolic processes. Both metals are potentially toxic elements when their consumption exceeded the admissible value. In contrast, cadmium (Cd) is very toxic even at small concentrations.

Based on the results of a number of Algerian researches, the water sources and the environment are threatened by the presence of heavy metals, which may lead to pollution and the possibility of contamination of natural waters in Algeria.

For all the dangerous impacts, it is mandatory to remove heavy metals (Cu(II), Cd(II), and Zn(II)) in order to preserve the environment, fauna and flora, and the human health for that many researchers have used different processes such as: chemical precipitation, adsorption, electrocoagulation, ion exchange , coagulation/ flocculation, ion flotation, and membrane technologies.

Among these techniques, chemical precipitation is the method selected and applied for experimental trials. The chemical precipitation is a physico-chemical process used to remove undesirable soluble metallic ions and certain anions from water or wastewater by conversion to an insoluble form. Its simplicity, low-cost and effectiveness over a wide range of temperature are among the significant advantages. Monitoring the pH and the solubility is the

key to this method's success. Hydroxide precipitation is the more commonly used type than sulfide and carbonate precipitation because it is economical, easily implemented, and controlled. The basic treatment processes for precipitating heavy metals includes: pretreatment, pH adjustment, flocculation/clarification, sludge thickening, sludge dewatering, sludge disposal, and effluent polishing.

The experimental part includes three chapters. The first one described the protocol used to carry out chemical precipitation tests on heavy metals in synthetic solutions and industrial effluents.

In the second chapter, the removal of heavy metals (Cu(II), Cd(II), and Zn(II)) from synthetic solution of distilled water has been investigated in two different media (simple and complex). The tests were carried out using: lime “Ca(OH)₂”, caustic soda “NaOH”, soda ash “Na₂CO₃”, and calcined eggshells “CaO_{Eggshells}”. The simple one represents the removal of each metal individually. However, the complex media studied the removal of the three metals together. The obtained finding showed that:

- The used precipitating agents were very effective for removing heavy metals (Cu(II), Cd(II), and Zn(II)) individually, and NaOH was the most suitable one.
- A good efficiency of metal removal required an important amount of precipitating agent. Otherwise, a precipitating agent deficiency will affect the precipitation process.
- Na₂CO₃ was more effective than Ca(OH)₂ and NaOH in removing the combined metal ions (Cu, Cd, and Zn). This may be due to the capacity of Na₂CO₃ to remove metals at a lower pH compared to hydroxide agents.
- The removal of metals in combination is more complicated than the removal of individual metals because the good removal efficiency for each metal occurs at different pH values. Therefore, it is difficult to get a good removal of all metals simultaneously.
- The re-use of waste eggshells is a great idea, especially for removing combined heavy metals.
- The calcined eggshell as an alternative to lime is a very good choice for the removal of Cu and Zn, but it is not the best one for removing Cd.
- Determining XRD, EDX/EDS, SEM, the volume, and the mass of precipitates helps to better understanding the mechanisms of chemical precipitation by analyzing the sludge characteristics (composition and particle size) and confirming the removal efficiency.

The last chapter is the most important: it is the real test of the efficiency and success of the chemical precipitation process. For that, this process was applied to remove heavy metals from two different industrial wastewaters (complex media). The first one was the *ENICAB* wastewater (from Algerian industry), which contains significant Cu(II) and Zn(II) concentrations. As a result, very good efficiency for Cu(II) and Zn(II) removal was achieved using Ca(OH)_2 , NaOH, and Na_2CO_3 at a smaller optimum dose only 300 mg/L.

The second industrial wastewater is galvanic wastewater (from Italian industries). Two similar agents were used: conventional lime (Ca(OH)_2) and calcined eggshells ($\text{CaO}_{\text{Eggshells}}$). This experiment had two different objectives. Firstly, the possibility of treating wastewater with a high Cu(II) and Ni(II) content was studied. The other objective was to compare Ca(OH)_2 and $\text{CaO}_{\text{Eggshells}}$ for removing Cu(II) and Ni(II) from galvanic wastewater.

