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**The American University in Cairo**

**School of Sciences and Engineering**

*Adsorption of Heavy Metals Cations in Wastewater  
Using Cement Kiln Dust*

By

Mohamed Abdel Kareem El Zayat

A Dissertation Submitted in Partial Fulfillment of the  
Requirements for the Degree of

**DOCTOR OF PHILOSOPHY**

Under the supervision of:

**Prof. Dr. Salah El Haggar**

Chair of the Department of Mechanical Engineering,  
American University in Cairo

**Dr. Sherien Elagroudy**

Director of Egypt Solid Waste Management Center of  
Excellence and Associate Professor at Public Works  
Department, Ain Shams University

**Fall 2014**

# DEDICATION

*This Work is dedicated to*

*My Dear Parents*

*My Beloved Wife*

*Kareem and Belal El Zayat*

## ACKNOWLEDGMENT

In the name of Allah and above all, Thanks God for giving me the strength and patience to complete this work after spending several months of hardworking in the laboratory. Thanks God for giving me this delightful feeling while writing these words after persistent research work to come up with this piece of work. I can say that a PhD degree is not only a destination to reach but it is a whole journey. By the time I'm writing these words, I can remember when I was working until very late hours and sometimes overnight leaving my wife and sons home alone. This was to make this work useful and the entire globe can get the benefit from it for a better and prosperous future for all of us and for our next generations. Thanks God who gave me this great opportunity to work under the supervision of Prof. Dr. Salah El Hagggar and Dr. Sherein Elagroudy who made my PhD journey a wonderful trip. Also, I'm very thankful to all the persons who give me unyielding support, assistance, and encouragement to finish this dissertation, and I hope I do not forget any of them in this acknowledgment.

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## PREFACE

The following peer reviewed international research publications have been conducted from this dissertation:

- ✓ *El Zayat, M., S. Elagroudy, and S. El Hagggar (2014), "Equilibrium Analysis for Heavy Metals Cations Removal Using Cement Kiln Dust" Water Science & Technology, doi:10.2166/wst.2014.325*
- ✓ *El Zayat, M., S. Elagroudy, and S. El Hagggar (2014), "Equilibrium and kinetic for heavy metals removal by using cement kiln dust (CKD)", Proceeding of the International Water Association 6th Eastern European Young Water Professionals Conference (East meets west): Istanbul- Turkey.*
- ✓ *El Zayat, M., S. Elagroudy, and S. El Hagggar (2013), "Characterization of Cement Kiln and Slaked Limestone for Potential Usage in Treatment of Domestic Wastewater", Proceeding of the 6th International Perspective on Water Resources and Environment 2013 by the Environment and Water Resource Institute of the American Society of Civil Engineers (EWRI/ASCE) : Izmir- Turkey.*
- ✓ *El Zayat, M., S. Elagroudy, and S. El Hagggar (2012), "Treatment of Various Types of Wastewater Using Cement Kiln Dust", Proceeding of the 5th International Perspective on Water Resources and Environment 2012 by the Environment and Water Resource Institute of the American Society of Civil Engineers (EWRI/ASCE): Marrakesh – Morocco*

The following research papers are under journals review:

- ✓ *El Zayat, M., S. Elagroudy, and S. El Hagggar (2014) "Equilibrium Adsorption Isotherms of Removal of Heavy Metals using Cement Kiln Dust "*
- ✓ *El Zayat, M., S. Elagroudy, and S. El Hagggar (2014) "Economic Viability of Removal of Heavy Metals Cations from Industrial Wastewater using Cement Kiln Dust"*

## ABSTRACT

Wastewater containing heavy metal constituents are mainly generated from industrial processes, such as electric battery manufacturing, lead smelting and glass industry. Heavy metals are very dangerous and carcinogenic due to the fact that they can bio-accumulate in our bodies resulting in increasing the concentration of chemicals in the biological organism compared to the chemical's concentration in the environment. A special emphasize in this study is on lead, cadmium, and copper since they are the most common toxic heavy metals in some inorganic industrial wastewater. Common techniques used in heavy metals treatment processes are chemical treatment, flotation, filter coalescence, and membrane filtration. However, they deemed too expensive to meet stringent effluent characteristics. Adsorption process is known with its effectiveness and high efficiency in heavy metals recovery from treated wastewater besides some other physiochemical constituents.

Cement Kiln Dust (CKD) as a low cost adsorbent for heavy metal cations uptake was examined for the removal of target heavy metals. Adsorption studies in completely mixed batch reactors were used to generate equilibrium pH adsorption edges. The adsorption behavior of the target heavy metals on the CKD was studied as a function of pH, contact time, sorbent dose and initial metal concentration. Studies showed the ability of CKD to remove the target heavy metals in a pH range below that of precipitation after an equilibrium reaction time of 24 hours maximum. The lead hydroxide precipitation is the dominant phenomenon at pH values  $> 6.0$  while for copper and cadmium, the precipitation started at pH 8.0 to reach approximately 90%. CKD is experimented in dynamic up-flow fixed bed reactors as well using stainless steel columns to study the dynamic breakthrough patterns. Synthetic metal solutes containing the target metals (lead, copper, and cadmium) are fed to the packed columns with the optimum conditions

resulted from the batch equilibrium experiments where the initial metal concentration is 30 mg/l. The experimental runs show that the CKD has a high affinity to adsorb the target metals. The column reactors have higher adsorption capacity than the batch ones for the same initial concentration of adsorbate. The surface concentration at exhaustion in a molar basis was found to be 240  $\mu\text{M/g}$ , 290  $\mu\text{M/g}$ , and 650 $\mu\text{M/g}$  for lead, copper and cadmium, respectively.

A surface titration experiment indicated negative surface charge of the CKD at pH below 10, meaning that electrostatic attraction of the divalent metals can occur below the pH required for precipitation. However, surface complexation was also important due to the substantive metal removal. Accordingly, a surface complexation model approach that utilizes an electrostatic term in the double layer description was used to estimate equilibrium constants for the protolysis interactions of the CKD surface as well as equilibria between background ions and the sorbent surface. Moreover, the experimental results were fitted to both Langmuir and Freundlich isotherm models to obtain the parameters of each. It was found that the adsorption capacity of CKD had the order  $\text{Pb} \geq \text{Cu} > \text{Cd}$  as depicted by Langmuir and Freundlich isotherm models, which is consistent with the electronegativity of these metals; 1.854, 1.85, and 1.52, respectively. The sorption capacity at the optimum conditions was 14.85, 14.65, and 14.1 mg/g for lead, copper, and cadmium respectively. The experiments were also supported by Fourier Transform Infra-Red (FTIR) spectroscopy. In addition, scanning electron microscope (SEM) together with energy dispersive X-ray (EDX) were performed to the CKD before and after the treatment process. The SEM and EDX were done using different magnifications in order to better understand the physical and elemental characteristics of CKD before and after adsorption. Hydrated lime as a prime source of CaO, the major constituent of CKD, was also examined at a bench scale as well and compared to CKD in heavy metals uptake.



This is to investigate whether the presence of other chemical composition in CKD, such as sodium, chloride, silicon, iron...etc., has any role in the treatment process or not.

A pilot scale of a full wastewater treatment plant of 20~25 l/hr capacity was fabricated to investigate the capability of CKD in treating selected industrial wastewater and scaling up of the proposed treatment facility. Raw industrial wastewater from glass manufacturing is introduced to the pilot scale unit. In glass manufacturing, lead oxide, potash, zinc oxide, and other metal oxides are used as coloring or de-coloring agents. Accordingly, liquid effluents resulted from grinding, polishing, coating and electroplating processes include suspended solids, heavy metals (i.e., lead), and variations in pH. The proposed treatment unit using CKD is able to reduce the total suspended solids (TSS) by 95% and biochemical oxygen demand (BOD) by 72%. In addition, heavy metals concentrations in the raw wastewater, such as lead, copper, chromium, nickel, and zinc, have been effectively treated to meet the international and national permissible limits for restricted irrigation. The highest metal concentration in the examined raw industrial wastewater is lead, and it has been reduced from 31.5 mg/l to 0.242 mg/l. The results were promising and indicated that the introduced methodology can be industrially applied.

Finally, the economic viability for the proposed treatment plant was evaluated. The economic indicators in terms of economic rate of return (11.5%) and the positive net economic present value proved that the system is economically and sustainably viable.

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# CHAPTER 1: INTRODUCTION AND OBJECTIVES

## 1.1 Background:

Preserving the environment is an increasingly pressing issue all over the world. Proper management of water resources as well as controlling water pollution is today's major area of interest. One of the most vital issues confronting many countries especially those threatened by water shortage is getting rid of their wastewater in a manner that is environmentally acceptable and economically viable.

The Egyptian water expenditure per capita is less than 38% of the international level which is 2,500 m<sup>3</sup> (Abdel Shafy, 2002). There has been increased effort in Egypt to reuse this amount of wastewater, after proper treatment, in irrigation purposes and hence increase our water budget (Nasr et al. 2011). Accordingly and in order to reuse treated wastewater, all wastewater contaminants, and especially inorganic constituents, should be in compliance with the national laws and international guidelines. Inorganic constituents, such as heavy metals are very dangerous and carcinogenic due to the fact that they can bioaccumulate in our bodies resulting in increasing the concentration of toxic chemicals in the biological organism compared to the chemical's concentration in the environment (Lentech, 2013). Unlike organic contaminants, heavy metals do not normally undergo biological decay and are thus considered a challenge for remediation (El Zayat, 2009).

Heavy metals may reach our bodies either by oral intake and inhalation, or dermal contact. Food and water are considered the major source of human oral exposure to heavy metals (Zheng et al., 2013). Therefore, there is a considerable concern over the possibility

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of disease transmission through the food chain as a result of untreated wastewater disposal and leaching to the soil.

Discharging heavy metals into sewage networks and water bodies is regulated by the Egyptian laws and guidelines. Accordingly, wastewater must be directly treated to recover heavy metals before discharging. Law 48/1982 and ministerial decree 93/1962 are the governing laws for water quality management in Egypt. Law 48 sets specific water quality standards for discharging into underground reservoir, Nile main stream and branches, and agricultural drains. Law 93 identifies the quality of discharge to sewer systems. The latter has been amended by the Ministerial Decree 44/2000 (by the Ministry of Housing, Utility, and Urban Communities) to distinguish the water quality requirements for unrestricted and restricted irrigation. All involved ministries and agencies should recognize the wastewater quality inspection and regulatory development follow the MHUUC Ministerial Decree 44/2000 to initiate restricted irrigation for the safe use of wastewater on selected crops (USAID, 2000). In an international level, the food and agricultural organization of the United Nations (FAO) and the world health organization (WHO) have identified the quality of treated wastewater effluent and disposal method. Based on the treated effluent quality, it is feasible to be used for either restricted or unrestricted irrigation. Restricted irrigation is limited to cereals, pasture, trees, and with no public access, while unrestricted irrigation is for eaten uncooked crops (World Bank, 2014). However, irrigating trees and shrubs might be the safest use of treated wastewater.

The most commonly used techniques for heavy metals removal are reduction, precipitation, ion exchange and adsorption. However, most of these methods are suffering from their high capital and operational costs (Barakat, 2011). Wastewater recovery from heavy metals by using abundant low cost and effective adsorbent materials is a field of



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interest for many researchers. Motivated by cost considerations, the influence of physical and chemical characteristics of cement kiln dust (CKD) on heavy metals recovery is investigated in this study.

Cement Kiln Dust (CKD) is an industrial secondary product which is considered a problematic source of air pollution, especially that the quantities of these product are increasing without finding any sustainable way to handle these valuable products. Many of these wastes might have feasible value if they have been reused. CKD is a fine material that is given off and carried out by the flow of hot gases within the cement kiln during the cement making process (Abo-El Hassan, 2008). Reusing this dust in the cement making industry and other fields becomes a potential due its lime content and cementitious properties (Maine, 2006). Cement Kiln Dust (CKD) has high content of calcium oxide (CaO) that results in using it as a replacement for lime in treating acidic wastewater (Mackie et.al., 2010). It has been also used as a chemical coagulant for wastewater treatment and it reveals promising results in enhancing the TSS, BOD<sub>5</sub>, COD, and P-total (El Zayat et al., 2012; Abo-El Hasan, 2008). Taha in 2003 investigated the effect of CKD on the mobility of the heavy metals present in the municipal wastewater and sewage sludge. Adding CKD on activated sludge process without primary settling achieved high removal efficiencies of the chemical and bacteriological pollutants which enabled using the sludge in compliance with the requirements of law 501/2005 (Mostafa, 2012). Moreover, many researches were conducted to investigate the influence of the physiochemical properties of CKD for soil and sludge stabilization (Peethamparan, 2006; Peethamparan et al., 2008; Khaled, 2000). The capacity of CKD, as heavy metals scavenger, for chromium up take from aqueous solutions has also shown good results (El Awady, 1997).

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## 1.2 Problem Statement:

Today's technology in cement industry minimizes the generation of CKD and allows most, and sometimes all of the cement kiln dusts to be reused, minimizing air pollution and disposal problems. In some facilities though, cement kiln dust is still an issue and some cement kilns do not reuse all of the dust they produce. The material is collected using pollution control systems like cyclones, electrostatic precipitators, or bag filter houses, and is then landfilled either on or off site. Cement kiln dust, CKD is considered a major pollutant resulting in respiratory tract irritations and infections due to its fine particle size and high pH (El Zayat *et al.*, 2013; Hawkins *et al.*, 2003).

The costs of the present methods of wastewater treatment are increasing rapidly and without beneficial economic return. Moreover, the development and implementation of wastewater collection and treatment schemes to serve the majority of urban populations are receiving increasing priority in most countries, even in developing ones. The fact that the generated wastewater will increase in a direct proportional with the population increase makes finding a cheap and efficient process for the destruction of inorganic constituents should be dealt with a high priority by the decision makers. Moreover, CKD has not been studied comprehensively for its effect on removing heavy metal constituents from wastewater.

The Guiding research question is: How could we produce high quality treated wastewater free from heavy metals and in compliance with the Egyptian laws and international guidelines using a sustainable solution.

The proposed solution is treating wastewater using CKD, *an industrial hazardous solid waste*, as a coagulant and adsorbent to overcome the high capital and operational costs, large footprint and huge energy consumption in the conventional wastewater

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treatment plants from one side and to mitigate the environmental and health impacts of such industrial waste from the other side.

### **1.3 Magnitude of the Problem**

The present cement production in Egypt is 46 million tons per year (Askar, 2010) and is expected to reach 77 million tons per year by 2015 (Riad, 2010). CKD is estimated to comprise 3 to 5 % from the produced cement (El Hagar, 2003). Thus, the present amount of CKD is around 1.3 million tons per year while it is expected to increase to more than 2 millions by year 2015 due to the increase in the cement production. These immense amounts of CKD have high potential to cause severe and chronic health effects due its very fine particle size and high pH (> 11.0) (Peethamparn, 2008; Mackie, 2010). A serious concern thus arises to properly manage CKD. This of course is raising the concern that there must be serious attempts to try to either reduce these huge amounts or efficiently use it in a proper environmental manner.

Untreated domestic wastewater quantity is approximately 2.4 BCM/yr while industrial wastewater is 1.3 BCM/yr (Egypt 2<sup>nd</sup> National Communication, 2010). Wastewater poses a threat to both rural and urban communities where the absence of wastewater treatment plants leaves individuals sometimes with no other alternatives other than wastewater disposal into fresh water bodies. Only 18 million capita in Egypt are served by wastewater treatment plants (Nasr, 2011) which means that more than 75% of the Egyptians has no access to any treatment facilities. Hence, improper discharge of the wastewater may lead to the destruction of the water bodies in addition to the destruction of aquifers and in turn precious underground water. Wastewater is a source of pollution to fresh water bodies as it contains various pathogens, parasites, and toxic metals. According to the Egyptian Environmental Affairs Agency (EEAA), 91 plants in Egypt were

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discharging their industrial wastewater into fresh water bodies resulting in releasing huge amounts of heavy metals contaminants (EEAA, 2007). Some of these industries could be allocated within residential areas, such as electroplating, metal finishing, glass manufacturing and leather tanning. Industrial wastewater constitutes 39% of the environmental problems of the industrial sector (Egypt Second National Communication, 2010).

According to the dramatic increase on the population, the water expenditure per capita is on the decrease. Reports on the state of freshwater and expenditure per capita in Egypt stated that severe water shortages are imminent by 2025 (Abdel Shafy, 2002). This may trigger an alarm that violent conflicts will raise in water-scarce regions. This also explains that in the coming few years Egypt will face a water shortage problem which needs to well manage our usage of water and to investigate new efficient solutions to reserve our water budget. Accordingly, treated sewage and industrial effluents will form a part of the water budget in Egypt.

#### **1.4 Objectives and Scope of the Research:**

Based on the severe problematic issues of both CKD and industrial wastewater on our health, the aims of this study are to:

- 1) Conduct a serious of bench scale studies to investigate the feasibility of using CKD as a sorbent in industrial synthetic aqueous solution.
- 2) Investigate the removal efficiency of heavy metals (in particular lead, cadmium, and copper) from wastewater using CKD.
- 3) Simulate and computationally model the adsorption capacity and equilibrium isotherm of CKD to be used later in designing a full scale project.

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- 4) Examine the proposed treatment technology on a pilot-scale. The proposed pilot scale will be designed to satisfy the following criteria:
- Compact design
  - Sustainable design: The possibility of effluent reuse or safe disposal
  - Minimal usage of energy and raw materials.
  - Utilizing a problematic industrial waste in a sustainable and environmental manner
- 5) Study the economic viability of the proposed treatment process in treating industrial wastewater using CKD.

These aims were predicted to result in the determination of new and promising alternatives for establishing and encouraging the use of such cost effective, easy to operate and highly efficient techniques for industrial wastewater treatment processes. This would produce an economic viable outcome to the community for the disposal of hazardous wastes, such as raw industrial wastewater and cement kiln dust, a solution which would be environmentally acceptable.

## 1.5 Hypothesis

The hypothesis behind this study is the adsorption isotherms and capability of CKD to particularly remove heavy metals from wastewater besides improving the physiochemical constituents, such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total suspended solids (TSS). In addition to adsorption isotherms, a pozzolanic reaction between wastewater and calcium hydroxide formed from free lime (CaO) during the hydration of CKDs is anticipated.

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The alkaline nature of CKD is a great potential for initiating the pozzolanic reaction with wastewater constituents with a relatively high rate. The presence of free-lime and alkalis is expected to elevate the pH values of wastewater and accelerate the chemical break down of both organic and inorganic constituents. That breakdown should precipitate the target heavy metals of this study (lead, copper, and cadmium) in addition to other wastewater constituents that can be adsorbed by CKD either through electrostatic reactions or more complex chemical reactions.

Considering chemical composition of CKD, formation of other reaction products (slag, ettringite, gypsum) is also expected but these materials are not predicted to play significant role in heavy metals recovery from wastewater. In order to figure out this issue, hydrated lime as a prime source of CaO (the major constituent of CKD) was examined at a bench scale as well and compared to CKD in heavy metals uptake.

## **1.6 Research Methodology**

The research plan comprises two main phases. In the first phase, a series of laboratory and bench scale experiments will be conducted particularly to determine the CKD adsorption isotherm and its affinity to remove heavy metals from synthetic aqueous solutions. In addition, the effect of CKD on other physiochemical constituents will be investigated. The hydrated lime as a prime source of CaO will be also examined at the same optimum conditions of CKD. This is to determine the effect of other chemical elements of the CKD on the treatment behavior.

A thorough analysis of the two materials (CKD and hydrated lime) followed by a pilot scale test will be carried out to examine up-scaling the process.

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Statistical software on design of experiments, namely Design-Expert® software package, will be utilized in order to make sure that the experiments are well-designed to obtain reliable results.

The first phase will lay the groundwork for the second phase. In the second phase, system computationally modeling will be conducted using surface complexation models to estimate the equilibrium isotherm constants. These equilibrium constants may be used later on for performing large scale units.

Finally, economic analysis will be conducted in order to investigate the viability of the proposed project.

## **1.7 Outline of Dissertation**

The background and the review of literature pertaining to the use of CKD in treating wastewater and heavy metals recovery is presented in chapter 2. In this chapter, a thorough analysis of the current state of the art treatment technology is presented and the requirements for further research have been outlined. In chapter 3, materials selection, experimental methods and sample preparation are described. This is followed by the data and analysis outcomes, discussion of the results, and modeling runs presentations in chapter 4. Chapter 5 shows the up scaling and pilot scale design, execution, procedures, experimental runs, and results. The economic viability analysis will be presented in chapter 6. A general discussion of all the results and the conclusions from the research study are reported in chapter 7.

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## CHAPTER 2: LITERATURE REVIEW

### 2.1 Introduction

First, this chapter presents an overview of the wastewater management problem in Egypt with a special focus on industrial wastewater. Commonly used wastewater treatment technologies are identified with a focus on the adsorption mechanism of heavy metals as toxic constituents in industrial influents. A comprehensive literature survey has been conducted on the adsorption mechanism. This is followed by determining the properties of the chosen adsorbent, cement kiln dust (CKD), which is an industrial waste from the cement manufacturing. The literature on the production process of the CKD, the details of the engineering property measurements to evaluate the effectiveness of using this material on industrial wastewater treatment facilities, and its environmental impacts are thoroughly presented. The properties of hydrated lime stone as a prime source of the CaO, the major elemental constituent of CKD, has also been discussed. Then, the Egyptian legislation framework and international environmental reform are quantified. Finally, the motivation for the present research study is established by identifying the areas of advancement needed for increasing the beneficial usage of CKD as a useful tool in industrial wastewater treatment. The present research study is motivated by the observation that the usage of CKD in treating wastewater might be increased by 1) correlating the performance of the material in wastewater treatment to its basic physical and chemical properties and 2) understanding the underlying mechanism of the selected material and industrial wastewater interaction.



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## 2.2 Wastewater Status in Egypt

Reports on the state of freshwater and the expenditure per capita in Egypt stated that severe water shortages are imminent by 2025 (Abdel Shafy, 2002). This may trigger an alarm that violent conflicts will raise in water-scarce regions. This also explains that in the coming few years Egypt will face a water shortage problem which necessitates proper management of water and investigating new efficient solutions to reserve our water budget. Treated wastewater represents important water resources that could form a valuable national asset if properly and effectively used.

Untreated domestic wastewater quantity in Egypt is approximately 2.4 BCM/yr while untreated industrial wastewater reaches 1.3 BCM/yr (Egypt 2<sup>nd</sup> National Communication, 2010). Both domestic and industrial wastewater pose a threat in rural and urban communities where the absence of wastewater treatment plants leaves individuals sometimes with no other alternatives other than disposal into fresh water bodies. Industrial Wastewater is a source of pollution to fresh water bodies as it contains various pathogens, parasites, and toxic metals (heavy metals). According to the EEAA, 91 plants in Egypt were discharging their industrial wastewater into the surface water bodies (i.e., Nile River and Natural Lakes) resulting in releasing huge amounts of heavy metals contaminants into water bodies (EEAA, 2007). Some of these industries could be allocated within residential areas, such as electroplating, metal finishing, glass manufacturing, and leather tanning. Industrial wastewater constitutes 39% of the environmental problems of the industrial sector (Egypt Second National Communication, 2010).

Therefore, economically viable techniques to treat industrial wastewater are essentially needed. Re-use of industrial wastewater in Egypt has many advantages. First,

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it will be an asset to the Egyptian water budget and will help to overcome the water shortage issue in the coming years. Second, the use of the treated wastewater for irrigation purposes will also help transforming our wasted desert lands into forests and hence increase our green areas. Moreover, treating industrial wastewater that finds its way to the surface water and aquifers will have a high positive socio-economic impact on the society through enhancing their health and well-being. This approach will effectively address several environmental and sustainable development aims, *inter alia*:

- Reduction of pollution loads to the water bodies and desert environment
- Protection of ecosystem and biodiversity
- Increase water availability and Egyptian water budget for further developments
- Build and enhance capacity of local and national expertise by establishing new and innovative wastewater treatment plants across the country

This research is more emphasizing on the industrial wastewater management problems. As a consequence, it is vital to understand the major wastewater constituents and pollutants and their health effects in order to find proper ways for alleviating them. The following sections determine the major industrial wastewater contaminates health effects and their sources with a great attention on heavy metals especially those subject to this study.

### **2.3 Industrial Wastewater Constituents**

Industrial wastewater is prominent with its toxicity due to the presence of high heavy metals concentrations (Katsou, 2011). Industries, such as metal plating operations, glass manufacturing, and tanneries, discharges an immense amount of contaminated wastewater with heavy metals and other constituents (Barakat, 2011). Many heavy metals such as lead, cadmium, and copper are widely used by modern industries resulting in

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releasing large quantities of pollutants to the environment. Heavy metals are widely used as input materials in many industries such as metal surface treatments, glass and pulp manufacturing, electroplating, iron and steel, textile, tanneries, petroleum refining, and other miscellaneous uses (European Commission, 2002).

Since there is a certain concern in this study for heavy metals, the following section (section 2.4) will identify sources of heavy metals and health effects especially the targeted heavy metals for this study, namely lead, copper, and cadmium. Moreover, other various physiochemical contaminants that could be mitigated before discharge will be highlighted. The Environmental Reform Section of this chapter presents the relevant Egyptian laws and its executive regulations besides the international guidelines.

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### 2.3.1 Soluble Organics

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Soluble organics can deplete the dissolved oxygen (DO) in water. The DO is essential to maintain the flourishing and surviving conditions for the existing living organisms and bacteria. These organisms use DO to digest organic material. However, if the decaying organic material increases without turnover of these organisms, the DO will be used faster (Fonderiest, 2013). Moreover, the DO levels affect the simulation of the nitrification and denitrification (Hocaglu, 2011). On the other hand, in some cases the transport of dissolved organic matter in runoff water causes an increase in the nutrients (Nitrogen and Phosphorus) inputs and heavy metals (Yang, 2013).

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### 2.3.2 Suspended Solids

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Suspended solids have an influence on water quality and aquatic biota. Besides the aesthetic effect of the suspended solids, the presence of suspended solids causes water quality deterioration and significant ecological degradation of aquatic ecosystem (Bilotta, 2008).

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### 2.3.3 Color and Turbidity

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Color is imparted to water by dissolved organic matter, natural metallic ions such as iron and manganese, and turbidity. Although color could not have a significant health impact, it is an aesthetic problem (Mihelcic, 2010).

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### 2.3.4 Oil and Floating Materials

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Like color and turbidity, the oil and floating materials have unsightly issues. They can be recovered through the coagulation treatment process to reach the allowable limits by law (Fu, 2011).

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### 2.3.5 Volatile Materials and Odor

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Volatile materials such as hydrogen sulfide and volatile organic carbons (VOC) would create odor nuisance. The most dominant odor-causing compounds come from the decay algae and aquatic biota. Also, excess chlorine dosing in the water treatment process would result in chlorine odor (Mihelcic, 2010).

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### 2.3.6 Nitrogen and Phosphorous

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Nitrogen and phosphorous can reach surface water bodies through water runoffs. The presence of nitrogen and phosphorous is undesirable since it enhances eutrophication and algae growth (Metcalf and Eddy, 2004).

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## 2.4 Heavy Metals Overview

The water industry worldwide is facing an increase in toxic substances in both surface and groundwater (Santos *et.al.*, 2014; Cartier *et.al.*, 2012). Heavy metals are considered the main constituent of these toxic substances. The term heavy metal refers to any substances in the d-block of the periodic table. Heavy metals are about 40 elements with a density greater than  $5 \text{ gm/cm}^3$  (e.g. Ag, Hg, Pb, Cr, Cd, As, Al, Cu. . .). They have

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a great affinity to bind with a wide variety of both organic and inorganic compounds (Kupper *et.al.*, 2014).

Alike the organic compounds where they are able to be degraded to inorganic ineffective pollutants, metal ions accumulate over time and are not subject to any degradation (Othman *et.al.*, 2011). Heavy metals can reach surface water either through industrial and consumer wastewater discharges or from acidic rain leached to the soils and releasing heavy metals into groundwater and surface water. Moreover, heavy metals can be found in the Earth's crust. Some heavy metals are vital to maintain the metabolism in our bodies at certain concentrations such as zinc. However, the excess of these heavy metals can lead to poisoning *via* drinking water contamination, high ambient air concentrations, or eating contaminated food. It's well known also that the specific gravity of heavy metal elements is more than five times the specific gravity of water where the specific gravity of water is 1 at temperature 4°C. For instance, the specific gravity of some toxic heavy metals is: lead, 11.34; copper, 8.93; and cadmium, 8.65 (Lef, 2013).

Heavy metals are very dangerous and carcinogenic due to the fact that they can bioaccumulate in our bodies resulting in increasing the concentration of chemicals in the biological organism compared to the chemical's concentration in the environment (Lentech, 2013).

The excess amount of heavy metals results in reducing the mental and nervous functions, damaging the blood composition, lungs, kidneys, liver, and other essential organs. Furthermore, long term exposure to heavy metals may induce Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. It is also known that heavy metals cause cancer. The recognition of these diseases is due to the fact that the symptoms are usually severe, rapid in onset, and associated with cramping, nausea,

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vomiting, pain, sweating, headaches, and difficulty breathing. There are some other symptoms resulting from the exposure to excess amount of heavy metals such as emotional instability, and insomnia (Lef, 2013).

Lead, copper, and cadmium are the most common toxic heavy metals (Lenntech, 2013). They are chemical elements in the periodic table that has the following symbols and atomic number respectively (Pb: 82; Cu: 29; and Cd: 48) (Louis, 2006). The main sources of these heavy metals in wastewater are discharged waste stream from electric battery manufacturing, lead smelting, glass industry, gasoline additive, electroplating, stabilizer in plastics, cable sheeting, tetraethyl lead manufacturing, mine drainage, paint and ink formulation, and ceramic and porcelain enameling industries. They can also leach directly into the water supply from water service lines and interior household pipes and fixtures (USEPA, 2014; Santos *et.al.*, 2014).

The following section (section 2.5) shows the health effect of the targeted heavy metals subject to this study, namely lead, copper, and cadmium.

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## **2.5 Heavy Metals Health Effects**

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### **2.5.1 Lead Health Effects**

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Lead has a significant role in many industries because it is ductile and easily shaped. It has been used in many sectors and products: batteries, petrol additives, chemical compounds, pigments, and cables (National Mining Association, NMA, 2014). Accordingly, lead can find a pathway to human beings through drinking water, food, air, soil and dust. Overdoses of lead and long term exposure can tend to severe impacts especially on infants. High concentrations of lead may cause problems in the synthesis of hemoglobin, effects on the kidney, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system. According to the Environmental

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Protection Agency (EPA) in 2014, the long-term exposure of lead can be severe and tends to decreased growth, hyperactivity, impaired hearing, and brain damage. Recent studies have stated that lead may have an impact on mental and psychological developments in children; for instance children may lose up to 2 Intelligence Quotient (IQ) points if the blood lead level rises from 10 to 20  $\mu\text{g}/\text{dl}$ . Lead mainly can be found in foods from the deposition of dust and rain containing lead on crops and soil. It can also accumulate in the human body from point source emissions. For example, lead can exist in drinking water from old lead piping and from illegal discharging of industrial wastewater of high concentrations into surface fresh water (Ferlemi *et.al.*, 2014; Osama, 2000).

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### 2.5.2 Copper Health Effects

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Copper can reach our bodies through drinking water in copper pipes. Although copper is a vital element that our body needs, high doses of copper can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Moreover, people that have Wilson's disease are at risk for health effects from overexposure to copper (Zhang *et.al.*, 2014; Lenntech, 2013).

Since copper has many practical uses ranging from coins to electrical wires and pipes, it can easily accumulate in the environment. Although our bodies need copper for good health, an excess amount of copper exposure or accumulation into human bodies can cause adverse health effects; for example, vomiting, diarrhea, stomach cramps, nausea, liver damage, and kidney disease. Unfortunately, children are more vulnerable to the toxic effect of copper much more than adults due to the fact that their bodies have not yet developed the mechanism needed to adapt to increased copper levels. The U.S. Environmental Protection Agency (USEPA) introduced a law to reduce the exposure if the level of copper in more than 10 percent of the collected tap water samples exceeds

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1,300 micrograms per liter (1,300 parts per billion).(Minnesota Department of Health, 2014).

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### 2.5.3 Cadmium Health Effects

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Cadmium could be produced as a byproduct during the refining of some heavy metals, namely zinc and lead; however, besides the detrimental impacts of cadmium, it has a significant use if it is recycled. Cadmium is commonly used in nickel/cadmium batteries for its high tolerance to physical and electrical stress. Furthermore, it can be used in coating for its high corrosion resistance, pigments, and electronic compounds such as batteries. Cadmium could reach our bodies through food if it has been added to agricultural soil or fertilizers in various ways, such as atmospheric deposition and discharging industrial wastewater into surface water. Long term exposure can lead to severe lung diseases and lung cancer. Moreover, high concentrations of cadmium cause bone defects, *osteomalacia and osteoporosis*. In addition to causing lung cancer and bone defects, high exposure to cadmium may cause hypertension. The average daily intake for humans is found to be 0.15 µg from air and 1 µg from water; furthermore, smoking a packet of 20 cigarettes can lead to increase the inhaling cadmium up to 4 µg (Chen *et.al.*, 2014; Lenntech, 2014).

The levels of Cd in organs such as liver and kidney increase with age. Cd persists in kidneys of humans for many years where the half life time could be estimated to be 30 years. This has been associated with occurrence of Cd toxicity, and increase in mortality risk by 40-100%. Besides, an excess amount of Cd may tend to pathologies such as renal failure, diabetics, and osteoporosis (USEPA; Qu *et.al.* 2014).



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## 2.6 Wastewater Treatment Process

Wastewater treatment is categorized into three different stages, primary, secondary, and tertiary. The need for one or all of these stages depends on:

- 1- Wastewater characteristics: this considers the form of the pollutant, i.e., suspended solids, colloidal, or dissolved compounds, the biodegradability, and the toxicity of the organic and inorganic components.
- 2- Required effluent quality and the aquatic toxicity limitation.
- 3- Costs and availability of land for any given wastewater treatment plant.

The following subsections describe each treatment stage:

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### 2.6.1 Primary Treatment

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The aim of the primary treatment is to remove solids through gravity precipitation. Most commonly, the precipitation is carried out in either circular or rectangular settling tanks or clarifiers. During settling, the solids precipitate to the bottom of the tanks and then can be removed as liquid-solid sludge. Primary treatment can remove up to 60 percent of the suspended solids (TSS) and 30 percent of the biochemical oxygen demand (BOD). Coagulants, such as alum, can be added to enhance the removal of the particulate matters. The primary treatment helps in reducing the energy needed to biologically convert these particles into CO<sub>2</sub>, water, and new biomass. The primary effluent is conveyed to the secondary treatment while the primary sludge is segregated for further treatment (Mehelcic, 2010; Metcalf, 2004).

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### 2.6.2 Secondary Treatment

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Secondary treatment which is usually a biological treatment utilizes microorganisms to digest organic compounds remaining after primary treatment. Secondary treatment is

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designed to substantially degrade the organic matter of the sewage. The majority of municipal plants treat the settled sewage liquor using aerobic biological processes. Secondary treatment systems are classified as *fixed-film (attached growth)* or *suspended-growth* systems (Jenkins, 2007). The selection of the appropriate technology depends on effluent quality needed, treated sludge quality, required footprint, odor nuisance levels, energy demand, ease of operation, etc (Daigger, 2007).

#### 2.6.2.1 Attached Growth Systems

Attached growth systems or fixed-film include trickling filters, biotowers, and rotating biological contactors, where the biomass grows on media and the sewage passes over its surface. The fixed-film principal has further developed into Moving Bed Biofilm Reactors (MBBR) and Integrated Fixed-Film Activated Sludge (IFAS) processes (Mehelcic, 2010; Metcalf, 2004).

#### 2.6.2.2 Suspended-Growth Systems

Suspended-growth systems include: 1) Activated Sludge (AS), where the biomass is mixed with the sewage and can be operated in a smaller space than trickling filters that treat the same amount of water; 2) Sequencing Batch Reactor (SBR), is a fill- and – decant system which uses the same unit processes (aeration and clarification) as for the conventional AS system; 3) Extended Aeration Process, the extended aeration process is similar to the conventional AS process, but it is operated under low organic loading conditions and uses a long aeration time; 4) Oxidation ditches typically operate in an extended aeration mode with long detention and solids retention times; 5) Membrane bioreactor (MBR), the membrane bioreactor process uses membrane treatment units submerged within an activated sludge tank to produce a very high quality effluent. The flow of treated effluent through the membrane units is controlled by the available gravity head (Mehelcic, 2010; Metcalf, 2004).

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### 2.6.3 Tertiary Treatment

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Tertiary treatment should be used as a polishing stage after secondary treatment to remove residual suspended solids. Filtration is widely used for removing small flocs or precipitated particles. There are two types of filtration which are granular media filtration and membrane filtration. Also, filtration may help in improving the color and odor of the treated effluent (Magdeburg, 2014). The tertiary treatment is associated with disinfection. Appropriate disinfection is needed to meet the effluent quality requirements. There are several disinfection options that could be adopted such as chlorination, ozonation and ultraviolet radiation (Chen, 2009; Mehelcic, 2010; Metcalf, 2004).

## 2.7 Heavy Metals Removal

This section focuses on the heavy metal removal from wastewater and identifies the various treatment techniques for heavy metals uptake. Heavy metals uptake from wastewater could be carried out using different techniques. Some of these techniques are phytoremediation, chemical precipitation, ion exchange, reverse osmosis, and adsorption (Gherasim, 2014). Most of these technologies are not economically viable and are complicated to control. In addition, they are not eco-friendly due to their demand on energy. Also, one of the major disadvantages of these technologies is incomplete uptake of the heavy metal constituents (Wang 2009; Ahalya, 2005; Voleskey, 2001). However, among these technologies, adsorption is considered the most reliable choice when both environmental and economic constraints are considered (El Zayat *et. al.*, 2014; Fenglian, 2011). The adsorption technique is still the favorable treatment process for heavy metals uptake due its easiness to operate, low cost, and high removal efficiency (Hua, 2014). The following sections describe thoroughly the adsorption process and all factors that affect

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the adsorption performance. The following subsections summarize the other removal technologies.

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#### 2.7.1 Reverse Osmosis:

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In reverse osmosis, heavy metals are segregated by a semi-permeable membrane at a pressure greater than the osmotic pressure. Reverse osmosis requires high capital and operational cost due to the high prices of the membranes (Zhao, 2014).

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#### 2.7.2 Phytoremediation:

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In recent years the use of certain types of plants to recover soil, sediment, and water from heavy metals contaminants has been widely used. This treatment process is called phytoremediation (Rungwaet. *al.*, 2013). However, this technology might need a long durations for heavy metals remediation (Ali, 2013).

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#### 2.7.3 Precipitation

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The precipitation is the widely applied technology for heavy metals removal. Metals are precipitated by increasing the pH through adding certain chemical. The main mechanism of the chemical precipitation is to de-solubilize the metal from the aqueous phase and precipitate the metal particles to the bottom of the settling chambers as sludge (Fu, 2012).

The chemical precipitation has many disadvantages as follows (Hua, 2014):

- The chemical doses should be highly adjusted and controlled.
- The chemical precipitation does not always comply with the allowable heavy metals limits.
- The generated sludge from the chemical precipitation needs high precaution in handling and disposal.

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#### 2.7.4 Ion exchange:

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Heavy metal ions are exchanged by electrostatic forces on an exchange resin. Ion exchange can efficiently remove dissolved metals; however, it is expensive and cannot be applied for large scale such as, mining effluent treatment (Pal, 2014; Rudnicki, 2014).

## 2.8 Adsorption

In general sorption may refer to either *adsorption* or *absorption*. *Adsorption* is a process where molecules accumulate at a surface or interface of another media. It can occur at an interface of any two phases, such as liquid-liquid, gas- liquid, gas-solid, or liquid-solid interfaces. The adsorption mechanism depends on the sorbent and sorbate behaviors. The adsorption can be based on a chemical binding which is called *chemisorption*, or surface-based physical forces attraction, such as Van Der Waals force, which is called *physiosorption* (Pang, 2013; Mihelcic, 2010). *Absorption*, on the contrary, is a process where the molecules or atoms of one phase interpenetrate uniformly into another phase to form a “solution”. It is simply the incorporation of an element or a molecule in one state into another of a different state, for example liquids could be absorbed by a solid or gases could be absorbed by water (Fomina, 2014). The accumulation of heavy metals on a solid phase, such as cement kiln dust (CKD), is an adsorption process (Salem, 2012; Ali, 2011; Zaki, 2007; El Awady, 1997). Accordingly, a great attention is given to discuss the adsorption process especially for the target heavy metals, the factors affecting adsorption, and how to identify the adsorption performance.

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#### 2.8.1 Lead Adsorption

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Lead adsorption depends on the agitation time, initial metal concentration, adsorbent dose, and the pH. Soltani, 2014 found that lead adsorption could be performed at pH 5.0. He also found that the adsorption performance increased by increasing the

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contact time between the adsorbate and adsorbent until reaching equilibrium condition. Soltani, 2014 also noted that increasing the empty-bed contact time (EBCT) in the continuous flow modes improved the adsorption mechanism (Soltani *et al.*, 2014).

Salem, 2012 investigated the use of manufactured Rasching ring for lead uptake from aqueous solutions. The Rasching rings were made of cement kiln dust, zeolite, and bentonite, and they were used as adsorbents in an industrial scale. The equilibrium result showed the possibility of lead immobilization by these fabricated rings. Moreover, Salem concluded that the strength and sorption capacity of these rings can be optimized by the addition of 47.5 wt.% cement kiln dust (Salem, 2012).

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### 2.8.2 Copper Adsorption

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Zaki in 2007 investigated the copper removal from synthetic solutions by using CKD leachate. The experiments were carried out on a batch wise runs using agitated flasks with an initial metal concentration of 100 mg/l. The removal efficiency of the Cu ions reached approximately 100%, and the removal started at pH > 5.5. Moreover, Zaki noted that at the addition of a solid material to a contaminated aqueous solution to adsorb heavy metals, the pH should be adapted otherwise a portion of the heavy metal will be precipitated as hydroxides (Zaki, 2007).

The removal of copper by cement kiln dust has not been comprehensively investigated. El Awady in 1997 investigated the effect of CKD as a metal scavenger to treat tannery influents from copper associated with other metals, such as chromium, iron, and cobalt. He found that the removal of the metal ions is increased by increasing the pH until equilibrium. The equilibrium breakthrough could be achieved at pH > 4.5. Also, it was observed that prolonging the equilibrium time up to 60 minutes is accompanied by a noticeable uptake percentage. Moreover, increasing the CKD dose from 5 to 20 g/l

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improves the removal efficiency to reduce the metal constituents to zero ml/l (El Awady, 2000).

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### 2.8.3 Cadmium Adsorption

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Hale in 2012 studied the effect of cement to recover soil from trace metals, such as cadmium. It was found that the cement can reduce the metals concentrations and mobility as the pH of the soil increased as a result of using cement. The cement increased soil pH which in turns improves both precipitation and adsorption of cadmium and any other existing elements. Soil samples contaminated by Cd, Co, Cu, Ni, Pb, Sb and Zn were subject to the treatment experiments using cement as a metal scavenger. The addition of cement or  $\text{Ca(OH)}_2$  reduced the mobility of every trace element (Hale, 2012).

The cement kiln dust was also recommended by the US Public Health Service to be used as an effective adsorbent to treat contaminated water from cadmium and other metal traces such as arsenic and lead. Waly in 2007 noted that the cadmium removal reached 90% at pH 5.5 and increased to 99% at pH 6.2. Batch adsorption experiments were conducted to investigate the use of the CKD as an adsorbent for the heavy metal ions, namely cadmium, zinc, aluminum, and cobalt. It was found that cadmium adsorption equilibrium was reached within 40-60 min and completed at 4 hrs. The influence of precipitation between pH 5.5 to 8 was negligible where the metal removal was mainly dominated by adsorption mechanism. The percent removal of the heavy metal ions increased as the pH increased to reach 99% removal at  $\text{pH} > 8.0$  except cobalt which reached 90% only. This study showed that CKD is effective in the removal not only Cd (II), but also Zn (II), Al (III) and Co metals in wastewater (Waly, 2007).

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## 2.9 Factors Affecting Adsorption

Adsorption is a physio-chemical treatment process for wastewater which is used to produce high effluent quality and free from either organic or inorganic elements (Du, 2014). The adsorption process generally depends on the following:

### 1- Adsorbent properties

- a. Surface area per unit weight must be high to increase the ability to adsorb much more amount of the adsorbate.
- b. The adsorbent must possess certain engineering properties depending upon the application to which they are put. If they are used in a fixed bed through which a liquid is to flow. For example, they must not offer too great pressure drop for flow nor must they easily be carried away by the flowing stream.
- c. They must have adequate strength and hardness so as not to be reduced in size during handling or crushed in supporting their own weight in beds of the required thickness.
- d. They must be cheap

### 2- Adsorbate properties:

- a. Substances of high molecular weight are easily adsorbed
- b. They must have the affinity to condensate on the surface of the adsorbent or to interact with it.

Adsorption of metal ions is affected by some external factors such as pH, temperature, the presence of other metal ions in solution, particle size of sorbent, adsorbent dose, initial metal concentration (Saad, 2008). The following sections discuss each factor that might affect the adsorption performance.



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### 2.9.1 Adsorbent Particle Size:

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The adsorption depends on the available surface area where the sorbate could be attached and interacts with. The adsorption capacity is directly proportional to the adsorbent surface area; the adsorption increases as the total surface area increases. In general, the adsorption increases as the grain size of the sorbent decreases; thus, the surface area increases (Gao, 2009). The physicochemical properties of the adsorbent surface also have a significant role in the adsorption process (Long, 2009).

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### 2.9.2 Temperature

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For practical applications of adsorption a reasonably narrow temperature range can be expected. In this narrow range, the effect of temperature is small (or neglected) as compared to other factors. The adsorption mechanism is an exothermic process. Accordingly, the sorbate removal efficiency increases when the temperature decreases. However, the adsorption performance does not significantly affected by small temperature variations. The normal temperature degrees of water and wastewater have minor effect on the adsorption mechanism (Wisniewska, 2013; Weber, 1972). The driving adsorption force could be determined by Gibbs free energy change. The adsorption reactions occur at a given temperature if  $\Delta G^o$  is a negative quantity. The following equation shows the free energy reaction considering the sorption equilibrium constant,  $K_o$ :

$$\Delta G^o = -RT \ln K_o$$

Where,  $\Delta G^o$  (free energy of the sorption) is standard free energy of change, J/gmol;  $R$  is the universal gas constant, 8.314 j/(gmol K);  $K_o$  is the thermodynamic equilibrium constant; and  $T$  is absolute temperature in Kelvin. The following equation also shows the relationship between the sorption equilibrium and the enthalpy and entropy change (Horsfall Jnr, 2005).

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$$\ln K_o = \frac{\Delta S_o}{R} - \frac{\Delta H_o}{RT}$$

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### 2.9.3 pH

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The adsorption mechanism is highly affected by the pH of the aqueous solution. Each metal has its own optimum pH. The pH as well has an effect on the metal solubility in water. If the pH of the water is acidic, the protonation behavior dominates the metal sorption. The chemistry of the metal adsorption plays a significant role at pH 5 – 6 (Saad, 2008).