The removal efficiency of Cu(II) and Ni(II) from *galvanic* wastewater was good using Ca(OH)_2 and $\text{CaO}_{\text{Eggshells}}$ ($R\% = 93\%$) at a basic pH above 12, using 1600 mg/L of precipitant. Despite this, the $R\%$ was insufficient if Algerian MCL standards were taken into consideration. Ca(OH)_2 performed better than $\text{CaO}_{\text{Eggshells}}$; this is related to the final pH, which increased rapidly with Ca(OH)_2 , unlike $\text{CaO}_{\text{Eggshells}}$, which required a higher dose.

Ca(OH)_2 and $\text{CaO}_{\text{Eggshells}}$ removed 93% of Cu(II) and Ni(II) from *galvanic* wastewater at a very basic pH (). While this removal did not conform to MCL standards, the pH_f increased rapidly with the use of lime, which is why it performed a bit better than calcined eggshells.

SEM and EDX results are discussed at three different precipitating agent doses with the purpose of following the chemical precipitation steps by showing the different changes in the structure of precipitates and the appearance and disappearance of new mineral elements at each step.

Finally, chemical precipitation is a very effective process for the removal of Cu(II), Cd(II), and Zn(II) in synthetic and industrial wastewater.

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SCIENTIFIC PRODUCTION WITHIN THE THESIS CONTEXT

1. *International publication*, in a category A journal indexed in SCOPUS

BENALIA, M.C., YOUCEF, L., BOUAZIZ, M.G. ACHOUR, S., MENASRA, H. (2021). Removal of Heavy Metals from Industrial Wastewater by Chemical Precipitation: Mechanisms and Sludge Characterization. Arab J Sci Eng .47, 5587–5599 <https://doi.org/10.1007/s13369-021-05525-7>

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RESEARCH ARTICLE-CHEMICAL ENGINEERING



Removal of Heavy Metals from Industrial Wastewater by Chemical Precipitation: Mechanisms and Sludge Characterization

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Abstract

Chemical precipitation using lime ($\text{Ca}(\text{OH})_2$), caustic soda (NaOH) and soda ash (Na_2CO_3) for the removal of simultaneous heavy metals ($\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$) from industrial wastewater of the cable industry was carried out in laboratory by jar tests. For each reagent used, an improvement in copper and zinc removal efficiency was obtained by increasing the precipitating reagent dose (10–400 mg/L). Efficiencies of over 90% can be achieved. Chemical precipitation efficiency is related to the pH of the treatment. At a high final pH level ($8 < \text{pH} < 10$), the removal efficiency of copper for each precipitating agent is slightly higher than that of zinc and the residual metal contents were in conformity with industrial discharge standards. In sludge product, zinc and copper were precipitated as amorphous hydroxides including $\text{Zn}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2$. Based on XRD analysis, the presence of an amount of other additional phases was noticed for copper. SEM images show that sludges produced are not large in size and are compact in structure. Corresponding EDX (energy-dispersive X-ray spectroscopy) shows that the amount of copper is higher than the amount of zinc in all recovered sludge. Wastewater treatment with soda ash resulted in a lower volume and a large product size of sludge. As a result, drying steps can be less expensive. This is a significant advantage comparably with the other precipitating agents. Soda ash may be considered as cost-effective precipitating agent for $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ in the industrial wastewater of the cable industry.

Keywords Industrial wastewater · Heavy metals · Precipitation · Mechanism · Sludge characterization

2. International communications

<p>1. BENALIA M C., YOUCEF L., ACHOUR S. (2019). Possibilité d'élimination des métaux lourds (Cu, Cd et Zn) par précipitation chimique, Séminaire International sur l'Hydrogéologie et l'Environnement 12 – 14 Mars 2019, Ouargla (Algérie).</p>	
<p>2. BENALIA M. C; YOUCEF L; ACHOUR S. (2021). Removal of Cu(II) and Zn(II) from ENICAB wastewater by chemical Precipitation, Colloque Maghrébin sur l'Eau et l'Environnement en Zone arides et Semi Arides (CMEEZASA'2021)-A travers Google Meet, 22-23 Mars, Laboratoire LARHYSS, Université de Biskra</p>	
<p>3. BENALIA M C., YOUCEF L., ACHOUR S. (2018). Etude de l'élimination du cuivre par précipitation chimique. 1^{er} Séminaire Maghrébin sur l'Eau et l'Environnement dans les Zones Arides (SMEEZA'1): Eau et Santé, 23-25 Avril, Ouargla, Algérie.</p>	

3. Research projects

Member of a PRFU research project approved in 01-01-2018, Code: **A17N01UN070120180001**, Title: Possibilités de l'élimination des métaux lourds par des procédés physico-chimiques.