The pH of the metal solution affects the adsorption because it identifies the available soluble metal ions for adsorption; moreover, it determines the adsorbent surface charge (Franco, 2004). Bennour in 2012 found that the Cu ion adsorption is obtained at 5.5 (Bennour, 2012). Soltani in 2014 studied the lead ions adsorption by silica nanopowder. He found that the Pb(II) ions adsorption has been performed at pH 5.0 (Soltani, 2014). Tajar in 2009 investigated the cadmium adsorption by using activated carbon. He investigated the effect of contact time, initial concentration and pH. He found that the high adsorption of cadmium ions was observed at pH > 8.0 (Tajar, 2009).

Osvaldo in 2007 has also found that the metal ions uptake from aqueous solutions is dominated by the pH as it affects the adsorbent surface charge. A maximum removal of Cd was observed at pH > 6 and pH greater than 5.0 for Pb and Cu.

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### 2.9.4 Time

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One of the advantages of adsorption is its relatively rapid occurrence. The rate of adsorption is very rapid during the initial 10 to 30 min of sorbent contact. The process of metal sorption by natural clay was investigated by Veli in 2007 and noticeable removal of metal ions (i.e., Cu and Zn) occurred after 5 minutes (Veli, 2007). In general, the adsorption time depends on the mechanism behavior. The adsorption is relatively fast for

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physical sorption and slow for chemical sorption mechanism. This is due to the fact that the chemical sorption (chemisorption) requires high energy to adsorb the sorbate into the sorbent cell (Saad, 2008).

El –Awady in 1997 studied the use of CKD to remove some heavy metal traces. He found that prolonging the contact time up to a certain limit is accompanied by improvement in the heavy metals removal. He found that the required time for equilibrium for many heavy metals ranges from 30 to 60 minutes (El Awady, 1997).

It was also shown by Ahalya in 2005 that the required equilibrium time does not change by changing the initial metal concentration. This might be attributed to the competition between metal ions to bind to the sorbent at higher metal concentrations (Ahalya, 2005).

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#### 2.9.5 Sorbent Dose

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Both the concentration of the metal ions and the sorbent doses have a significant impact on the adsorption behavior. Many researchers stated that the increase in sorbent dose resulted in rapid increase in heavy metal ions adsorption. However, this uptake values sometimes showed a reverse trend with the increase of the sorbent dose (Saad, 2008; Veli, 2007)

El Awady in 1997 investigated using different cement kiln dust doses to remove heavy metal ions from an aqueous solution, namely chromium, iron, copper, and cobalt. He used CKD doses in the range of zero up to 40g/l. It was obvious that the removal efficiency was on the increase by the increase of CKD. The same was discovered by Akpomie in 2012 by using another sorbent material which is Nsu Clay. Akpomie observed the high removal efficiency of Cadmium with 100 mg/l initial concentration by increasing the sorbent dose from 1 gram to 5 grams (Akpomie, 2012).

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### 2.9.6 Metal Concentration and Solubility

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As mentioned in the previous section, the initial concentration is a vital parameter in the adsorption mechanism and is much affected by the adsorbent dose. Accordingly, the adsorption of highly contaminated aqueous solutions by heavy metals could be properly performed as long as the binding sites of the adsorbent are not saturated (Venkatesham, 2012; Lacina, 2003).

On the other hand, the nature of the sorbate and its affinity to be adsorbed is another important aspect in the adsorption process. The adsorption performance is inversely proportional to the sorbate solubility. If the solubility of metals in solution is high, the uptake capacity will be challenging (Lo, 2009). Kim in 2005 also found that the adsorption is linearly and inversely proportional with the metal solubility (Kim, 2005). The solubility of the metal ions in aqueous solutions depends mainly on the pH of the solution. The effect of both pH values together with ionization of the metal on the adsorption process was studied by Stafiej in 2007. It was observed that the pH value plays an essential role on the metal solubility and hence its adsorption. Moreover, it was found that the low adsorption that could happen in the acidic region can be attributed for the strong solute-solvent bond and the competition between  $H^+$  and the metal ion  $M^{+2}$  on the adsorbent surface (Stafiej, 2007).

### 2.10 Adsorption Performance

The performance of the adsorbent material is measured as how much sorbate it can be adsorbed and retained in an immobilized form. Accordingly, the adsorption capacity is calculated by using the following mass equilibrium equation (Volesky, 2003):

$$q = (C_o - C)V/W$$

Where:

**q** is the adsorbed quantity of heavy metal per gram of sorbent (mg/g)

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$C_0$  is the initial heavy metal concentration (mg/l)

$C$  is the final heavy metal concentration (mg/l)

$V$  is the volume of the solution, L

$W$  is the weight of dry sorbent, gm

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### 2.10.1 Sorption Isotherm Model

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The equilibrium distribution of ions between solid and liquid phases in the adsorption mechanism is of high interest before the implementation of any sorption operation. The relationship between the quantities of adsorbate to the adsorbent at equilibrium ( $Q_{eq}$ ) and the equilibrium concentration of the sorbate ( $C_{eq}$ ) is called the sorption isotherm. The adsorption isotherm is affected by the type of adsorbent and adsorption conditions (Milmile, 2011).

The most widely used isotherm models are the simple *Langmiur* model and *Freundlich* model. In Langmiur the sorption mechanism is assumed to be in monolayer type while it is assumed to be multilayer type in Freundlich (Mihelcic, 2010).

#### 2.10.1.1 Langmuir Isotherm Model:

The Langmuir isotherm (1918) had been performed based on homogenous binding between the sorbate and sorbent and the following assumptions (Mihelcic, 2010; Metcalf and Eddy, 2004):

- Metal ions are chemically adsorbed at a fixed number of well defined sites;
- Adsorption cannot proceed beyond monolayer coverage;
- Each site can hold only one ion;
- All sites are energetically equivalent; and
- There is no interaction between the ions adsorbed on neighboring sites (i.e. the ability of molecule to adsorb at a given site is independent of the occupation of neighboring sites).

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- Adsorption is reversible.

The equilibrium is reached once the rate of adsorption onto the material site surface equals the rate of desorption. In other words, once the adsorption capacity reaches its breakthrough. The Langmuir isotherm could be explained by the following equation:

$$\frac{1}{q_e} = \frac{1}{b} + \frac{1}{abC_e}$$

Where:

**q<sub>e</sub>** mass of heavy metal adsorbed per gram of adsorbent

**C<sub>e</sub>** equilibrium heavy metal concentration in liquid phase, mg of heavy metal/liter

**a** Langmuir constant, liter/mg of heavy metal

**b** Monolayer coverage, mg of heavy metal/gm of adsorbent

#### 2.10.1.2 Freundlich Isotherm Model

Unlike the Langmuir model, Freundlich is based on the heterogeneity of the surface. Freundlich has been empirically driven assuming that the sorbents can be adsorbed in a multilayer manner.

The Freundlich isotherm could be explained by the following equation (Mihelcic, 2010):

$$\text{Log}q_e = \text{Log}K_f + \frac{1}{n}\text{Log}C_e$$

Where:

**q<sub>e</sub>** mass of heavy metal adsorbed per gram of adsorbent

**C<sub>e</sub>** equilibrium heavy metal concentration in liquid phase, mg of heavy metal/liter

**k<sub>f</sub>** and **n** are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of adsorption

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## 2.11 Cement Kiln Dust

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### 2.11.1 Cement Kiln Dust Production

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The cement industry is a relatively small but significant component of the U.S. economy, with annual shipments valued at around \$8.6 billion. In the United States, 39 companies operate 118 cement plants in 38 states. Worldwide, the United States ranks third in cement production, behind China, the world's leading producer, and India (Simmons, 2003). In 2008, the cement industry produced 86.3 million tons of portland and masonry cement in the U.S.A. and the world output was about 1.9 billion tons. The cement industry has a limited number of by products that result from the manufacturing process, such as cement kiln dust (Oss, 2008). Compared to Egypt production from cement, Egypt has 22 cement factories which produce approximately 46 million metric ton/ year (Askar, 2010). Askar also stated that the most voluminous by product generated is cement kiln dusts (CKDs). An overview of the cement manufacturing process and the generation of CKDs are outlined below.

Portland cement, the fundamental ingredient in concrete, is calcium silicate cement made with a combination of calcium, silicon, aluminum, and iron. Producing cement that meets specific chemical and physical specifications requires careful control of the manufacturing process. There are three main stages in the manufacturing process (Oss, 2008):

Stage I - Raw material extraction: The first step in the portland cement manufacturing process is obtaining raw materials. Generally, raw materials consisting of combinations of limestone, clay, sand, and iron ore are mined from a quarry probably near the plant. At the quarry, the raw materials are reduced by primary and secondary crushers. Stone is first reduced to 12 cm (5-inch size), then to 19 mm (3/4-inch).

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Stage II - Blending and clinkerization: Once the raw materials arrive at the cement plant, the materials are proportioned to create cement with a specific chemical composition. Two different methods dry and wet are used to manufacture Portland cement. In the dry process, dry raw materials are proportioned, ground to a powder, blended together and fed to the kiln in a dry state. In the wet process, slurry is formed by adding water to the properly proportioned raw materials. The grinding and blending operations are then completed with the materials in slurry form. After blending, the mixture of raw materials is fed into the upper end of a tilted rotating cylindrical kiln. The mixture passes through the kiln at a rate controlled the slope and rotational speed of the kiln. Burning fuel consisting of powdered coal or natural gas is forced into the lower end of the kiln. Inside the kiln, raw materials reach temperature of ~2600°F (1430°C). At that temperature, a series of chemical reactions cause the materials to fuse and create cement clinker-grayish-black pellets. Clinker is discharged from the lower end of the kiln and transferred to various types of coolers to lower the clinker to handling temperatures.

Stage III- Grinding and distribution: Cooled clinker is combined with gypsum and ground into a fine gray powder. The clinker is ground so fine that nearly all of it passes through a No. 200 mesh (75 micron) sieve. This fine gray powder is the portland cement.

#### *2.11.1.1 CKD Generation and the Need for its Disposal*

Cement kiln dust is generated in the second stage of the cement manufacturing process. During the burning of raw materials in the cement kiln, large quantities of air are used for carrying fuel to the burning zone and for combustion. The air and combustion products entrain particles of clinker, raw materials, and partially calcined raw materials with the exhaust gases. The finely divided dry particulate matter, carried from the cement kiln by exhaust gas is captured by the kiln's air pollution control device (APCD) and is known as the cement kiln dusts (CKDs). The generation of CKDs is affected by a wide



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variety of factors including raw materials used, required product specifications, kiln type, fuel type, and secondary material substitutes for raw materials and fuels. CKD may be returned as a component of raw feed in cement manufacturing if it is low in alkalis. For some facilities, the dust from the APCD is directly returned to the kiln, and in other systems, some segregation or processing is required. Operators of some kiln systems that use electrostatic precipitators (ESP) and high alkali raw materials have found that the CKD in different ESP fields or sections will have different chemistries (Hawkins *et al.*, 2003). The finest materials captured in the last portion of the ESP often have the highest percentage of alkalis. For that reason, CKD in the first ESP field(s) may be appropriate for return to the kiln, while the dust in the final field(s) may be removed from the process for other uses, processing, or disposal (Hawkins *et al.*, 2003).

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#### 2.11.2 Factors Affecting CKD Generation

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Numerous factors associated with the cement manufacturing process influence CKD generation. The following sub sections show the significant factors that have an influence on the CKD generation.

##### *2.11.2.1 Type of Dust Collection System*

Air pollution control devices (APCDs) are used to control dust emissions from the kiln system to the atmosphere. APCDs are sensitive to a variety of operating conditions (i.e., temperature, moisture, sulfur content) which affect their removal efficiency. The most commonly used APCDs with their efficiency are electrostatic precipitator (99.75%), bag house (99.95%) and multi-clones (85-94%) (Pudasainee, 2009; USEPA, 1987).

##### *2.11.2.2 Chemical Specification of Cement*

The chemical characteristics of the raw material affect the alkalinity of the cement kiln dust. Therefore, in order to produce low alkali cement, control facilities to reduce the

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build-up of certain elements should be introduced. Accordingly, cement facilities with high alkali raw materials tend to waste more CKDs in order to meet the low alkali specification (Alexandra, 2008; USEPA, 1987).

#### *2.11.2.3 Process Type*

Individual characteristics of the cement process are determined by kiln type and design. When design parameters are changed or modified, they have the potential to greatly impact each other. This could result in increased dust suspension in the gases traveling within the system, which, in turn, impacts the amount of CKDs generated. A few of the several design parameters which impact the process are temperature profile of the system, gas velocity, kiln diameter/cross sectional area and kiln rotation speed.

The comparison made between wet kilns and dry kilns indicates that wet kilns generate less gross CKDs per ton of clinker produced. However, wet kilns generate more net CKD per ton of clinker produced. This is due to the recycling limitations associated with wet kilns, based on the more complex challenge of mixing a pulverized dry material into the slurry mix. As a countermeasure, wet kilns are able to sell their CKD at a greater rate than dry kilns because the composition of the net CKD is less concentrated in alkalis and other impurities (IPPC, 2001).

#### *2.11.2.4 Physical and Chemical Characteristics of CKD*

CKD mainly consists of calcium carbonate, silicon dioxide, iron oxide, calcium oxide, sodium and potassium chlorides and sulfates, metal oxides, and other salts. In 2003, a preliminary analysis of chemical composition of CKDs gathered from 20 different plants in USA was performed. The analysis showed that the CaO varies from 38 - 63%, total alkali range is from 2 to 11%, sulfate content is 3-17%, and the free lime contents 1 - 25% (Peethamparan, 2006). Peethamparan also stated that 50 to 90% of

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CKDs has a diameter below 10 $\mu$ m which is within a respirable range for humans. Furthermore, it was observed that dry precalciner kilns generate larger CKD amounts than wet kilns or long dry kilns. However, the produced CKD particles from long dry kilns are smaller and in the respirable range.

#### 2.11.2.5 Environmental Impact of CKD

As mentioned previously, great efforts were exerted to reduce the generated quantities of the CKDs by using advanced control technologies (Hawkins *et al.*, 2003). However, further CKD reduction cannot be easily achieved due to technical issues and cement manufacturing efficiency. On the other hand, the disposal of CKD faces many challenges and environmental concerns. Accordingly, discovering new innovative ways to utilize CKD as a value added product are of high interest to the cement industry. The chemical compositions of CKDs are similar to that of cement. However, the alkalinity of the CKD is higher than the cement. Also, the CKD particle size is very fine where it is in the range of 10 micron. Due to its alkalinity and very fine size, CKD is considered a major pollutant resulting in respiratory tract irritations and infections (El Zayat *et al.*, 2013; Peethamparan, 2006). On the other hand, the CKD would have some positive impacts and beneficial uses. CKD would be used for soil stabilization, waste solidification, cement additive, mine reclamation, agricultural soil amendment, sanitary landfill liner, wastewater treatment, pavement works, and concrete blocks (Adaska, 2008). The amount of alkalis and sulfates, calcium carbonate/calcium oxides are substantially higher in CKDs compared to cement. The higher alkalinity and finer particle size, in addition to its cementitious properties, make this material usable for several applications. Some of the potential uses of CKDs, that take advantage of its favorable chemical and physical properties, are waste solidification (Mohamed and EL Gamal, 2011), replacement for Portland cement in concrete block manufacturing and ready mix concrete and in

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supplementary cementitious materials (Prusinski *et al.*, 2006; Hawkins *et al.*, 2003), hydraulic barrier in a landfill liner/cover (Moses and Afolayan, 2011), land application as agricultural soil amendment (Khaled, 2000), flowable fill (Howard, 2012; Khalifa, 2002), mineral filler in asphalt paving and mine reclamation, and sorbent to remove sulfur dioxide from cement kiln flue gas. Occasionally, CKDs contain large amounts of free-lime (CaO) making it a potential candidate for substituting traditional soil stabilizer (lime), fertilizers, sludge stabilizers etc. (Prusinski *et al.*, 2006). Studies reported in the past have shown that treating soils with CKDs improves its various properties and hence some CKDs have great potential to be used as an effective soil stabilizer (Peethamparan, 2006; Khaled, 2000).

Cement dust by pass, or the cement kiln dust, is a hazardous by-product from the cement industries. Egypt currently has 22 cement factories. The factories already operating, although they have different air pollution control devices (APCD), still have a major problem with its final disposal (Askar, 2010). Currently, the cement dust is pumped into transportation trucks and dumped in the desert. Due to the nature of the dust, it tends to be dispersed into the air and carried by wind to the surrounding areas, causing significant health hazards. This is witnessed currently in the Helwan area, where one of the oldest and largest cement factories is located. According to Sinai Cement Factory, 70 tonnes/day of cement dust is generated at its factory. Accordingly, significant amounts of CKD are produced annually. The Egyptian Environmental Affairs Agency (EEAA) is studying the possibility of using cement dust as an amendment with sludge, as well as other bulking agents, in an attempt to produce safe and sanitized compost and to consume some of the cement dust in a beneficial way.

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## 2.12 Lime Stone

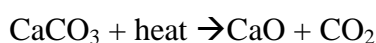
Considering chemical composition of CKDs, formation of other reaction products (slag, ettringite, gypsum) is also expected but these materials are not predicted to play significant role in heavy metals recovery from wastewater. As such, hydrated lime as a prime source of CaO (the major constituent of CKD) was examined and compared to CKD in heavy metals uptake in this study. Accordingly, the following sub sections identify the formation of the hydrated lime stone and its physio-chemical properties.

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### 2.12.1 Lime Manufacturing Process

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Lime is the product of the calcination process of limestone. Limestone deposits widely exist in Egypt in the Eastern desert, Western desert and Sinai (Mahrous, 2010). The rock shall contain 50 percent calcium carbonate (CaCO<sub>3</sub>) in order to be classified as limestone. If the rock contains 30 to 45 percent magnesium carbonate (MgCO<sub>3</sub>), it is identified as dolomite or dolomitic limestone. Not only can lime be produced by the calcination of limestone, but also it can be manufactured from aragonite, chalk, marble, and sea shells (EPA, 1995). According to the lime manufacturing process in the EPA's guidebook (1998), the selected limestone, based on its chemical composition and granulometry, is calcinated at about 1000°C in various types of kiln fired by such fuels as natural gas, coal, fuel oil, lignite...etc. The produced calcinated lime is called quicklime. Quicklime is produced according to the following endothermic reaction:



The resulted quicklime is followed by hydration, i.e. combined with water. Hydrated lime, known as hydrated lime, is produced according to the exothermic reaction shown below:



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### 2.12.2 Chemical and Physical Characteristics of Lime

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As a result of the nature of the raw material used in the lime process, hydrated lime consists mainly of  $\text{Ca}(\text{OH})_2$ . As discussed in the previous sections, hydrated lime is obtained by treating quicklime ( $\text{CaO}$ ) with water and hence oxides convert to hydroxides. The generated hydrated lime depends on the type of the quicklime and hydration conditions. In 2007, a preliminary analysis of chemical and physical properties of lime was conducted by the National Lime Association (NLA) in USA following the standards of the American Society for Testing and Materials (ASTM). According to the NLA specifications the lime is classified into three different types. First, High calcium hydrated lime which is generated from high calcium quicklime contains approximately 73%  $\text{CaO}$ . Second, Dolomitic hydrated lime produced from dolomitic quicklime under normal atmospheric pressure composes of approximately 47%  $\text{CaO}$ , 33%  $\text{MgO}$ . Third, Dolomitic hydrated lime produced from dolomitic quicklime under pressure contains 40%  $\text{CaO}$  and 30%  $\text{MgO}$ . In general, lime is strongly alkaline possessing a pH greater than 11.0.

Mahrous et al. (2010) evaluated the several hundred limestone samples obtained from eight different Egyptian quarries. It was found that the densities of limestone deposits and their calcium carbonate contents vary from  $2250 \text{ kg/m}^3$  for Aswan limestone to  $2700 \text{ kg/m}^3$  for both Suez and Minia deposits.

### 2.13 Environmental Reform

Egypt has committed many environment laws and regulations in order to preserve the nature. Many of these laws give high consideration for heavy metals recovery. These laws are summarized in the following table (Table 1). Among the summarized laws in the following table, we are mainly concerned about Law 93/62, Law 48/82, and Law 4/94 with respect to heavy metals.

**Table 1: Egyptian Environmental Laws**

<b>Law Number</b>	<b>Regulation</b>
Law 116/1983	Controls the use of land for non-agricultural purposes.
Law 48/1982	Addresses the protection of the Nile and related fresh waterways from pollution.
Law 38/1967 and its amendment 31/1976	Deals with municipal solid wastes.
Law 106/1976	Addresses housing construction, density, lighting and ventilation, permitting, plumbing and sanitary connection.
Law 3/1983	Deals with planning of urban settlements.
Law 145/1988	Delineates authorities and responsibilities of local government units
Law 102/1982	Designates natural reserves and related conservation measures
Law 93/1962	Details responsibilities and authorities of General Organizations for Sanitary Drainage in licensing and limitations of discharges to public sewers.
Law 117/1983	Defines criteria for designation of historical structures, protection of antiquities and regulation of excavation in historical sites.
Law 24/1983	Concerning protection of marine life and regulations of fisheries.
Law 27/1981	Deals with regulations of handling toxic chemicals in industry
Law 4/94	Has a greater role with respect to all

	governmental sectors as a whole. The law has been designated as the highest coordinating body in the field of the environment that will formulate the general policy and prepare the necessary plans for the protection and promotion of the environment.
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### 2.13.1 Law No. 93/62

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Law No. 93/62 limits the heavy metals concentration in industrial water flows according to the discharged water. The law has stated that the following metals either in a single form or mixed should not exceed 10 ppm if the discharge is less than 50 m<sup>3</sup>/d, or 5 ppm if the discharge is greater than 50 m<sup>3</sup>/d: copper, zinc, cadmium, chromium, mercury, silver, nickel, and tin. Furthermore, the concentration of mercury and silver should not exceed 1 ppm regardless of the amount of the discharge. Interestingly, the law does not mention the allowable limits for lead.

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### 2.13.2 Law No. 48/82

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The law was advanced in order to control the concentration of heavy metals in industrial discharges and the ambient concentrations in agricultural drains. The law stated that the total heavy metals in the industrial effluents discharged to non-fresh water bodies should not exceed 1 ppm where non-fresh water bodies include agricultural drains and lakes. Not only is the law concerned about non-fresh water, but also underground water reservoirs and fresh water areas. Moreover, the law has given the following allowable limits for heavy metals in case of discharging agricultural drain water into fresh water bodies: (1) copper should not exceed 1 ppm, (2) cadmium should not exceed 0.01 ppm, and (3) zinc should not exceed 0.01 ppm.



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### 2.13.3 Law No. 4/94

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This law includes a whole chapter on hazardous materials and wastes. It prohibited discharging or dumping wastes without license from the competent authority. It has also banned their importation or passage through the Egyptian territories. Furthermore, law no.4/94 prohibits the passage of ships carrying hazardous waste in the territorial waters without permission from the competent authority. Violators of the rule will be penalized by not less than five years imprisonment and a fine not less than twenty thousands up to forty thousand Egyptian Pounds; moreover, he will be responsible to re-export this waste at his own expense.

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### 2.13.4 International Regulations

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The food and agricultural organization of the United Nations (FAO) and the world health organization (WHO) have identified the quality of treated wastewater effluent and disposal method. Based on the treated effluent quality, it is feasible to be used for either restricted or unrestricted irrigation. Restricted irrigation is limited to cereals, pasture, trees, and with no public access, while unrestricted irrigation is for eaten uncooked crops (World Bank, 2014). According to the FAO guidelines the heavy metals concentrations should not exceed 5 mg/l, 0.2 mg/l, and 0.01 mg/l for lead, copper, and cadmium respectively.

## **2.14 Research Motivation**

The Guiding research question is: How could we produce high quality treated wastewater free from heavy metals and in compliance with the Egyptian regulations and international guidelines using a sustainable solution. The proposed solution is treating wastewater using industrial solid wastes as coagulants and adsorbents to overcome the high capital and operational costs, large footprint and huge energy consumption in the

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conventional wastewater treatment plants from one side and to mitigate the environmental and health impacts of industrial wastes from the other side.

In order to answer this guiding question, we are concerned about comprehensively studying the Cement Kiln Dust (CKD) as an industrial solid waste that exists in abundance. It will also be compared to hydrated lime in a bench scale study. Accordingly, our main concerns are to:

1. Simulate and computationally model the proposed treatment system in order to know the equilibrium adsorption isotherm of CKD.
2. Investigate the design of a new pilot-scale system that provides a new integrated system for advanced recovery of heavy metals from an industrial wastewater treatment using Cement Kiln Dust.
3. Study the economic viability of this new technology.

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## CHAPTER 3: METHODOLOGY

### 3.1 Introduction

This chapter describes the materials selection, experimental methods and sample preparation of the laboratory work conducted at the Environmental Laboratory at the American University in Cairo. Laboratory experiments presented in this chapter were carried out in order to evaluate the impact of using cement kiln dust in wastewater treatment and heavy metals up take. Statistical software on design of experiments, namely Design-Expert® software package, was utilized to ensure the experiments are well-designed to obtain reliable results. Research work focused on three types of heavy metals, namely; lead, copper and cadmium. The research plan proceeded in two phases.

In the first phase, a series of experiments were conducted to determine adsorption capacity of the cement kiln dust on heavy metals; namely, lead, copper and cadmium. The experiments were conducted twice; once as completely mixed batch reactors, and the second time as continuous flow columns. Both systems are used in wastewater treatment plants. The column experiments also give a picture of the dynamic (or kinetics) of the adsorption process. In addition to the adsorption experiments, a surface titration experiment was carried out in order to know the surface charge characteristics of the cement kiln dust used in these experiments. Finally, the full set of equilibrium constants were then used as input in a dual rate dynamic model (FITEQL) to simulate the breakthrough curve of the target metals. The ultimate objective is to use the model as a scale-up tool for design of full-scale units. Verification of a modeling tool to simulate performance and facilitate design for adsorption units with CKD is an important contribution to the literature and to engineering practice pertaining to the advanced treatment of heavy metals in wastewater. In addition to the conducted bench scale

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experiments to evaluate the CKD as a heavy metal scavenger, the CKD effect on the physiochemical and bacteriological characteristics of raw wastewater was examined. This is to know the influence of CKD on the organic constituents in the raw wastewater as well.

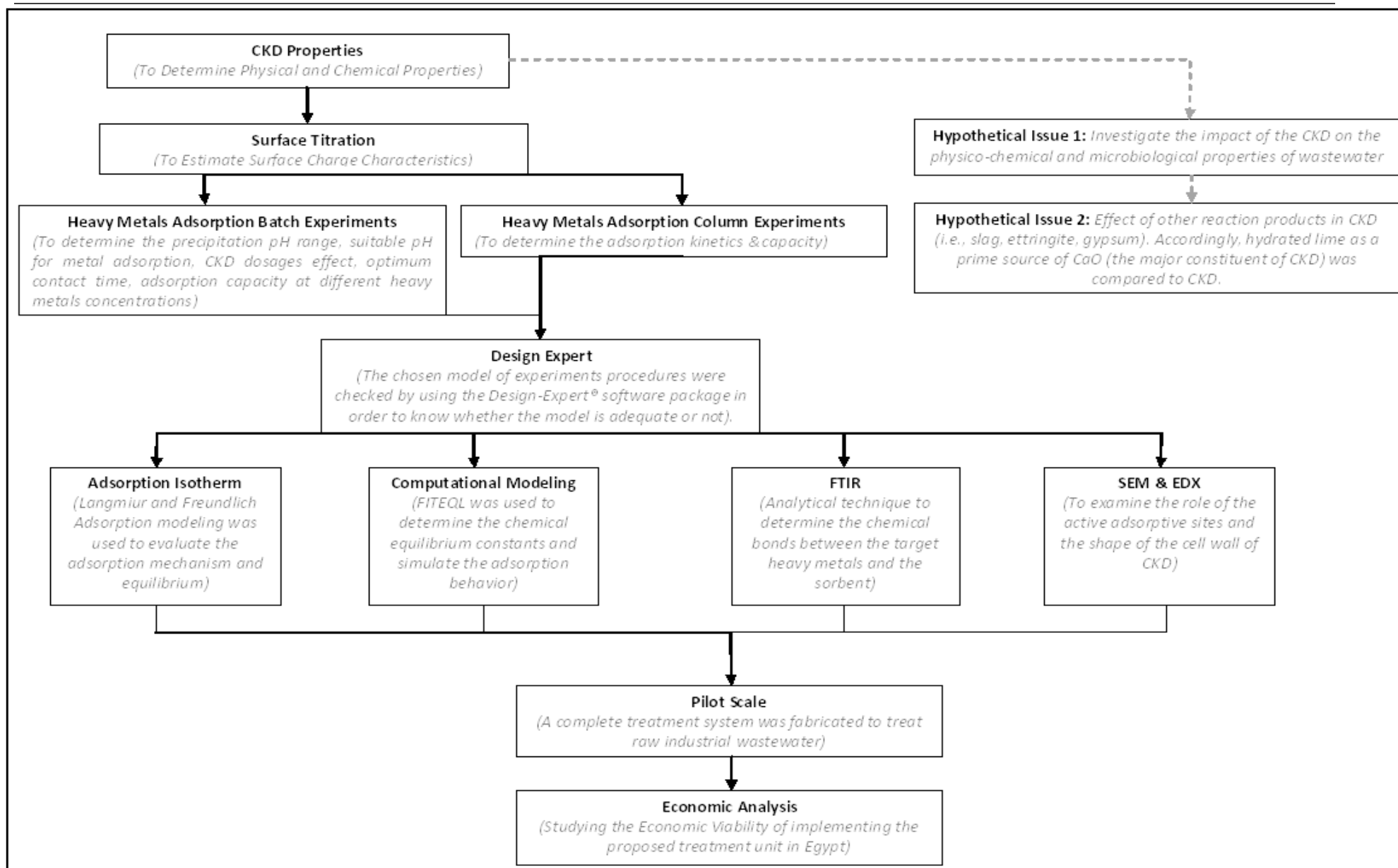
The first phase will lay the ground to the second phase. In the second phase, a pilot scale test was performed in order to know the properties of the CKD and its removal capacity of the pollutants found in wastewater. Chapter five will thoroughly discuss the design, manufacturing, and the operation of the pilot scale.

Hydrated lime stone, a prime source of CaO (the major constituent of CKD), was also examined for heavy metals removal from wastewater. Hydrated lime was examined on bench scale batch equilibrium experiments and compared to CKD in wastewater recovery from heavy metals, physiochemical and biological constituents. The purpose behind testing hydrated lime is to investigate whether the formation of other reaction products found in CKD (slag, ettringite, clay...) has an effect on heavy metal removal behavior or not.

System computational modeling was conducted using surface complexation models to estimate equilibrium constants from experimental results. These equilibrium constants can be used later in up-scaling the treatment unit.

Finally, economic analysis has been conducted in order to investigate the viability of the proposed project. The economic viability of the proposed project will be discussed separately in chapter six.

The following flow chart (Figure 1) summarizes and shows the experimental work done.



**Figure 1: Experimental Methodology**

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## 3.2 Experimental Design

Design-Expert 8.0.1, software by Stat-Ease Inc, was used for checking the design and analysis of experimental work. The output from the batch experiments optimization experiments were analyzed using Design-Expert software and are presented in Chapter 4.

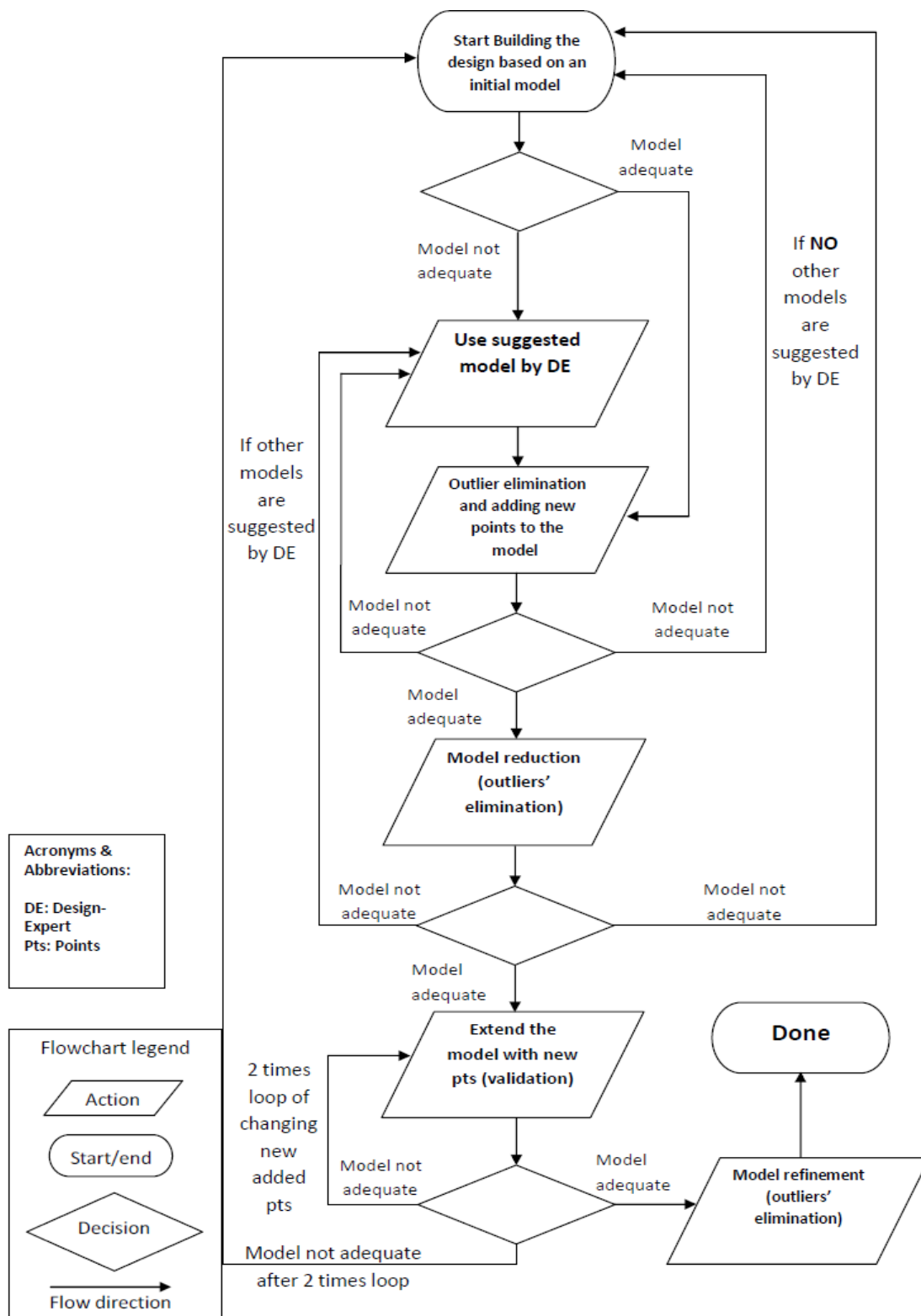
The application of this software helped reaching a final model with appropriate fitting equation, minimum possible error, and lack of fit. The flowchart shown in Figure 2 explains the steps of the software. The initial design of the optimization experiments started with a quadratic model till reaching a partial quadratic model.

The *Decision* of an adequate model or not was based on the model analysis; represented in “Fit Summary”, “ANOVA”, “Case statistics”, and “Graphical displays”, obtained from Design-Expert output. Each one will be explained further in chapter 4.

## 3.3 Materials and Reagent

### 3.3.1 Cement Kiln Dust (CKD)

Cement Kiln Dust (CKD) samples were taken from BeniSuef Cement Plant located in BeniSuef Governorate in Egypt. The cement manufactory has rotary kilns that operate in the temperature range of 1370–1480°C. It uses a dry feed process and collects the CKD by the means of electrostatic precipitator. The production of CKD in this plant is around 5% of the total production of the dry kilns which is 3 million metric tons of clinker. Accordingly, the amount of CKD produced is in the range of 150,000 ton/year. Therefore, the daily generation of CKD at BeniSuef plant is approximately 470 ton assuming that the plant operates for 320 days/year. The generated CKD is disposed in the desert which is the usual practice by most of the cement companies in Egypt. In some cases, CKD, also known as bypass dust, is disposed of after granulation or pelletizing using water. These huge amounts of CKD cost a fortune to get rid of them (Kunal, 2012).

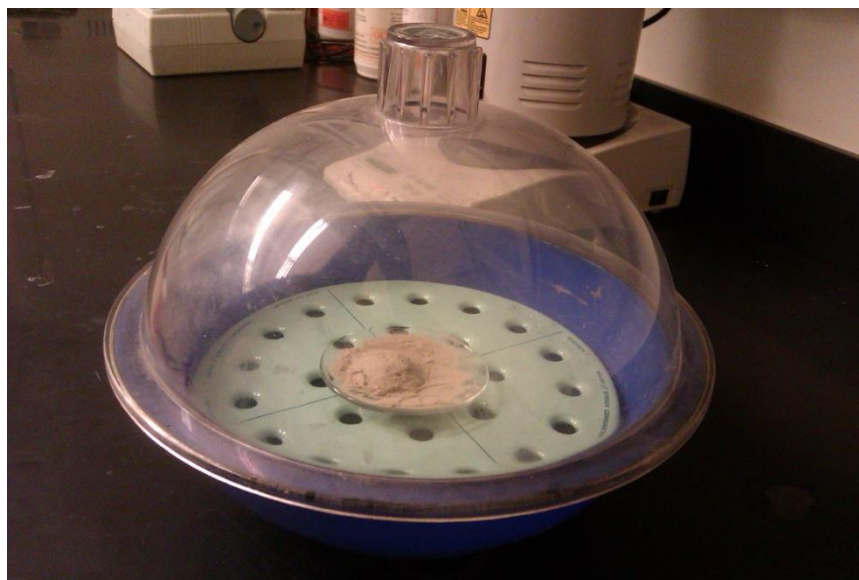


**Figure 2: Design Expert Navigation Algorithm**

The collected CKD were stored in sealed containers made of plastic, and kept all the time on a desiccator to avoid the conversion of CaO to CaCO<sub>3</sub> (Figure 3). The CKD is

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produced in a powder form with particle size approximately equal to 74 microns. The pH of suspended CKD in distilled water was 11. Figure 4 shows the CKD collected samples. The physiochemical properties of CKD were examined as shown in section 3.5 of this chapter: Laboratory Experiments.



**Figure 3: CKD Sample in the Dissecator**



**Figure 4: CKD Collected Samples**

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### 3.3.2 Hydrated Lime Stone

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The quicklime was provided by a lime factory that uses Mazout to calcinate limestone to quicklime. The quicklime was converted to hydrated lime at the American University in Cairo Environmental Engineering laboratory by pouring water until complete hydration of the quicklime has been reached.

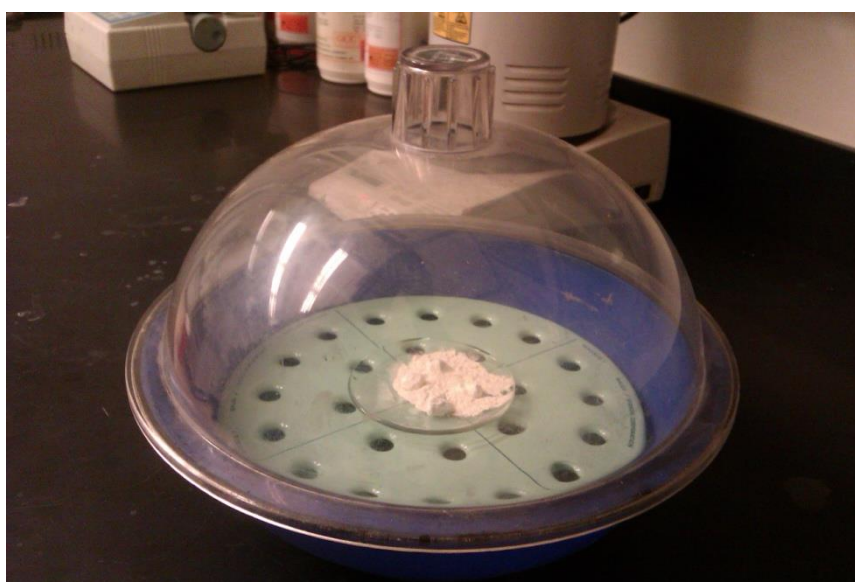


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The collected hydrated lime stone, shown in Figure 5, were stored in sealed containers made of plastic. The same as CKD, the hydrated lime stone was kept all the time in a desiccator at a room temperature to preserve its characteristics (Figure 6). The hydrated lime stone is a powdered material with a pH ~ 11.0.



**Figure 5: Hydrated Lime Stone Samples**



**Figure 6: Hydrated Lime Stone Sample in the Dessicator**

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### 3.3.3 Salts of Heavy Metals and Reagents

The synthetic heavy metal solutions were prepared at the laboratory using reagent grades following the standard methods released by Perkin Elmer (Elmer, 1995). The desired concentrations of the target heavy metals were prepared by diluting the stock solutions in de-ionized distilled water (DDW). The stock solutions were MERCK type grade, and were used in preparation of both the heavy metal solutions and standards.

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An ionic background, sodium nitrate ( $\text{NaNO}_3$ ) with assay of 99% (Gainland Chemical Company GCC, reagent grade), was added. The sodium nitrate was added to the heavy metal solutions to adjust the ionic background to 0.01 M for the solution to more realistically simulate untreated water and to ensure the same total dissolved solids concentration in all cases.

#### 3.3.3.1 Synthetic Lead Solution

The working lead solutions were prepared by dissolving the lead stock solution (1000 ppm), manufactured by MERCK, in DDW. The experimental lead solutions were diluted to reach the desired concentration of lead used in the experiments by diluting the standard stock solution.

In the equilibrium batch experiments, the desired concentrations were 200 mg/L, 150 mg/l, 100 mg/l, 70 mg/l, 50 mg/l, 30 mg/l, and 10 mg/l.

In the column experiments where large volumes were needed, the experimental lead solution was prepared by diluting 1.598  $\text{Pb}(\text{NO}_3)_2$  manufactured by American Chemical Society (ACS) with assay 99% in 1000 ml DDW in order to get 1000 ppm. The lead solution was then acidified by adding 1%  $\text{HNO}_3$  (10 ml) as per the standard methods. As such, 300 ml of the prepared stock solution was added to 10L DDW to reach the desired concentration of 30 ppm.

All the experimental lead solutions were used with the same ionic background of 0.01 M by adding 0.85 gm  $\text{NaNO}_3$  for every liter. The used  $\text{NaNO}_3$  was manufactured by Gain Land Company (GCC) in UK with an assay of 99%.

The standard solutions used in the calibration procedure for the atomic absorption spectrometer were prepared with the same dilution procedure as the samples.

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### 3.3.3.2 Synthetic Copper Solution

The working copper solutions were prepared by dissolving the copper stock solution (1000 ppm), manufactured by MERCK, in DDW. The experimental copper solutions were diluted to reach the desired concentration of lead used in the experiments by diluting the standard stock solution as follows:

In the equilibrium batch experiments, the desired concentrations were 200 mg/L, 150 mg/l, 100 mg/l, 70 mg/l, 50 mg/l, 30 mg/l, and 10 mg/l.

In the column experiments where large volumes were needed, the experimental copper solution was prepared by diluting 3.8 (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O) manufactured by Oxford Laboratory UK with assay 99% in 1000 ml DDW in order to get 1000 ppm. The copper solution was then acidified by adding 1% HNO<sub>3</sub> (10 ml) as per the standard methods. As such, 300 ml of the prepared stock solution was added to 10L DDW to reach the desired concentration of 30 ppm.

All the experimental copper solutions were used with the same ionic background of 0.01M by adding 0.85 gm NaNO<sub>3</sub> for every liter. The used NaNO<sub>3</sub> was manufactured by Gain Land Company (GCC) in UK with an assay of 99%.

The standard solutions used in the calibration procedure for the atomic absorption spectrometer were prepared with the same dilution procedure as the samples.

### 3.3.3.3 Synthetic Cadmium Solution

The working cadmium solutions were prepared by dissolving the cadmium stock solution (1000 ppm), manufactured by MERCK, in DDW. The experimental cadmium solutions were diluted to reach the desired concentration of cadmium used in the experiments by diluting the standard stock solution as follows:

In the equilibrium batch experiments, the desired concentrations were 200 mg/L, 150 mg/l, 100 mg/l, 70 mg/l, 50 mg/l, 30 mg/l, and 10 mg/l.

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In the column experiments where large volumes were needed, the experimental cadmium solution was prepared by diluting 2.74 (Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O) manufactured by Oxford Laboratory UK with assay 99% in 1000 ml DDW in order to get 1000 ppm. The cadmium solution was then acidified by adding 1% HNO<sub>3</sub> (10 ml) as per the standard methods. As such, 300 ml of the prepared stock solution was added to 10L DDW to reach the desired concentration of 30 ppm.

All the experimental cadmium solutions were used with the same ionic background of 0.01M by adding 0.85 gm NaNO<sub>3</sub> for every liter. The used NaNO<sub>3</sub> was manufactured by Gain Land Company (GCC) in UK with an assay of 99%.

The standard solutions used in the calibration procedure for the atomic absorption spectrometer were prepared with the same dilution procedure as the samples

#### 3.3.3.4 De-ionized Distilled Water (DDW):

De-ionized distilled water (ASTM type one grade water) was used in the preparation of synthetic metal solutions as well as heavy metals standards. Also, it was used in calibration standards preparation, all experimental work, blanks, experimental analyses, and as dilution water. All references to reagent water in this research study refer to ASTM type 1 grade water. The DDW produced from two consecutive water treatment units model Fistream Glass Still and model NANOpure UV manufactured in USA by Barnstead.

#### 3.3.3.5 Lead Nitrate Pb (NO<sub>3</sub>)<sub>2</sub>:

American Chemicals Society (ACS) grade was used in the preparation of lead (Pb<sup>+2</sup>) solutions of large volumes. The molecular weight of the lead nitrate salt is 331.2 gm/mo. For small volumes and standards, Pb standard solution manufactured by MERCK Germany was used.

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#### *3.3.3.6 Copper Nitrate $Cu(NO_3)_2 \cdot 3H_2O$*

Oxford laboratory reagent grade manufactured in UK was used in preparing large stocks of copper metal ( $Cu^{+2}$ ). The molecular weight of the used copper nitrate salt is 241.60. For the other copper synthetic solutions and standards, copper standard solution manufactured by MERCK Germany was used.

#### *3.3.3.7 Cadmium Nitrate $Cd(NO_3)_2 \cdot 4H_2O$*

Oxford laboratory reagent grade was used in preparation large stock solutions of cadmium metal ( $Cd^{+2}$ ). The cadmium nitrate salt has molecular weight of 308.47 gm/mol. For the other cadmium synthetic solutions and standards, cadmium standard solution manufactured by MERCK Germany was used.

#### *3.3.3.8 Nitric Acid ( $HNO_3$ ) concentrated:*

Reagent grade manufactured by MERCK Germany was used.

#### *3.3.3.9 Sodium Hydroxide ( $NaOH$ ) pellets*

Reagent grade manufactured by GCC in UK with an assay of 99% was used.

#### *3.3.3.10 Sodium Nitrate ( $NaNO_3$ ):*

Reagent grade manufactured by GCC in UK with an assay of 99% was used.