République Algérienne Démocratique et Populaire
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ÉVALUATION DES NOUVEAUX PROJETS DE RECHERCHE UNIVERSITAIRE
État d'agrément

Etablissement: Université de Biskra
 Domaine: SCIENCES ET TECHNOLOGIES
 Filière: Hydraulique

Session: 2018

Intitulé du Projet	Chef de Projet	Membres de l'équipe	Grade	Observations
Possibilités de l'élimination des métaux lourds par des procédés physico-chimiques	Mme. Youcef Leila Grade: PR	Mme. Guergazi Saadia M. Ouakouak Abdelkader M. Youcef Soufiane M. Benalla Mohamed Charif M. BOUAZIZ Mohamed Ghrissi	PR MCB Doctorant Doctorant Doctorant	- Projet agréé à partir du : 01/01/2018 - Durée du projet: 04 ans - Code de projet: A17N01UN070120180001

Official stamp of the Ministry of Higher Education and Scientific Research, Algiers, with a handwritten signature in Arabic script over it.

1. Scholarship

Erasmus + KA107 exchange program at Padova University (Italy), period from 14 March 2021 to 31 July 2021. Realization the experimental topic: Removal of heavy metals from wastewater using CaO extracted from eggshells by chemical precipitation.



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Higher Education
Evaluation form for thesis work

SHORT EVALUATION REPORT for THESIS WORK

Benalia Mohamed Charif ERASMUS STUDENT'S NAME		
Università degli Studi di Padova, Italy RECEIVING INSTITUTION		I-PADOVA01 ERASMUS CODE
From 14/03/21 to 31/07/21 PERIOD (from dd/mm/yy to dd/mm/yy)		
Professor Maria Cristina Lavagnolo NAME AND FUNCTION OF THE SUPERVISOR		
Removal of Heavy metals from Wastewater using CaO extracted from eggshells by chemical precipitation TITLE OF THE WORK		
Environmental Protection / Removal of toxic metals SUBJECT AREA/STUDY FIELD OF THE WORK		
KIND OF THESIS WORK : <input type="checkbox"/> BACHELOR THESIS <input type="checkbox"/> MASTER THESIS <input checked="" type="checkbox"/> DOCTORAL PROJECT		
RESEARCH APPROACH : <input type="checkbox"/> THEORETICAL <input checked="" type="checkbox"/> EXPERIMENTAL(PROJECT WORK) <input type="checkbox"/> BASED ON INTERNSHIP/TRAINING <input type="checkbox"/> REVIEW WORK		
PROPOSED NUMBER OF ECTS CREDITS*:	18	
NUMBER OF HOURS of the activity (if applicable):		

EVALUATION OF STUDENT'S WORK (if necessary, this part can be substituted by a Supervisor letter attached to the present document)

Dr. Benalia worked with great seriousness, professionalism and enthusiasm on the project that he himself wanted to explore. This project is of great value because it fits perfectly into the new lines of research for sustainable environmental engineering and the so-called blue economy (Gunter Pauli, 2010). Competence and the ability to work in a team were fundamental characteristics for the success of the research even if unfortunately, due to the COVID19 pandemic, he was only able to attend the laboratory for a few weeks. Although he was unable to stay in the laboratory, dr Benalia attended the water and wastewater treatment course (12 ECTS) as a doctoral student.

The results obtained will be presented at a conference in late July in Crete at the conference on Industrial and Hazardous Waste Management (<http://hwm-conferences.tuc.gr/>)

Padova, 9th July 2021



***Supervisor's signature.....

*This activity will not be reported in the Official Register of Records. The proposed number of ECTS credits is just a suggestion for your University of Origin

**Stamp of the receiving University of the Supervisor's Department / Structure

***This declaration is not valid without the Supervisor's original signature and the Institution's stamp