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### 3.3.4 Raw Wastewater

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Raw wastewater samples were collected from wastewater treatment plant (WWTP), pumping station, and an industrial glass manufacturing facility. The target of examining different sources of wastewater was to examine the CKD effect on different constituents' concentrations and wastewater characteristics. All samples were delivered to the laboratory within 1 h and were refrigerated at 4°C for subsequent experiments. The wastewater samples were collected from the following locations:

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#### *3.3.4.1 Abu Rawash Wastewater Treatment Plant*

AbuRawash WWTP, located 15 km west of Cairo, has a daily average capacity of 800,000 m<sup>3</sup>. It treats domestic wastewater and consists of preliminary and primary treatment units only. Effluent wastewater is discharged to Barakat drain and eventually reaches the Nile River. Preliminary treatment consists of mechanical screens. Samples were taken after the screen at the inlet of the primary sedimentation tanks. To compare the efficiency of using CKD in treating wastewater with that of the current primary treatment at Abu Rawash, another set of samples were taken at the effluent of WWTP.

#### *3.3.4.2 New Cairo Wastewater Treatment Plant*

The WWTP of New Cairo is conceived to treat domestic wastewater with a daily average capacity of 250,000 m<sup>3</sup>. It is located in the eastern desert of Egypt 35 km away from Cairo. It treats domestic wastewater and consists of preliminary, primary, and secondary treatment (biological) units. Effluent wastewater is chlorinated by >0.5 mg/l prior using it for irrigating the landscapes in New Cairo. Raw wastewater enters mechanical screens, then to grit removal chambers before entering the primary sedimentation tanks. In secondary treatment, biodegradable organics and nutrients are removed from the sewage by biological treatment. Finally, the effluent is settled in clarifier tanks. The sludge is collected and treated by thickening and drying beds. Samples were taken at the inlet of the primary sedimentation tanks. To compare the efficiency of using CKD with that of the current secondary treatment at New Cairo, another set of samples were taken at the effluent of this WWTP after the secondary treatment process. Given the fact that the New Cairo WWTP was the only plant among the chosen sources that applies biological treatment, another set of experiments were run using hydrated lime stone. The results of the hydrated lime stone experiments were compared with the corresponding ones for CKD.

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#### *3.3.4.3 New Cairo City Center Pumping Station*

The city center wastewater pumping station is located in the fifth settlement, New Cairo. The station serves almost 300,000 capita. It pumps daily 40,000 m<sup>3</sup> of the collected wastewater from the neighborhood to New Cairo WWTP. The station passes the wastewater on mechanical screens as a preliminary process before pumping it. Hence, the samples were taken after the screens.

#### *3.3.4.4 Abu Rawash Industrial Zone*

Samples were collected from a glass manufacturing facility. The generated wastewater was highly contaminated with different heavy metal constituents. The generated wastewater is treated on site by industrial wastewater treatment unit before conveying it to the public sewers. Samples were taken directly before treatment and were used in running the pilot scale experiments. The samples were analyzed before being used in the pilot scale to investigate the concentrations of the heavy metals as well as the physiochemical and biological characteristics. After running the pilot scale experiments, the effluent's characteristics were identified and the treatment efficiency of the pilot scale treatment system was determined. Chapter five describes thoroughly the design of the pilot scale and shows the results of these experimental runs.

### **3.4 Equipment and Supplies**

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#### 3.4.1 Equipment

- **Atomic Absorption Spectrometer (A.A.S):** GBC flame spectrophotometer model SensaAA dual flame atomization system was used to determine any element in a sample. The device uses an analytical technique for the qualitative and quantitative determination of an element in a sample. In this method the sample, in the form of homogeneous liquid, is introduced into a flame where

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thermal and chemical reactions create “free” atoms capable of absorbing, emitting or fluorescing at characteristic wavelengths. Flame spectroscopy can be subdivided into the different processes occurring, to give us Flame Emissions Spectroscopy, Atomic Absorption Spectroscopy and Atomic Fluorescence Spectroscopy. The GBC flame spectrophotometer was manufactured by GBC scientific instruments in USA. It has very high performance in measuring heavy metals with high concentrations, and it has asymmetric modulation with 2:1 sample-to-reference ratio for noise reduction. All its reflective system is with quartz overcoating on mirrors and dust cover for optical system. Its monochromator is Ebert-Fastie designed with 333 mm focal length and 175 – 900 nm wavelength range. The Hyper – Pulse background corrector takes 200 (50 HZ) or 240 (60HZ) sample readings per second for correction of fast background peaks and interpolation between measurements. High intensity deuterium arc lamp provides 175-423 nm correction to 2.5 total absorbance. The Flame atomization system is Permixon design with solid polypropylene mixing chamber, integrated liquid trap. Furthermore, it is all-titanium burner construction. Nebulizer has platinum- iridium capillary and titanium Venturi. Quick change mounting to enable easy changeover to graphite furnace is allowed. Figure 7 shows the used atomic absorption spectrometer (A.A.S.).

- **Fourier Transform Infrared (F.T.I.R) spectrometer:** the FTIR spectrometer used is the Bruker vector 22 model. It is capable of acquiring data over the near-IR (12,000-4,000  $\text{cm}^{-1}$ ), mid – IR (4,000- 400  $\text{cm}^{-1}$ ), and far – IR (680-30  $\text{cm}^{-1}$ ) regions.



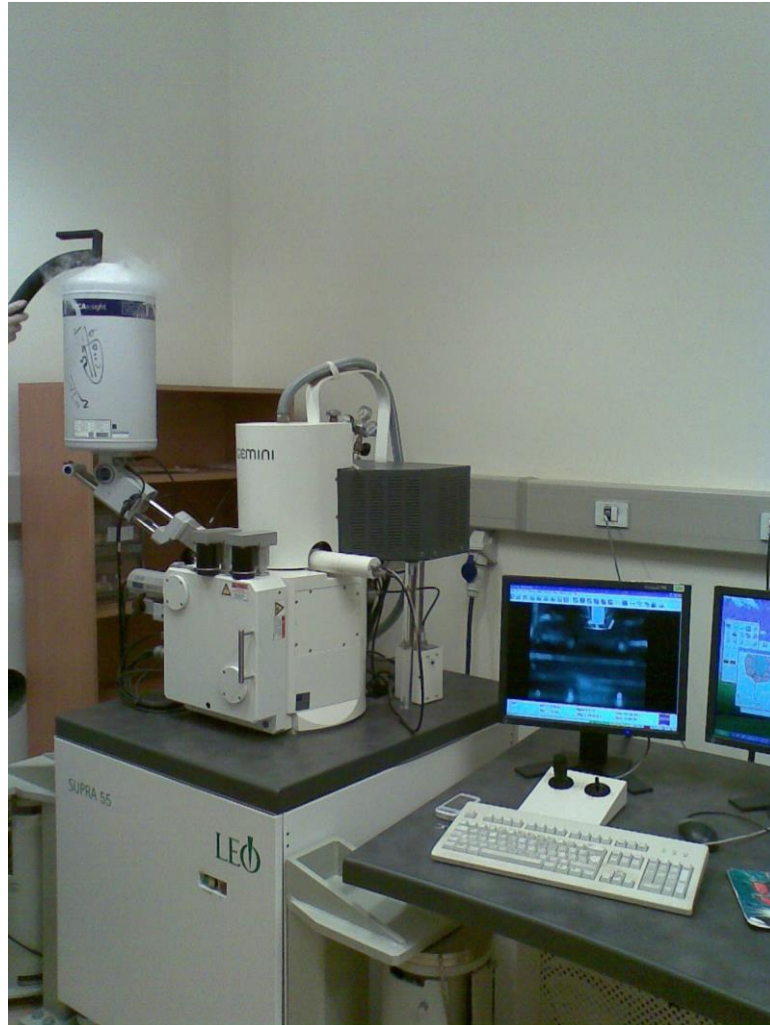


**Figure 7: SensAA Atomic Absorption Spectrometer (A.A.S)**

- **Scanning Electron Microscope (SEM) & Energy Dispersive X-ray (EDX) unit:**

A LEO SUPRA 55 Scanning Electron Microscope (SEM) manufactured by ZEISS Germany was used to obtain SEM images of both CKD and Hydrated Lime samples. It has an accelerating voltage of 30 kv, magnification 10 xs up to 400,000 x and resolution for W. (3.5 nm).

An INCA Oxford Energy Dispersive X-Ray (EDX) was conducted in order to detect the type of the attached crystals for each raw material that appeared in the Scanning Electron Microscope (SEM). The EDX also shows the elemental and chemical formations of the CKD and Hydrated Lime. Figure 8 shows the used SEM and EDX in the experiments.



**Figure 8: A LEO SUPRA 55 Scanning Electron Microscope (SEM) together with Energy Dispersive X-ray (EDX) unit**

- **Incubator:** temperature range is from 0 to 49.9°C and accuracy  $\pm 2^\circ\text{C}$
- **Autoclave:** sterilizing temperature is approximately 121° C under steam pressure 15 psig.
- **Orbital Shaker:** manufactured by Cole-Parmer Industrial Company in USA
- **JAR Tester:** manufactured by PHIPPS and BIRD in USA
- **Analytical Balance:** it has the capability to measure 0.1 mg up to 220 gm, and it was used for weighing solids, chemical salts, standards...etc.
- **Drying Oven:** thermostatic control type JEIO Tech manufactured in Korea, and it is capable to maintain temperature up to 300°C

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- **pH Meter:** pH electrode combined with integrate temperature sensor manufactured by SCHOTT Germany
  - **Deionize System:** This system was used to obtain high grade DDW. It contains of distiller unit, Barnstead FI-streem III glass still distiller, followed by Barnstead Nanopure UV unit. The DI system was manufactured by NANOpure USA.

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### 3.4.2 Glassware and Supplies

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All reusable lab ware were cleaned by washing with a detergent solution, rinsing with tap water, soaking with diluted HNO<sub>3</sub> (20% V/V), and then rinsing with reagent water and stored clean according to EPA method 209.9 (USEPA, 2001). The following shows the list of glassware and supplies that were used during all the experimental work:

- Volumetric flasks (Kimax brand) class A: 10 ml to 1 L capacities.
- Volumetric Jar (SELECTA brand): 1 L capacities
- Narrow mouth bottles, high density polyethelene (HDPE), Nalgene USA brand with 125 ml to 10 L capacities.
- 250 ml Erlenmeyer flasks.
- Disposable sterilized Petri dishes for bacteria culture: 47 mm<sup>2</sup>
- Disposable plastic graduated pipits: 1 ml to 10 ml
- Adjustable glass micropipettes with disposable polypropylene tips
- Polypropylene graduated cylinders: 25ml to 100 ml
- Micro filters
- Teflon reaction vessels for filtration Nalgene USA brand
- The column set up: 3- way valve, stainless steel column, high pressure liquid pump manufactured by Eldex Laboratory USA.

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- HACK COD glassware

### 3.5 Laboratory Experiments

#### 3.5.1 Physical and Chemical Characteristics of Cement Kiln Dust and Hydrated Lime Stone

Particle size, density and surface area of CKD and hydrated limestone influence their efficiency in treating wastewater. Surface properties such as surface area, and surface groups were measured using Le Chatelier flask according to standard methods (ASTM C188-95). Density, more usefully expressed as specific gravity, the latter being a dimensionless number was also measured according to standard methods (ASTM C188-95). The surface area was calculated based on the mercury displacement method according to the standard methods (ASTM C 204). An INCA Oxford Energy Dispersive Microscopy (EDM) was conducted in order to detect the type of the attached crystals for each material that appeared in the Scanning Electron Microscope (SEM). The EDM, also known with EDX, shows the elemental and chemical formations of the CKD and Hydrated Lime stone.

#### 3.5.2 Surface Titration

Sorbent samples were titrated potentiometrically in order to estimate surface charge characteristics. In this study, 0.1 g of dry sample was suspended in a Teflon reaction vessel containing 50 ml of DDW at room temperature to yield a solid concentration of 2 gm/L. The suspension was continuously stirred and purged by ultra-pure nitrogen gas prior to titration in order to remove CO<sub>2</sub> that would interfere with an acid-base titration. Standard HNO<sub>3</sub> (of assay 65%) with a molarity of 0.1 M and NaOH with a molarity of 0.1 M were added precisely to adjust the pH. The pH was measured by a pre-calibrated SCHOTT pH meter and probe (Figure 9). Na NO<sub>3</sub> was used as an ionic background in

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order to standardize the solution. The NaOH was incrementally added to the suspended solution to raise the pH, and the HNO<sub>3</sub> was incrementally added to lower the pH. The total volume of acid and base added was less than 5% of the sample volume (5 ml) to minimize the dilution effects. The pH was measured for increments of 0.1 ml for both acid and base. The experiment was done for ionic backgrounds of 0.1M, 0.01M, and 0.001M in order to examine the impact of background total dissolved solids concentration on surface charge of the cement kiln dust.

The experiment was conducted as follows:

1. 8.5 g NaNO<sub>3</sub> was added in 1L DDW to give 0.1M solution.
2. 2 g of NaOH was added in 500 ml DDW to give 0.1M solution.
3. 3.2 ml of HNO<sub>3</sub> (assay 65%) was added in 500 ml DDW to give 0.1 M solution.
4. 50 ml from the ionic background (NaNO<sub>3</sub> with 0.1 M) was taken and then 0.1 gm CKD was added. The solution was stirred and purged continuously by nitrogen gas while measuring the pH.
5. For the alkaline leg, NaOH of 0.1 M was used. 0.1 ml was added until reaching 5% of the total volume of the solution (5 ml). The pH was measured every 0.1 ml.
6. For the acid leg, HNO<sub>3</sub> of 0.1 M was used. 0.1 ml was added until reaching 5% of the total volume of the solution (5 ml). The pH was measured every 0.1 ml.

The experiment was repeated for ionic backgrounds 0.01 and 0.001 M by diluting the stock solution used in the first step to the desired molarities as follows:

- For 0.01 M: add 10 ml from the NaNO<sub>3</sub> stock solution (0.1 M) into 100 ml DDW.
- For 0.001 Mole: add 1 ml from the NaNO<sub>3</sub> stock solution (0.1 M) into 100 ml DDW.



**Figure 9: pH Meter**

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### 3.5.3 Batch Equilibrium Experiments

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The most appropriate method for assessing adsorbent capacity and the equilibrium relationship between adsorbent and adsorbate is the derivation of a whole sorption isotherm. The sorption isotherm is the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium.

To investigate the optimum environmental factors that mainly affect the adsorption equilibrium; initial pH, contact time, initial CKD dose, and initial metal concentration were studied in this group of experiments. After then, the effect of hydrated lime on metal recovery compared to CKD at the same optimum conditions was also studied.

The purpose of this set of experiments was:

- 1) To determine the precipitation pH range of the synthetic solutions of lead, copper and cadmium
- 2) To determine the most suitable pH for metal adsorption.
- 3) To test several CKD dosages and their effect on metal uptake from solution.

- 
- 4) To determine the optimum contact time for metal recovery
  - 5) To determine the adsorption capacity of CKD at different heavy metals concentrations.
  - 6) Compare the effect of hydrated lime stone on heavy metal uptake capacity to CKD at the same optimum conditions.

This set of experiments was carried out using 125 ml high density polyethylene, HDPE, manufactured in USA by Nalgene Company. The experiments done are presented in the following sections.

#### *3.5.3.1 Identifying pH Profile for Metal Hydroxide Precipitation*

The experiments were performed for the three target metals, namely lead, copper and cadmium, using a synthetic metal solution of 30 mg/l. This solution was poured into 10 bottles (125 ml narrow mouth HDPE), each one with 50 ml sample. The pH of the solutions in these 10 bottles was adjusted to a value that varies from 3 to 11, as follows: 3,4,5,5.5,6,6.5,7,8,9 and 11 ( $\pm 0.05$ ); respectively. The pH was adjusted using either 0.1 M HNO<sub>3</sub> or 0.1M NaOH solutions. Then, the solutions were centrifuged to separate the precipitated metal and then acidified to pH<2. The concentration of metal in the solutions was measured using the A.A.S., as described in Section 3.4“Equipment and Supplies”. The experiments and the analyses were replicated to confirm the results.

#### *3.5.3.2 Identifying the Optimum pH for Heavy Metals Removal (Effect of pH)*

Table 2 summarizes the list of experiments carried out to investigate the effect of pH on the adsorption equilibrium.

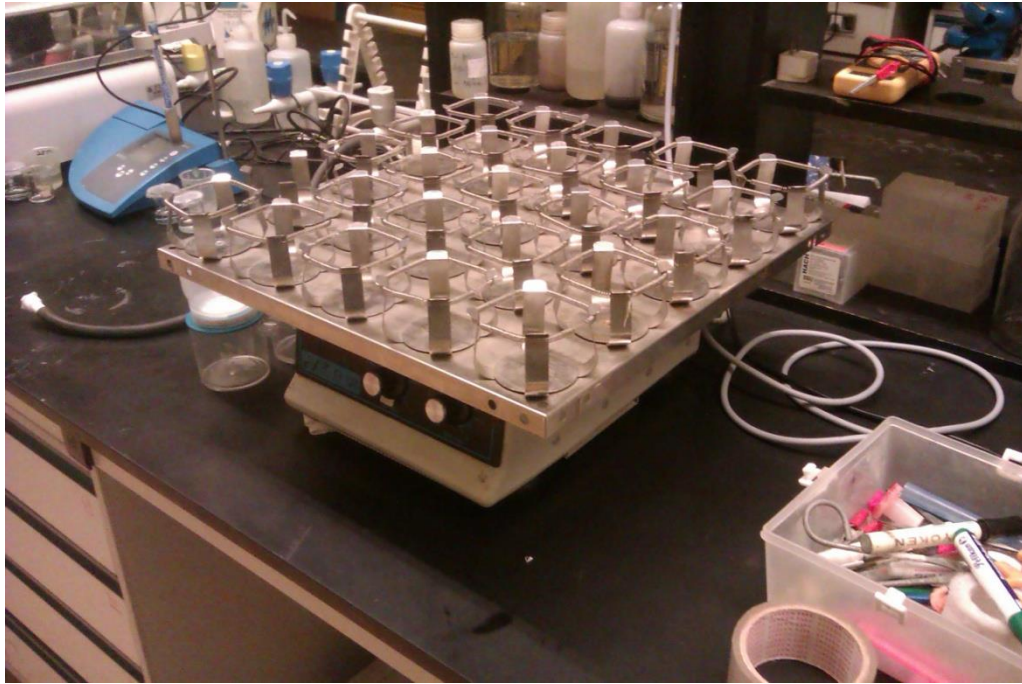
**Table 2: Identifying the Optimum pH for Heavy Metals Removal**

Experiment No.	CKD Dose (g/l)	Heavy Metal	Heavy Metal Concentration (mg/l)	pH Range	Reaction Time (days)	No. of Samples
1	2.0	Pb	30	3-11	1	9 + blank
2	2.0	Cu	30	3-11	1	9 + blank
3	2.0	Cd	30	3-11	1	9 + blank

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To investigate the optimum pH value, the batch equilibrium experiment was performed using a synthetic metal solution of 30 mg/l. This solution was poured into 10 bottles (125 ml narrow mouth HDPE), each one with 50 ml sample. The experiment was performed at pH values from 3 to 11 and compared with the results of the previous experiment. The pH of solutions in these bottles was adjusted into the desired experimental values from 3 to 11 as follows: 3, 4, 5, 6, 7, 8, 9, 10, and 11 ( $\pm 0.05$ ) using either 0.1 M HNO<sub>3</sub> or 0.1 M NaOH solutions. After addition of 0.1 g of CKD into 9 bottles while the 10th was left as reagent blank (control sample), bottles were agitated at 175 RPM on the orbital shaker (Figure 10) at room temperature ( $22 \pm 1$ ) for a time deemed appropriate for the equilibrium to take place, approximately 1 day. The pH value was readjusted periodically at (15, 30, 45, 60, 90) minutes. After the equilibrium had been established (pH tends to be stable), the experiment was stopped. Then, the solutions were filtered to separate the CKD from the solution using the laboratory built-in vacuum filtration setup after rinsing the filter papers with DDW. The filter papers used in the filter cups were 0.7  $\mu\text{m}$  membrane filters. The filter cups were manufactured in U.S.A by Nalgene. All samples including the blank ones were acidified to reach  $\text{pH} < 2.0$  as required by the analytical technique. The concentration of metals in the solutions was measured by using the AAS. The experiments were replicated to confirm the results. The much better adsorption was observed at pH varies from 5.5 to 6.0 for the three metals. Therefore, the pH value is controlled at this value for all adsorption experiments in the research.





**Figure 10: Orbital Shaker**

*3.5.3.3 Identifying the Optimum Contact Time Effect*

Table 3 shows the experiments performed in order to study the effect of contact time on the adsorption equilibrium.

**Table 3: Identifying the Optimum Contact Time Effect**

Experiment No.	CKD Dose (g/l)	Heavy Metal	Heavy Metal Concentration (mg/l)	pH	Reaction Time	No. of Samples
1	2.0	Pb	30	Optimum pH for Pb removal from the previous set of experiments	0	1 + blank
2					5 min.	1 + blank
3					20 min.	1 + blank
4					30 min.	1 + blank
5					45 min.	1 + blank
6					1 hr	1 + blank
7					1.5 hrs	1 + blank
8					2 hrs	1 + blank
9					4 hrs	1 +

						blank
10					8 hrs	1 + blank
11					24 hrs	1 + blank
12	2.0	Cu	30	Optimum pH for Cu removal from the previous set of experiments	0	1 + blank
13					5 min.	1 + blank
14					20 min.	1 + blank
15					30 min.	1 + blank
16					45 min.	1 + blank
17					1 hr	1 + blank
18					1.5 hrs	1 + blank
19					2 hrs	1 + blank
20					4 hrs	1 + blank
21					8 hrs	1 + blank
22					24 hrs	1 + blank
23	2.0	Cd	30	Optimum pH for Cd removal from the previous set of experiments	0	1 + blank
24					5 min.	1 + blank
25					20 min.	1 + blank
26					30 min.	1 + blank
27					45 min.	1 + blank
28					1 hr	1 + blank
29					1.5 hrs	1 + blank
30					2 hrs	1 + blank
31					4 hrs	1 + blank
32					8 hrs	1 + blank
33					24 hrs	1 + blank

To determine the contact time required for equilibrium sorption, the experiments were designed to measure the metal concentrations at different times (0, 5, 20, 30, 45, 60, 90, 120, 240, 480, and 1440) minutes.

A metal solution, namely lead, copper and cadmium, of 30 mg/l was poured into 12 bottles (125 ml narrow mouth HDPE), each one with 50 ml sample. Then, pH was adjusted at 5.5( $\pm$ 0.05) by using either 0.1 M HNO<sub>3</sub> or 0.1M Na OH. After addition of 0.1g of dried CKD into 11 bottles while the 12th one was leaved as reagent blanks (control sample), bottles were agitated at 175 RPM on the orbital shaker at room temperature (22  $\pm$  1). At each time one of the bottles was taken off, rapidly the solution was filtered by the vacuum pump to separate it from the sorbent, and then acidified to pH  $\leq$  2. The concentration of metal in the solutions was measured by using the AAS. The experiments were replicated to confirm the results.

#### 3.5.3.4 *Identifying the optimum CKD dose*

The effect of CKD concentrations was studied in order to determine the optimum CKD dose and its effect on the batch equilibrium experiment. Table 4 shows the list of experiments performed in order to investigate the optimum CKD dose.

**Table 4: Identifying the Optimum CKD Dose**

Experiment No.	CKD Dose (g/l)	Heavy Metal	Heavy Metal Concentration (mg/l)	pH Range	Reaction Time (days)	No. of Samples
1	0.15	Pb	30	Optimum pH for Lead removal	Optimum Reaction Time for Lead removal	1 + blank
2	0.30					1 + blank
3	0.50					1 + blank
4	0.75					1 + blank
5	1.0					1 + blank
6	1.5					1 + blank

						blank
7	2.0					1 + blank
8	0.15	Cu	30	Optimum pH for Copper removal	Optimum Reaction Time for Copper removal	1 + blank
9	0.30					1 + blank
10	0.50					1 + blank
11	0.75					1 + blank
12	1.0					1 + blank
13	1.5					1 + blank
14	2.0					1 + blank
15	0.15					Cd
16	0.30	1 + blank				
17	0.50	1 + blank				
18	0.75	1 + blank				
19	1.0	1 + blank				
20	1.5	1 + blank				
21	2.0	1 + blank				

The sorption concentration is an important parameter, which affects sorption efficiency and capacity. So, the experiment was carried out with the purpose of observing the effect of this parameter on the rate of metal adsorption. In the experiment, all the initial conditions remain constant (30 mg/l of metal concentration in 50 ml sample, pH was adjusted at 5.5, and 240 minutes for equilibrium); the amounts of adsorbent added to 50ml reactors is the only variable factor, which are 0.0075, 0.015, 0.025, 0.0375, 0.05, 0.075, 0.1gm respectively. These amounts are equivalent to the following concentrations respectively (0.15, 0.3, 0.50, 0.75, 1.0, 1.5, and 2.0 g/l). Then, bottles were agitated at 175

RPM on the orbital shaker at room temperature ( $22 \pm 1$ ), also the pH was readjusted each 15 minutes. After the equilibrium had been achieved, the experiment was stopped. Finally, the solutions were filtered by the vacuum pump to separate it from the sorbent, and then acidified to  $\text{pH} \leq 2$ . The concentration of metal in the solutions was measured by using the AAS. The experiments were replicated to confirm the results.

### 3.5.3.5 *Effect of Initial Metal Concentration*

Table 5 shows the experiments carried out to investigate the CKD impact on heavy metals removal with different concentrations.

**Table 5: Identifying the Effect of Initial Metal Concentration**

Experiment No.	CKD Dose (g/l)	Heavy Metal	Heavy Metal Concentration (mg/l)	pH Range	Reaction Time (days)	No. of Samples
1	Optimum dose for lead removal from previous set of experiments	Pb	10	Optimum pH for Lead removal	Optimum Reaction Time for Lead removal	1 + blank
2			30			1 + blank
3			50			1 + blank
4			70			1 + blank
5			100			1 + blank
6			150			1 + blank
7			200			1 + blank
8	Optimum dose for Copper removal from previous set of experiments	Cu	10	Optimum pH for Copper removal	Optimum Reaction Time for Copper removal	1 + blank
9			30			1 + blank
10			50			1 + blank
11			70			1 + blank
12			100			1 + blank
13			150			1 + blank
14			200			1 + blank

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15	Optimum dose for Cadmium removal from previous set of experiments	Cd	10	Optimum pH for Cadmium removal	Optimum Reaction Time for Cadmium removal	1 + blank
16			30			1 + blank
17			50			1 + blank
18			70			1 + blank
19			100			1 + blank
20			150			1 + blank
21			200			1 + blank

The concentration of both the metal ions and the adsorbent is a significant factor to be considered for effective adsorption. It determines the sorbent/sorbate equilibrium of the system. The rate of adsorption is a function of the initial concentration of ions (Ahalya, 2005). So, the experiment was carried out with the purpose of observing the effect of this parameter on the rate of metal adsorption.

In the experiment, all the initial conditions remain constant (0.1 g of adsorbent in 50 ml sample, pH was adjusted at 5.5, and 90 minutes for equilibrium); the metal concentration in each bottle is the only variable factor, which are 10, 30, 50, 70, 100, 150, 200 mg/l respectively. The same metal concentration was repeated for lead, copper, and cadmium. Then, bottles were agitated at 175 RPM on the orbital shaker at room temperature ( $22 \pm 1$ ), also the pH was readjusted each 15 minutes. After the equilibrium had been achieved, the experiment was stopped. Finally, the solutions were filtered by the vacuum pump to separate it from the sorbent, and then acidified to  $\text{pH} \leq 2$ . The concentration of metal in the solutions was measured by using the AAS. The experiments were replicated to confirm the results.

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### 3.5.3.6 *Effect of Hydrated Lime on Metal Recovery Compared to CKD at Optimum Conditions*

Based on the optimum conditions for CKD obtained from the previous set of batch equilibrium experiments, hydrated lime was also tested. These conditions are: 0.1g hydrated lime in 50 ml synthetic metal solution with initial concentration of 30 mg/l and pH of 5.5 ( $\pm 0.5$ ). The samples were agitated for 4 hours at an ambient temperature 22 ( $\pm 1$  °C). The objective of this set of experiments is to test the effect of hydrated lime in removal of heavy metals and to compare that to CKD results. The following table shows the list of experiments conducted on hydrated lime stone.

**Table 6: The Hydrated Lime Batch Equilibrium Experiments**

Experiment No.	Lime Dose (g/l)	Heavy Metal	Heavy Metal Concentration (mg/l)	pH Range	Reaction Time	No. of Samples
1	2.0	Pb	30	5.5	4 hrs	1 + blank
4	2.0	Cu	30	5.5	4 hrs	1 + blank
7	2.0	Cd	30	5.5	4 hrs	1 + blank

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### 3.5.4 Column Experiments

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The purpose of this set of experiments was:

- 1- To observe the adsorption kinetics of the solutes,
- 2- To determine the adsorption capacity of the CKD, for the target metals, Pb, Cu, and Cd

This set of experiments was conducted using stainless steel columns of internal diameter 7 mm and 80 mm length. The solutions were pumped to the column by a positive displacement pump, reciprocating type (manufactured in U.S.A by Eldex), that delivers the solution from a polypropylene container manufactured by Nalgene USA (with a tight cover) to the bottom of the column. At the bottom of the column there is a three-way valve that directs the influent either to the column or to waste. The setup of the experiment is shown in Figure 11. The experiments done are presented in Table 7.

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**Table 7: Column Experiments**

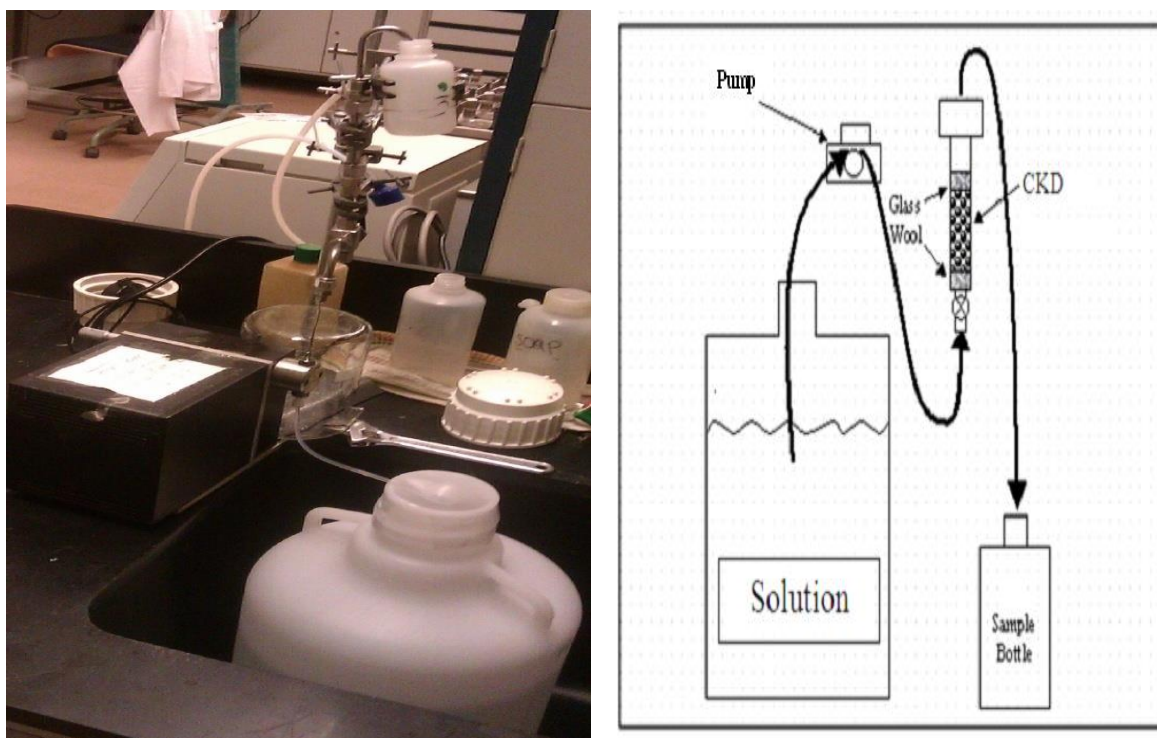
Solute	Column Diameter (mm)	CKD bed depth (mm)	Concentration (mg/l)	Influent flow rate ml/min	pH	Run Time (Hrs)
Pb	7	30	30	6	5.5	24
Cu	7	30	30	6	5.5	24
Cd	7	30	30	6	5.5	24

The experiment was conducted as follows:

- 1- 1000 ml of the solution was prepared in a volumetric flask by diluting the stock solution to the desired concentration. The dilution step utilizes 10 L flask in order to fill the polypropylene container.
- 2- The ionic background of the solution was adjusted to 0.01M as  $\text{NaNO}_3$ .
- 3- The pH of the prepared solution was adjusted to the specified pH, by using  $\text{HNO}_3$  and  $\text{NaOH}$  solution.
- 4- The column was packed by adding 2.5 cm glass beads followed by 3 cm CKD and finally 2.5 cm glass beads. For uniform packing, a glass rod was used for uniformly tapping and tamping the column.
- 5- Distilled water was passed through column for 1 hr to cleanse any CKD fines from the system.
- 6- The three way valve was switched to waste and plugged in the metal solution for 10 minutes.
- 7- The three way valve was switched to the column and then the starting time zero started after 30 seconds. This accounts for the travel time of the solution through the glass beads to the bed.



- 
- 8- The influent and effluent samples were collected at the specified times in small test tubes.
  - 9- The pH of the samples was measured immediately after collecting them.
  - 10- The effluent samples were filtered to make sure that there is not any passed sorbent to the solution.
  - 11- The samples were then acidified to reach  $\text{pH} < 2.0$  for analysis purpose.
  - 12- Finally, the samples were analyzed using the atomic absorption spectrometer.



**Figure 11: The Column Experiment Setup**

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### 3.5.5 Fourier Transform Infrared (FTIR)

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Fourier Transform Infrared (FTIR) analysis is a powerful tool for studying the mechanism of adsorption (Volesky, 2003). It is an analytical technique used to identify organic and inorganic materials by measuring the absorption of various infrared light wavelengths by material of interest. These infrared absorption bands identify specific molecular components and structures (functional groups involved in

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the adsorption). Absorption bands in the range of 4000-1500 wave numbers are typically due to the functional groups (e.g. OH, C=O, N-H, CH<sub>3</sub>, etc). The range between 1500-400 wave numbers is referred to as fingerprint region (Mee, 2014).

Samples were analyzed by FTIR spectrometer (model Bruker vector 22) specified in section 4: Equipment and Supplies. The translucent disks of the CKD samples were obtained by milling 5 mg of each sample with 400 mg potassium bromide to form fine powder. Then, this powder is compressed into a thin pellet and analyzed in mid-IR region (4,000-400 cm<sup>-1</sup>).

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### 3.5.6 Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX)

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It has previously been proposed that metal accumulation on the surface of some sorbents is a result of a series of complex reactions that happen between metal and the sorbent surface walls (Smith, 2000). Thus, the role of the active adsorptive sites and the shape of the cell wall of CKD were examined by SEM and EDX.

The EDX analysis system works as an integrated feature of a scanning electron microscope, and cannot operate on its own without the later. During EDX analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms own electrons, knocking some of them in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher – energy electron from an outer shell. To be able to do so, however, the transferring outer electron must give up some of its energy by emitting an X- ray. The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. The atom of every element releases X-ray with unique amounts of energy during the transferring process. Thus, by measuring the amounts energy

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present in the X-rays being released, the identity of the atom from which the X-ray was emitted can be established. Few particles of native and metal exposed sorbents were dried and coated with carbon for scanning and analyzing by SEM and EDX unit, which specified in section 4 of this chapter.

Electron micrographs with different magnifications were taken from SEM to make a comparison between the cell wall appearance before and after metal uptake.

As well as EDX spectra of the sorbent before and after the adsorption were taken, to elucidate the dominant mechanism.

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### 3.5.7 Laboratory Analysis

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#### 3.5.7.1 *pH Measurements*

The pH value of samples was measured and adjusted using the pH meter (model SCHOTT pH meter). The pH meter was calibrated each time with buffers over anticipated range (pH 4 and 7 buffers). Its accuracy equals to  $\pm 0.05$  pH units.

#### 3.5.7.2 *Heavy Metals Analyses*

All metals, which were studied in this research, were analyzed by the atomic absorption spectrometer (AAS). After adjusting the working conditions of the (AAS) and allowing the hollow cathode lamp to warm up for a period of about 20 minutes, the instrument was calibrated in the beginning of each batch of analysis using the calibration blank and calibration standards.

The percent removal of heavy metal ions was determined using the following equation:

$$\%R = \left(1 - \frac{c}{c_0}\right) 100 \quad [Equation 1]$$

Where:

**% R** is the percent removal of heavy metal ions

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$C_o$  is the initial heavy metal concentration (mg/l)

$C$  is the final heavy metal concentration (mg/l)

The adsorbed phase concentration was calculated using the following equation:

$$q = (C_o - C)V/W[\text{Equation 2}]$$

Where:

$q$  is the adsorbed quantity of heavy metal per gram of sorbent (CKD/ hydrated lime stone) (mg/g)

$C_o$  is the initial heavy metal concentration (mg/l)

$C$  is the final heavy metal concentration (mg/l)

$V$  is the volume of the solution, L

$W$  is the weight of dry sorbent (CKD/ hydrated lime stone), gm

### 3.5.7.3 Physiochemical and Biological Constituents

#### 3.5.7.3.1 Biochemical Oxygen Demand (BOD)

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Raw and treated wastewater from either bench scale or pilot scale experiments were analyzed for their BOD following the standard method published jointly by the APHA, AWWA and WEF (STM No. 5210).

#### 3.5.7.3.2 Chemical Oxygen Demand (COD)

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The COD was measured by HACH DR/2000 device following HACH methods (HACH 8000-COD).

#### 3.5.7.3.3 Total Suspended Solids (TSS)

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The total suspended solids (TSS) were determined as the standard method procedures by filtration and drying at 105°C (STM No.2540).

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#### 3.5.7.3.4 Microbiological (E-Coli)

To investigate the fate of pathogens after treating the raw wastewater, raw and treated samples were investigated for the presence of E-coli. E-coli were counted using the MSC coliform micro-plates technique (Standard Method: STM 9000).

#### 3.5.7.4 *Sorption Mechanism Investigation*

Knowledge of the sorption mechanism for heavy metals removal using CKD is not a straight forward process since we are not dealing with simple clearly defined chemical compounds. Sorbents comprise different types of cells with a highly complex structure which can display several binding sites. Moreover, even one binding site can participate in different binding mechanisms. Consequently, several mechanisms often act in combination (Volesky, 2003). So, one of the research objectives- as noted in Chapter One - is to investigate the dominant mechanism in the sorption of the target metals (Pb, Cu and Cd) by CKD in principal.

To achieve this aim, the sorbent was subjected to various chemical treatments and then the native and the modified sorbent were analyzed by F.T.I.R, to determine the functional groups responsible for metal uptake. As well as, Energy Dispersive X-ray (EDX) and Scanning Electron Microscope (SEM) analyzed the sorbent (CKD) before and after the adsorption process.

#### 3.5.7.5 *Quality Control and Assurance*

Quality assurance is an essential and integral part of research study. The purpose of any QA plan is to insure that valid and reliable procedures are used in collecting and processing research data. Quality control represents the specific procedures that are performed to ensure that the quality of the process remains within the acceptable limits blank, multipoint, while quality assurance represents the specific mechanisms employed to evaluate the effectiveness of quality control program to satisfy the laboratory data objectives (Standard Methods: APHA, AWWA, and WEF, 1992).

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Quality Control and Quality assurance (QC / QA) procedures were applied to the analyses in the terms of U.S.EPA method 200.9 (USEPA, 2001):

- All the sorption experiments were conducted twice and mean values of the analyses were used.
- Laboratory control standard (calibration verification standard) was used to periodically verify the instrument calibration during analysis.
- Calibration blank- An aliquot of reagent water acidified with the same acid matrix as the calibration standard. The calibration blank is a zero standard and is used to auto zero the A.A.S instrument.
- Method blank (reagent blank) – An aliquot of reagent solution that is treated exactly as a sample including exposure to all glassware, equipment, and reagent. It is used to determine if any interference are present in the laboratory environment, reagent, or apparatus.
- Calibration line was represented by 3-4 points of calibration standards. The calibration was acceptable if the correlation coefficient ( $R^2$ ) is greater than 0.995.

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#### 3.5.8 Sorption Isotherm Model

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The constant equilibrium relationship between the quantity of adsorbate per unit of adsorbent ( $Q_{eq}$ ), and the equilibrium concentration of adsorbate in the solution ( $C_{eq}$ ) is called the adsorption isotherm.

Adsorption modeling could enable us to evaluate to what extent an adsorption system can be improved as well as estimate the necessary operating conditions for the system in order to be more efficient.

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The most extensively used models are the simple isotherms of *Langmuir*, which suggests adsorption in monolayer type, and *Freundlich*, which suggests adsorption in multilayer type.

#### 3.5.8.1 *Langmuir Isotherm*

The Langmuir isotherm could be explained by the following equation:

$$\frac{1}{q_e} = \frac{1}{b} + \frac{1}{abC_e} \text{ [Equation 3]}$$

Where:

**q<sub>e</sub>** mass of heavy metal adsorbed per gram of adsorbent

**C<sub>e</sub>** equilibrium heavy metal concentration in liquid phase, mg of heavy metal/liter

**a** Langmuir constant, liter/mg of heavy metal

**b** Monolayer coverage, mg of heavy metal/gm of adsorbent

#### 3.5.8.2 *Freundlich Isotherm*

The Freundlich isotherm could be explained by the following equation:

$$\text{Log}q_e = \text{Log}K_f + \frac{1}{n}\text{Log}C_e \text{ [Equation 4]}$$

Where:

**q<sub>e</sub>** mass of heavy metal adsorbed per gram of adsorbent

**C<sub>e</sub>** equilibrium heavy metal concentration in liquid phase, mg of heavy metal/liter

**k<sub>f</sub>** and **n** are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of adsorption

#### 3.5.8.3 *Computational Modeling*

A computer program for determination of chemical equilibrium constants from experimental data, namely FITEQL, was used. FITEQL 4.0 is a non-linear least-squares optimization program (Herbelin and Westall, 1999) that is available from John C. Westall of the Oregon State University.

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First, a triple-layer surface complexation model (TL-SCM) was used for the determination of sorbent surface equilibrium constants from potentiometric titration data. These values were then used to estimate adsorption equilibrium constants from pH adsorption edge data for the three target heavy metals; lead, copper, and cadmium.



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## CHAPTER 4: RESULTS AND DISCUSSION

### 4.1 Design Experiment

The selected design of batch equilibrium experiments was checked using the Design-Expert® software package in order to know whether the design of the experiments is adequate or not. The analysis is based on a 5% significance level ( $\alpha=0.05$ ). This level is the preset level utilized by the model and adopted in many experimental design applications (Design-Expert, 2014). This statistical tool could give us an indicator whether the experiments were well designed or need further improvements. The Design Expert is a statistical analysis tool where a full factorial design takes into account all possible combinations besides each discrete possible level. It allows analysis of the effect of each factor as well as the effect of interactions among those factors (Aghahosseini, 2013).

In order to run the program, we assumed that we have four factors that might affect the heavy metal adsorption process which are: 1) pH; 2) Agitation Time; 3) Sorbent Dose; 4) Heavy Metal Initial Concentration. Design Expert® was used in order to cross check if the chosen adsorption factors are adequate. All the obtained experimental results were used in this statistical tool in order to know how far the adsorption optimization experiments were adequate. The results of the Design Expert show that the four factors are significant model terms. The “predicted R-Squared” of 0.9934 is in reasonable agreement with the “Adjusted R-Squared” of 0.9952. Therefore, the model is adequate. Figure 12 shows also the normal plot of residuals that indicates that the experiments were well designed and no further improvement is required. It is also shown that residuals

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clearly follow a linear pattern which indicates a completely linear correlation between adsorption and operating parameters.

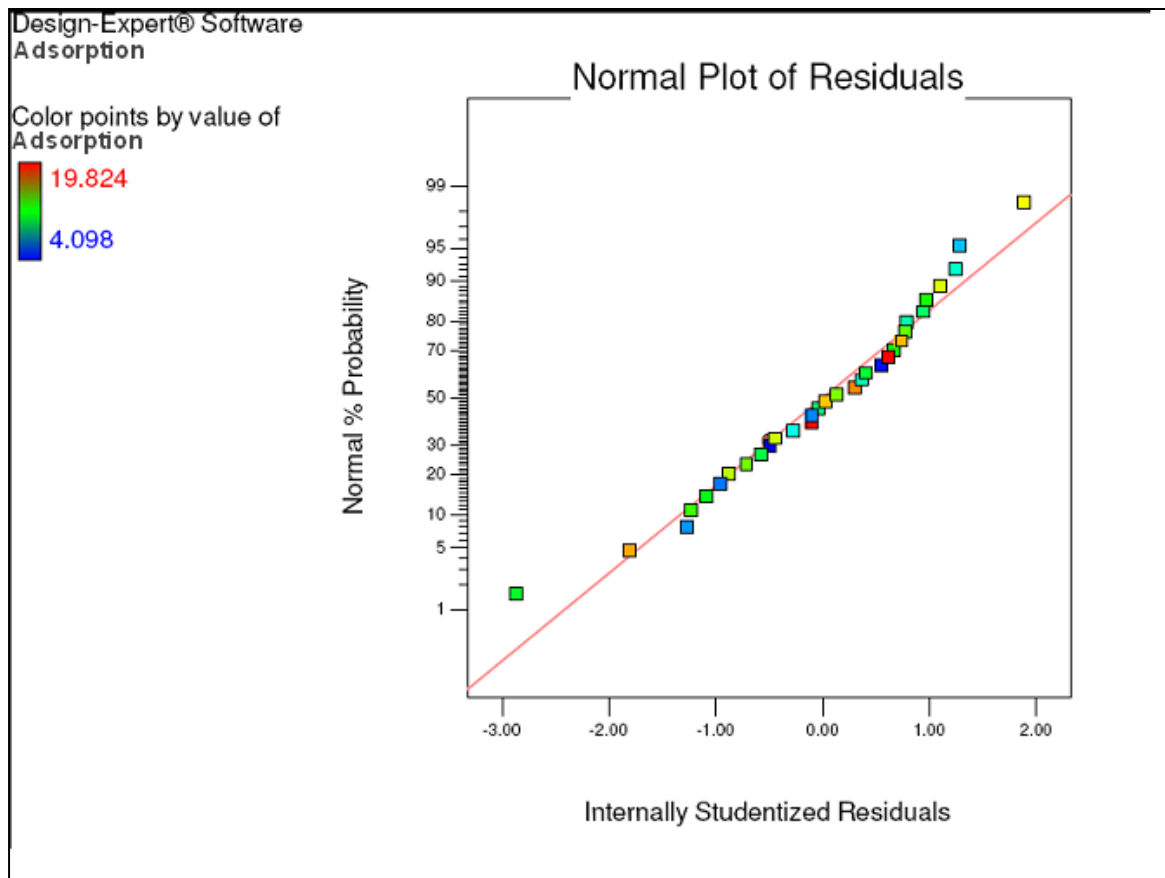


Figure 12: Normal Plot of Residuals for Adsorption Experimental Analysis (Design Expert®)

## 4.2 Cement Kiln Dust and Hydrated Lime Stone Physical and Chemical Characteristics

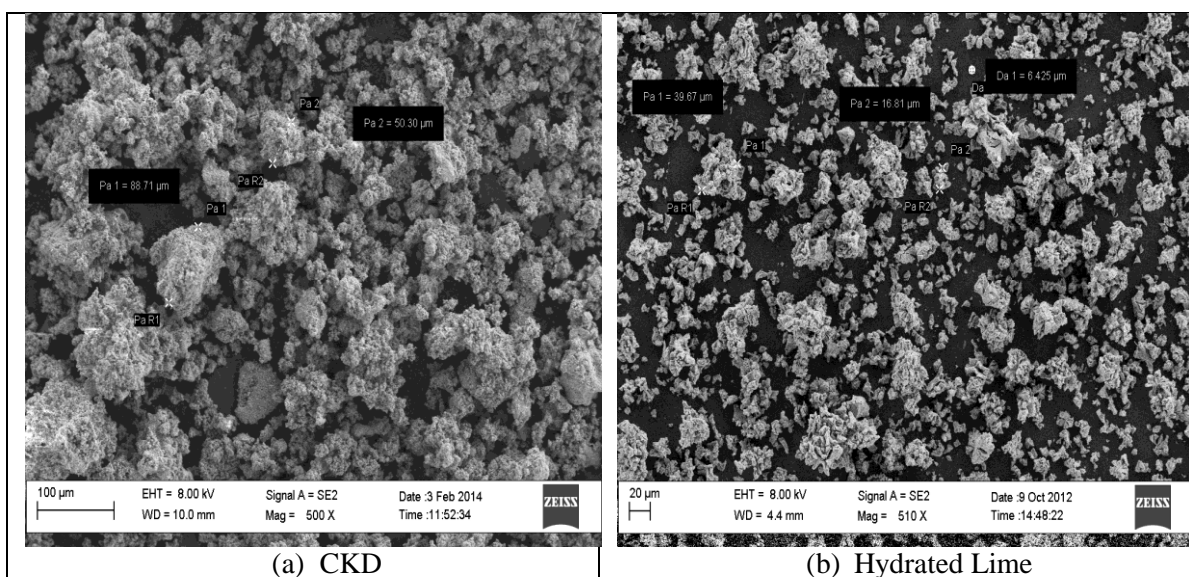
### 4.2.1 Physical Analysis

The physical properties of CKD depend on the cement process type and manufacturing. Dry kilns generate larger CKD than wet processes (Peethamparan 2006). CKD usually has a diameter below  $10\mu\text{m}$  which is within the range of respiration for humans. However, it might vary between 10 to  $50\mu\text{m}$  based on the storage process (Gdoutos, 2003). Physical properties of both CKD and hydrated lime were measured as per the methodology procedures stated in the previous chapter. Particle size, bulk density,

specific gravity and surface area values for each of CKD and hydrated lime have been measured and are shown in Table 1. Hydrated lime samples were found to be notably finer than the CKD. In addition to measuring the particle size of both CKD and Hydrated Lime, the scanning electron microscope (SEM) was hired to qualitatively show the relative particle sizes of both materials. Figure 13 shows the particle size of both CKD and Hydrated Lime by using SEM. Collectively, the results demonstrate that the CKD particles have a higher specific surface area than Hydrated Lime. Due to the fineness of the CKD particles, a larger surface area is available for the reaction of CaO with water to produce Ca(OH)<sub>2</sub>. This indicates that the oxide particles present in CKD may demonstrate greater reactivity compared to hydrated lime due to the increase in surface area. Increased surface area also allows more space for metal adsorption, since CKD has been demonstrated to act as both a neutralizing agent and sorbent (Mackie et al. 2010).

**Table 8: Physical Properties of both CKD and Hydrated Lime Stone**

Parameter	CKD	Hydrated Lime
Particle Size (microns)	~ 70	40
Bulk Density (gm/cm <sup>3</sup> )	~ 0.7	0.4~0.64 *
Specific Gravity	2.5	-
Surface Area (cm <sup>2</sup> /gm)	~ 4000	≥ 2200**
* National Lime Association – Lime Fact Sheet		
**Egyptian Code		



**Figure 13: Particle Size of CKD and Hydrated Lime by Using SEM**

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#### 4.2.2 Chemical and Elemental Analysis

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As a direct result of the nature of the raw materials used in the cement manufacturing process, CKD consists primarily of finely ground particles of calcium carbonate, silicon dioxide, iron oxide, calcium oxide, sodium and potassium chlorides, sulfates, metal oxides, and other salts. In 2007, a preliminary analysis of chemical and physical properties of lime was conducted by the National Lime Association (NLA) in USA following the standards of the American Society for Testing and Materials (ASTM). According to the NLA specifications, lime is classified into three different types. First, high calcium hydrated lime which is generated from high calcium quicklime and contains approximately 73% CaO. Second, dolomitic hydrated lime produced from dolomitic quicklime under normal atmospheric pressure and composes of approximately 47% CaO, 33% MgO. Third, dolomitic hydrated lime produced from dolomitic quicklime under pressure and contains 40% CaO and 30% MgO. In general, both CKD and hydrated lime are strongly alkaline possessing a pH greater than 11.0.

The Energy dispersive X-ray (EDX) analyses performed on collected samples of both CKD and hydrated lime to determine major elemental analysis are presented in Table 9 and Table 10 respectively. Available Ca is an indicator of the CaO content that is readily available for reactions and was of interest in this study. It can be noted that Ca content in CKD was 55.30% by weight compared to 85.02% by weight for hydrated lime. These results match those of Mackie, 2010 who proved that CKD can contain up to 61.3% by weight of total CaO while a total of 90% for quicklime. Moreover, it is obvious that both elements are rich in CaO content which is known to have positive effect on treating wastewater (Abo- El Hassan 2008; Ayoub 2011).

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**Table 9: Chemical and Elemental Analysis for CKD using EDM**

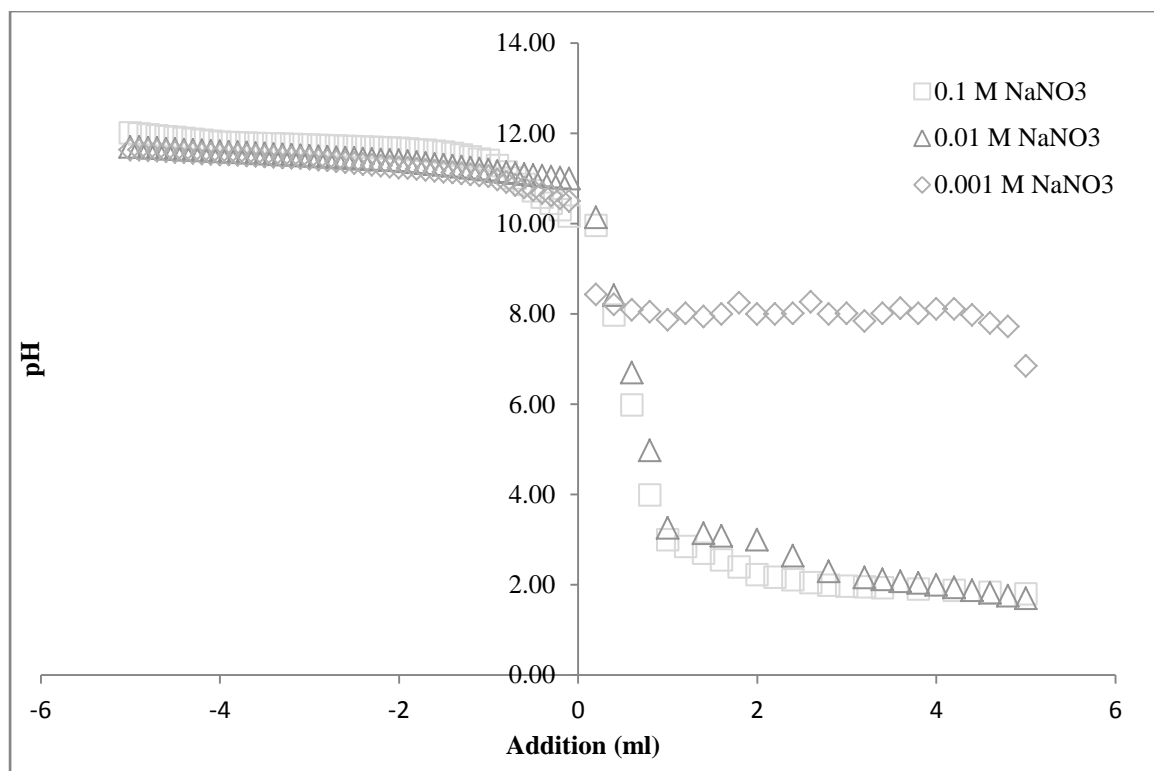
Element	Weight%	Atomic%
Na K	9.91	15.38
Al K	1.02	1.35
Si K	3.92	4.98
S K	2.63	2.92
Cl K	18.74	18.86
K K	6.88	6.28
Ca K	55.30	49.21
Fe K	1.60	1.02
Totals	100.00	

**Table 10: Chemical and Elemental Analysis for Hydrated Lime using EDM**

Element	Weight%	Atomic%
Mg K	0.66	1.17
Al K	0.41	0.67
Si K	0.88	1.36
Ca K	85.02	92.20
Sb L	9.18	3.28
IL	3.85	1.32
Totals	100.00	

### 4.3 Surface Titration

Sorbent samples were titrated potentiometrically at room temperature in order to observe the acid-base nature of the CKD surface. The experiment was conducted for different ionic backgrounds of 0.1M, 0.01M, and 0.001M. The surface titration results show that the CKD is an alkaline material due to the fact that the DDW pH increased by about 4 pH points regardless the ionic background. Moreover, it was obvious that the CKD has a consistent behavior during titrating it with NaOH. On the other hand, the CKD behavior did not show regular behavior when titrated with HNO<sub>3</sub>. This means that the CKD has a significant resistance to pH change with acid addition. This might be due to the affinity of CKD to absorb H<sup>+</sup> ions by its naturally alkaline surface when HNO<sub>3</sub> is added. Figure 14 shows the surface titration data of the CKD at different ionic background strengths.



**Figure 14: Surface Titration Data of CKD at Three Different Ionic Strengths**

Figure 14 shows the acid-base titration curve of the CKD aqueous solution. It is characterized by a weak acid system at the different ionic background strengths. The three curves intersect at  $\approx$  pH 10.0. This means that the system will thermodynamically tend to drive toward this point. It also indicates that the surface charge on the sorbent surface is neutral at pH 10, which is referred to as the  $\text{pH}_{\text{zpc}}$ , or pH of zero point of charge. The points of zero charge (PZC) are used to characterize the materials engineering, catalysis, geo-chemistry, agriculture, wastewater management, etc. (Kosmulski, 2011).

The surface charge of CKD was calculated from the titration data using the following equation (Lützenkirchen *et al.*, 2012; El Zayat *et al.*, 2010):

$$\sigma = \frac{F}{AS} [C_A - C_B - (H^+) + (OH^-)]$$

Where;

---

$F$ : Faraday Constant = 96485.339 Coulomb/mole

$S$ : Sorbent concentration = 2 g/l according to this study

$A$ : Surface area of sorbent = 0.4 m<sup>2</sup>/g

$H^+$ :  $10^{(\text{pH value})}$

$OH^-$ :  $10^{(14-\text{pH value})}$

$C_A, C_B$ : Acid or base added (moles/L)

$\sigma$ : The surface charge density

As shown in Figure 15 for the 0.1 M ionic background case, it is obvious that the CKD surface was positively charged at pH more than  $\approx 10.0$  (alkaline conditions) and negatively charged under pH= 10.0. The CKD has weak negative charges from pH<10.0 to pH> 3.0, while it has strong negative charge at the acidic conditions. It was observed that the surface charge varies from 63.7 C/m<sup>2</sup> to -130 C/m<sup>2</sup>. The negative charge of the CKD has a significant impact on adsorbing heavy metals by electrostatic attraction where heavy metals have positive charge (M<sup>+2</sup>). However, the identification of the preferable pH for adsorption could be a complicated issue. Accordingly, one of the main roles of batch experiments is to identify the optimum pH value for adsorbing the target heavy metals.

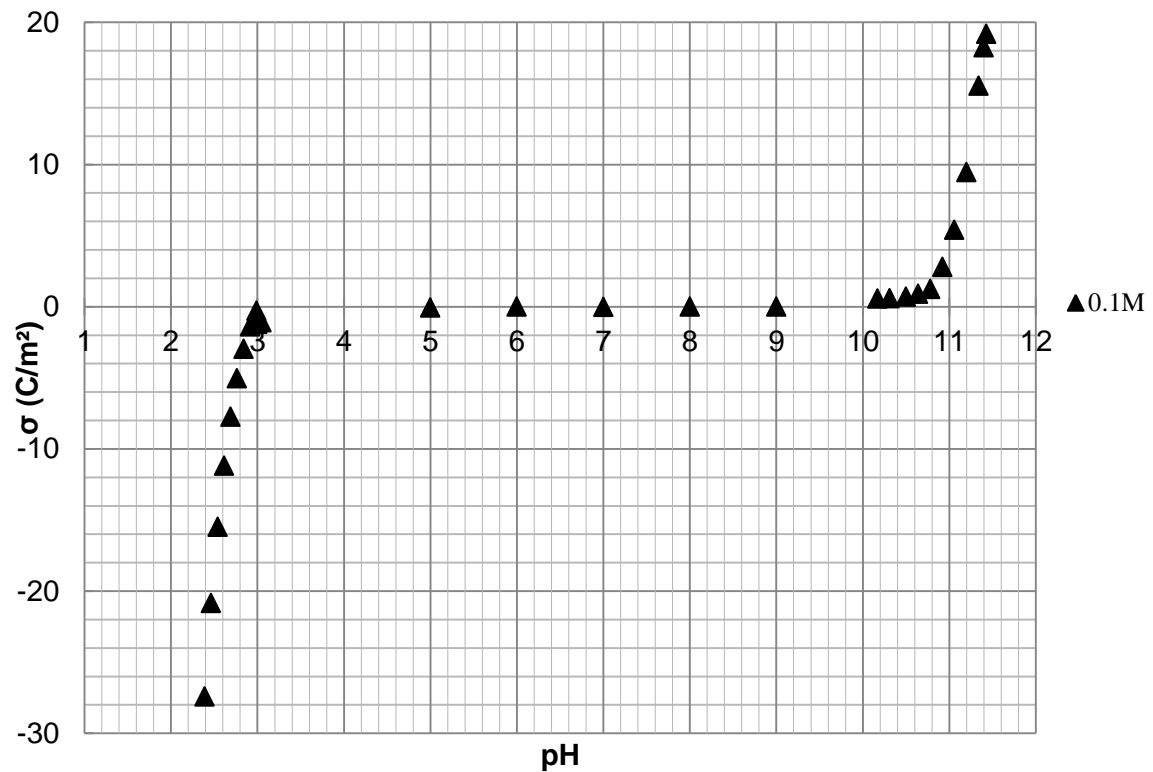


Figure 15: Sorbent Surface Charge at different pH values at Ionic Background of 0.1 M

#### 4.4 Batch Equilibrium Experiments

CKD was experimented to recover wastewater from heavy metals, namely Pb (II), Cu (II), and Cd (II). The parameters affecting metal ( $M^+$ ) removal from synthetic solutions were thoroughly investigated in this set of experiments. These parameters are the pH, contact time, CKD dose, and initial metal concentration. The optimum conditions for heavy metals uptake for the three target metals were determined. The CKD also has been compared to hydrated lime stone at the optimum adsorption conditions. The hydrated lime stone was used since it is the prime source of CaO (the major constituent of CKD) so that we can know whether any other chemical constituent in the CKD can play a significant role in the adsorption mechanism or not. Moreover, both sorbent materials have similar physical and chemical characteristics as mentioned in section two of this chapter “Cement Kiln Dust and Hydrated Lime Stone Physical and Chemical



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Characteristics”. However, a special emphasize on CKD was considered since it is a troublesome industrial waste in cement manufacturing.

Studying the sorption equilibrium, provides data for adsorption models to describe the equilibrium that had been established between metal ions adsorbed on the CKD ( $q_{eq}$ ) and metal ions remaining in the solution ( $C$ ,  $C_o$ , and  $C_e$ ) at constant temperature.

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#### 4.4.1 Metal Hydroxide Precipitation

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The metal hydroxide precipitation experiments showed that the hydroxide precipitation of the metal ions ( $Pb^{+2}$ ,  $Cu^{+2}$ , and  $Cd^{+2}$ ) from the synthetic metal solutions limits the suitable operation pH for adsorption. This is due to the fact that at higher pH values the insoluble metal hydroxides precipitate which makes the actual adsorption mechanism hard to study. The experiment was carried out at different pH values (3– 11) to investigate the metal hydroxide precipitation pH range of 30 mg/l for each target metal individually without using of CKD.

Figure 16 shows the percentage removal of  $M^{+2}$  (Pb, Cu, and Cd) as hydroxides from the synthetic wastewater solution as a function of pH, and Figure 17, shows the theoretical hydroxide precipitation curves of common metals as a function of pH. From Figure 16, it can be seen that drastic change in lead precipitation started at pH value of 6.0 to reach 87%. From this pH and beyond, the precipitation is the dominant mechanism of lead removal from the solution. This observation has been also confirmed by other authors (Venkatesham *et al.*, 2013; Cechinel *et al.*, 2014). Therefore, lead hydroxide precipitation is the dominant phenomenon at upper pH values ( $pH > 6.0$ ). While for both copper and cadmium, the precipitation started at pH 8.0 to reach approximately 90%. Accordingly, the dominant mechanism of copper and cadmium removal from the aqueous solution is the hydroxide precipitation at  $pH > 8.0$ . The pH values that are higher than 8.0 reduces the solubility of different heavy metals (Jiang, 2013; Sun, 2005). Therefore, the

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metal aqueous solution pH should be controlled to avoid amphoteric metal ions dissociation (Rojas, 2014).

#### 4.4.1.1 *Effect of pH*

Adsorption of metal from aqueous solution was related to the pH of the solution, as the later affects the surface charge of the metal binding sites in the sorbent, and the degree of ionization and the species of the metal (Pitsari, 2013). Therefore, the experiment was carried out to investigate the optimum pH value for metal adsorption by CKD.

The batch equilibrium experiment was performed using a CKD dose of 2 gm/l in metal synthetic solutions for lead, copper, and cadmium separately. The metal solution initial concentration was chosen to be 30 mg/l and the initial pH values were adjusted to be in the range of 3 to 11.

Figure 18 and Figure 19 show that CKD has significantly lower sorption capacity for metal uptake at pH values below 4. At a pH value higher than 4, a considerable jump in the adsorption capacity of the CKD was observed to reach 38% for lead, 57% for copper, and 47% for cadmium at pH = 5.0. The metal adsorption reached its optimum capacity (>90%) at pH 5.5 ~6.0 for the three target metals. The metal uptake ( $Q_{eq}$ ) was 15 mg lead/ g of CKD and 13.5 mg/gm CKD for copper and cadmium. This binding behavior between the adsorbent and the adsorbate might be due to the effect of hydroxyl (-OH) and carboxyl (-COOH) groups, since the ionization constant for a number of these groups range between 4 and 5 (Saad, 2008). Above pH 6, the heavy metals tend to form insoluble micro-precipitates complexes that make a distortion in the sorption results (Kim *et. al.*, 2002). Therefore, the pH value of the metal solution shall not exceed pH 6 to determine actual adsorption capacities. The results can also indicate that the adsorption process took place before substantial precipitation began to occur in accordance with the pH scale.

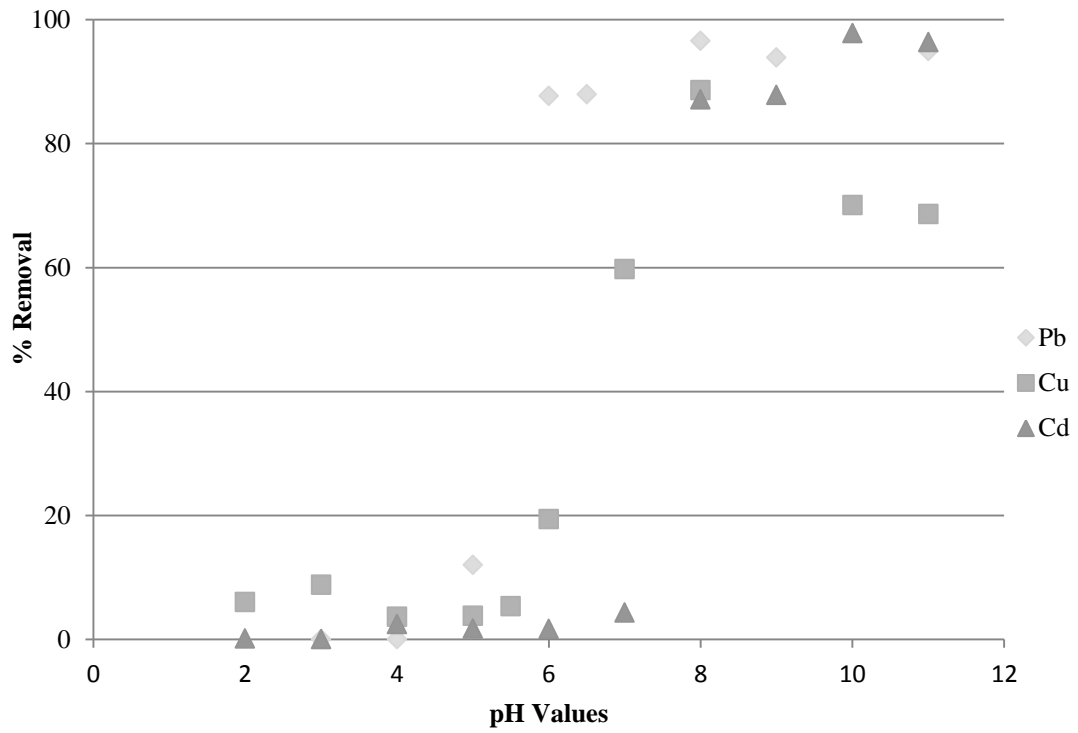


Figure 16: Metal Removal by Hydroxide Precipitation

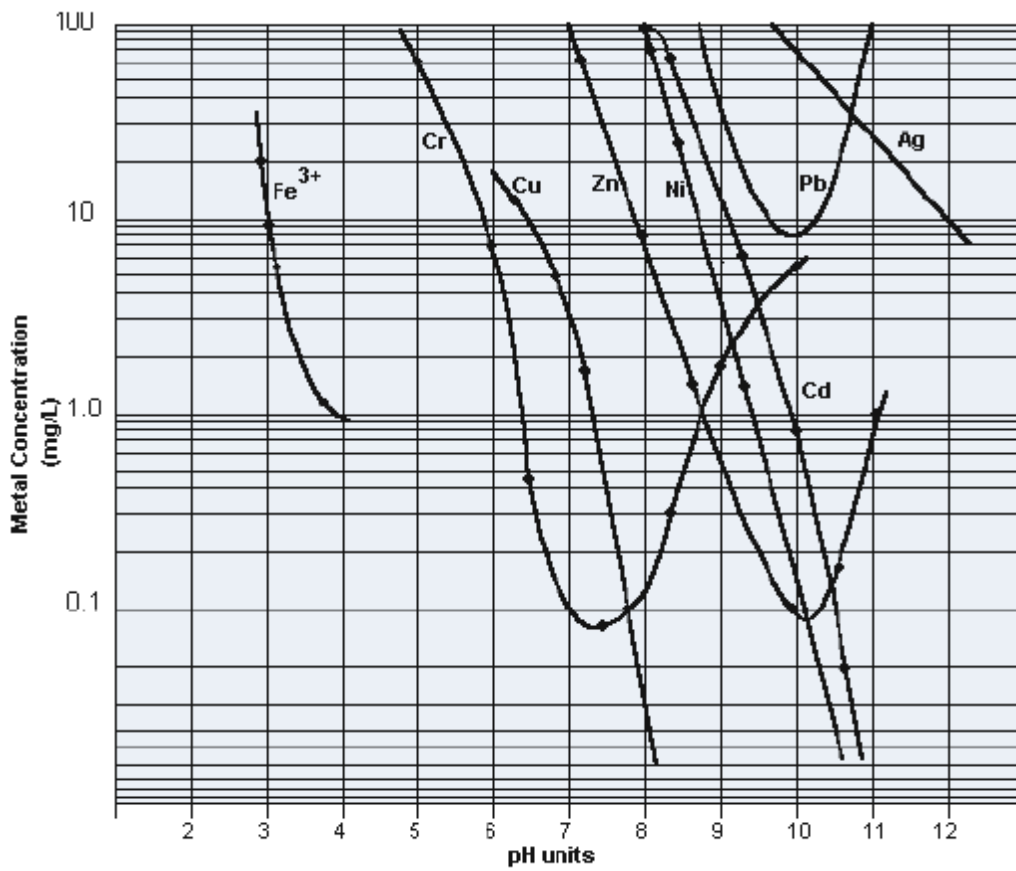


Figure 17: Theoretical Metal Hydroxides Precipitation Ranges (Hoffland, 2014)

According to the surface charge results that showed the negative charge of the sorbent at pH <10, a surface reaction involving electrostatic attraction of  $M^{2+}$  is likely responsible for the sharp increase in the adsorption of metal ions onto the surface of the CKD at pH <6. On the other hand, there was a notable removal of the target heavy metals (Pb, Cu, and Cd) at higher pH values and after the zero point of charge which is likely due to metal precipitation. The following table (Table 11) shows the equilibrium data analysis for the adsorption of heavy metals by using CKD at different pH values.

**Table 11: Equilibrium Data for Heavy Metal Adsorption by CKD at Different pH Values**

<b>Pb Removal</b>			<b>Cu Removal</b>			<b>Cd Removal</b>		
<b>pH</b>	<b>% Removal</b>	<b>Q(eq)</b>	<b>pH</b>	<b>% Removal</b>	<b>Q(eq)</b>	<b>pH</b>	<b>% Removal</b>	<b>Q(eq)</b>
	%	mg/gm		%	mg/gm		%	mg/gm
3	2.3	0.35	2	0.0	0	2	1.3	0.2
4	19.0	2.85	2.5	1.3	0.2	3	5.0	0.75
5	37.9	5.68	3	3.3	0.5	4	40.0	6
5.5	99.0	14.85	4	6.7	1	5	46.7	7
6	99.6	14.94	4.5	50.0	7.5	6	90.0	13.5
7	98.0	14.70	5	56.7	8.5	7	97.7	14.65
8	99.9	14.99	5.5	90	13.5	8	98.3	14.75
9	99.9	14.99	6	91.0	13.65	9	97.3	14.6
10	95.5	14.33	7	94.7	14.2	10	98.5	14.77
11	93.3	14.00	10	99.0	14.85	11	99.8	14.97

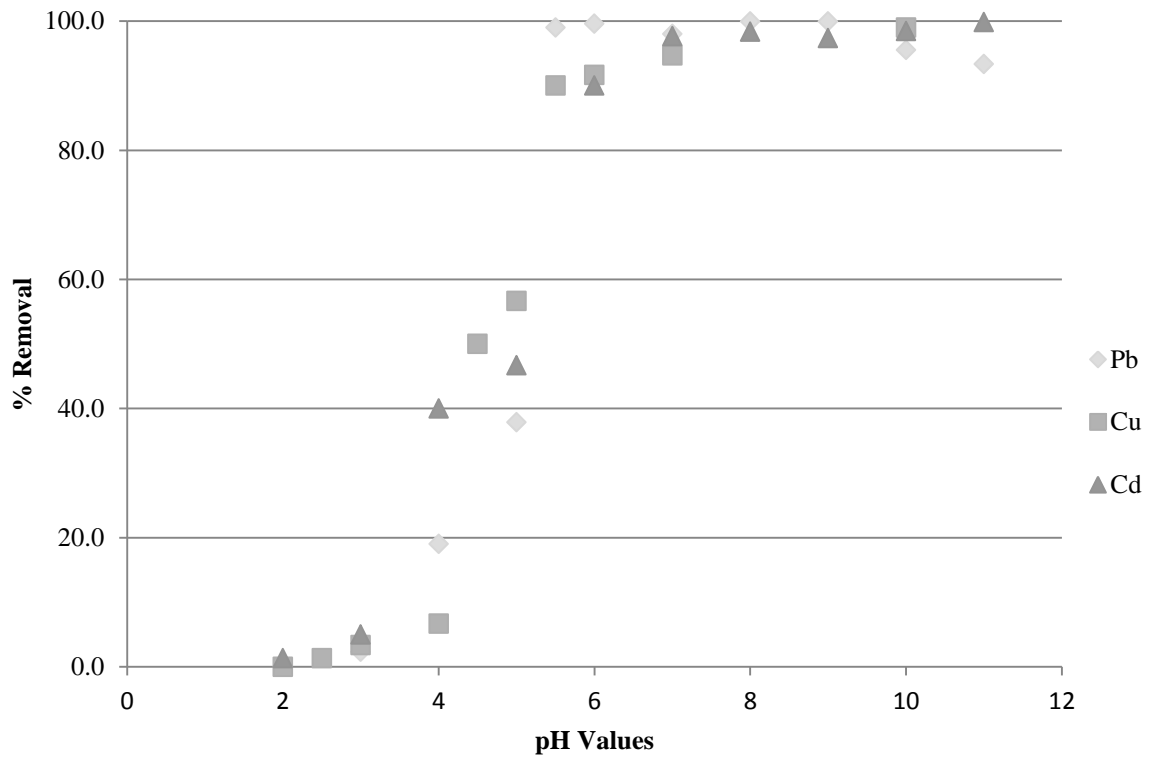


Figure 18: Effect of pH on Adsorption of 30 mg/l Heavy Metal Removal by using 2g/l CKD – Percentage Removal

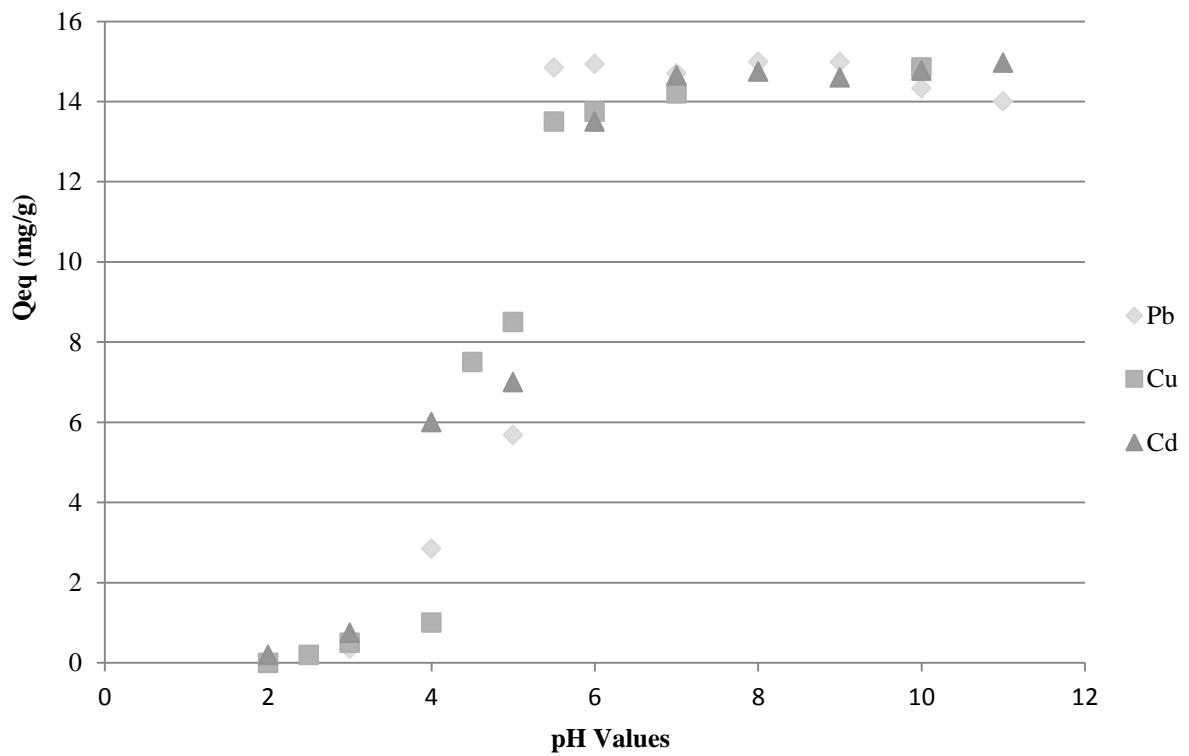


Figure 19: Effect of pH on Adsorption of 30 mg/l Heavy Metal Removal by using 2g/l CKD – Sorbent Uptake Capacity

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#### 4.4.1.2 *Effect of Contact Time*

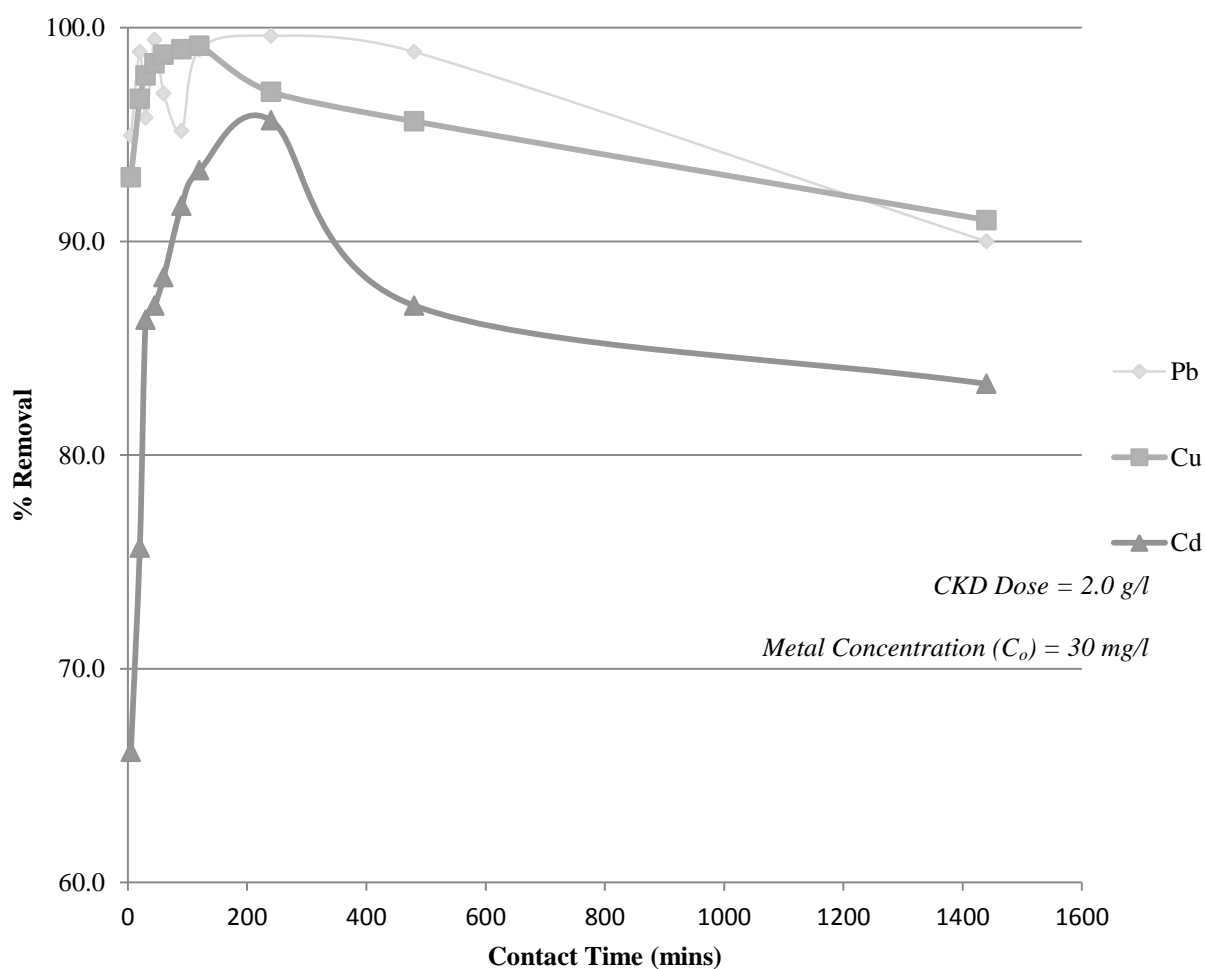
The required contact time in order to reach equilibrium depends on the system behavior; therefore, it is vital to determine the required contact time to reach equilibrium. To identify the required time for equilibrium sorption, the batch equilibrium experiments were performed using a CKD dose of 2.0 gm/l in a metal solution of 30 mg/l. The initial pH was adjusted at the optimum pH obtained from the first set of experiments mentioned previously (pH value of 5.5). The percentage of metal uptake was measured at time intervals from 5 minutes to 24 hours. The results show that the CKD has a rapid adsorption mechanism.

Figure 20 shows that the rate of metal adsorption is high during the first 20 minutes of the experiment runs. The lead and copper uptake amazingly reached more than 90% in the first 5 minutes while it took 90 minutes for the cadmium to achieve 90% recovery. After then, the uptake capacity of the CKD increased slowly until it reached its breakthrough after approximately 4 hours. Accordingly, the required contact time to reach equilibrium for the target heavy metals is 4 hours at which the uptake efficiency of CKD reached more than 95% for the three target metals, namely lead, copper, and cadmium. After reaching to the equilibrium, the sorption process reversed by time and the percentage of metal removal was on the decrease as shown in Table 12.

Figure 21 also shows the specific uptake of the CKD versus the contact time. The adsorption capacity of the CKD at equilibrium is 14.8 mg/gm, 14.6 mg/gm, and 14.4 mg/gm for lead, copper, and cadmium respectively.

**Table 12: Equilibrium Data for Heavy Metal Adsorption by CKD at Different Contact Times**

Contact Time (mins)	Pb Removal		Cu Removal		Cd Removal	
	% Removal	Q <sub>eq</sub> (mg/gm)	% Removal	Q <sub>eq</sub> (mg/gm)	% Removal	Q <sub>eq</sub> (mg/gm)
5	94.9	14.242	93.0	13.95	66.1	9.9
20	98.9	14.831	96.7	14.5	75.7	11.35
30	95.8	14.3675	97.8	14.666	86.3	12.95
45	99.4	14.9167	98.3	14.75	87.0	13.05
60	96.9	14.54	98.7	14.8115	88.3	13.25
90	95.2	14.2755	99.0	14.85	91.7	13.75
120	99.0	14.846	99.2	14.873	93.3	14
240	99.6	14.9435	97.0	14.55	95.7	14.35
480	98.9	14.831	95.6	14.3435	87.0	13.05
1440 (24 hrs)	90.0	13.5	91.0	13.65	83.3	12.5



**Figure 20: Effect of Contact Time on Heavy Metal Adsorption at pH 5.5 – Percentage Removal**

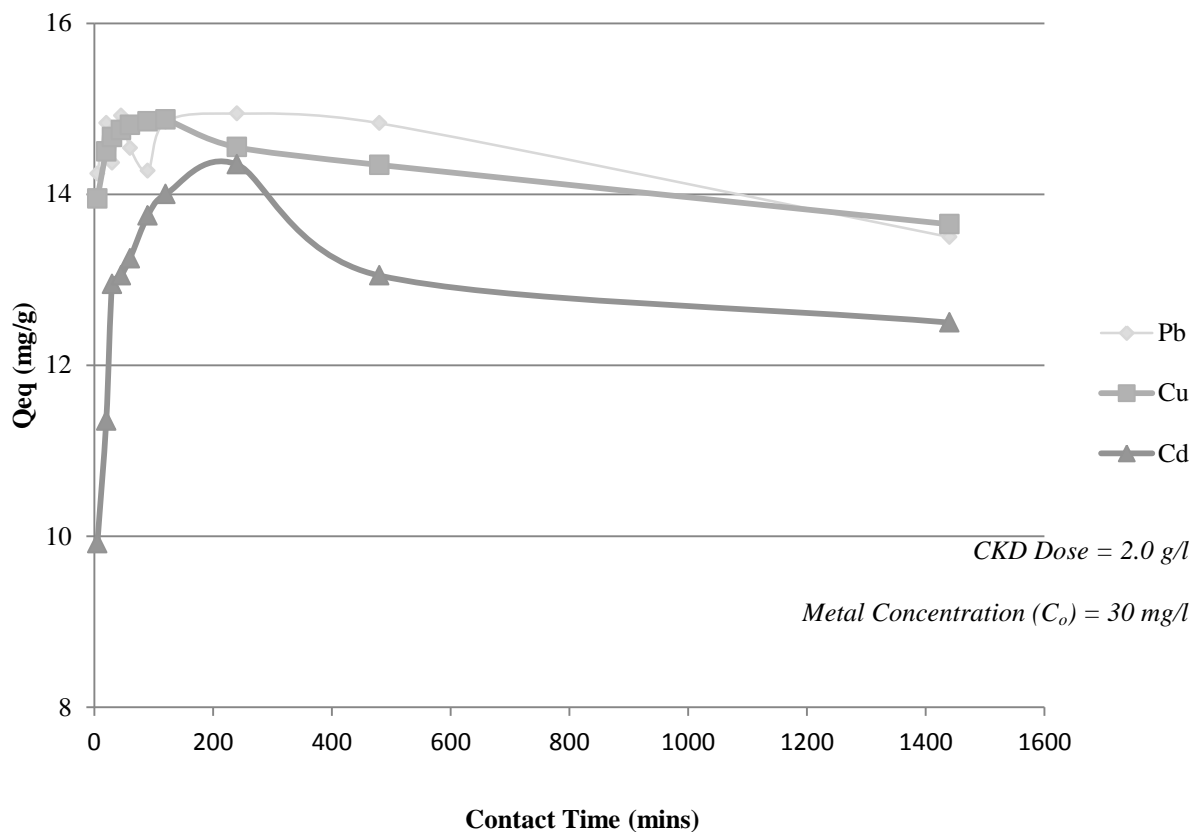


Figure 21: Effect of Contact Time on Heavy Metal Adsorption at pH 5.5 – Specific Uptake

#### 4.4.1.3 Effect of Sorbent Dose

One of the significant adsorption parameters is the sorbent dose. The efficiency of the adsorption mechanism is affected by the sorbent to sorbate ratio (Chang, 2002). In order to determine the effect of CKD concentration on the adsorption process, the batch equilibrium experiment was performed using a different adsorption doses; 0.015%, 0.03%, 0.05%, 0.075%, 0.1%, 0.15%, and 0.2% (W/V), with an initial metal concentration of 30 mg/l at the optimum pH of 5.5 and contact time of 4 hours.

Figure 22 and Figure 23 depict the influence of adsorption dose on the heavy metal uptake capacity. It is obvious that the increase in adsorption dose from 0.05% to 0.2% (W/V) resulted in increasing the uptake of metal ions dramatically. However, this uptake values showed a reverse trend in the specific uptake ( $Q_{eq}$ ) from 43 mg Pb / gm - to



14.85mgPb / gm CKD, 27mg Cu/gm CKD to 14.55 mg/gm, and 20 mg/gm to 14.25mg/gm for cadmium. This phenomenon might be attributed to the reduction in sorbent concentration (X) in the suspension at a given metal concentration (Co) which in turn increases the metal / sorbent ratio (Co/X). Hence, the metal uptake per gram sorbent (Qeq) increases. The increase in specific uptake (Qeq) with increasing in (C/X) ratio has two possible explanations: 1) the reduction in sorbent concentration decreases the electrostatic interaction between cells which increase the adsorption rate. 2) Increasing the ratio of initial metal concentration versus sorbent dose might cause an increase in the available number of ions around the sorbent particles, and hence more easily bound to the active sites will occur as long they are not saturated (Saad, 2008).

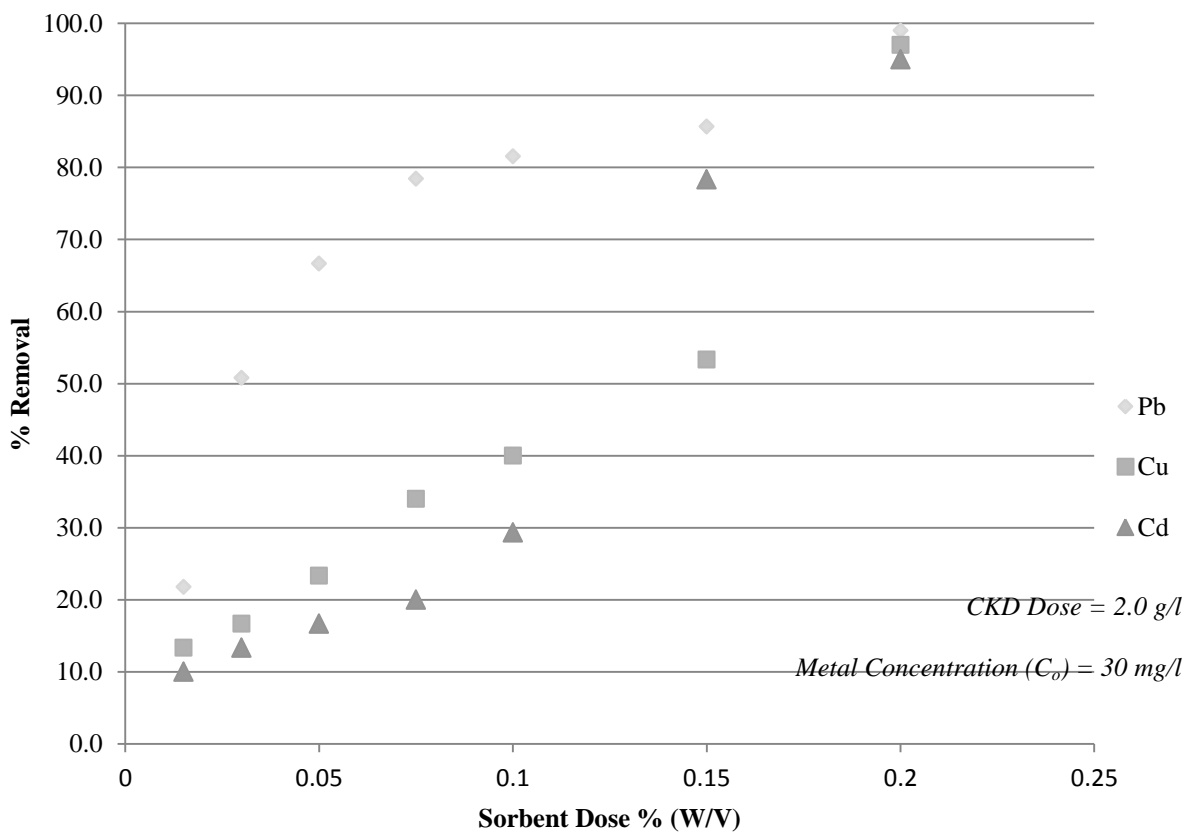


Figure 22: Effect of CKD Doses on Heavy Metal Adsorption at pH 5.5 for 4hrs Contact Time – Percentage Uptake

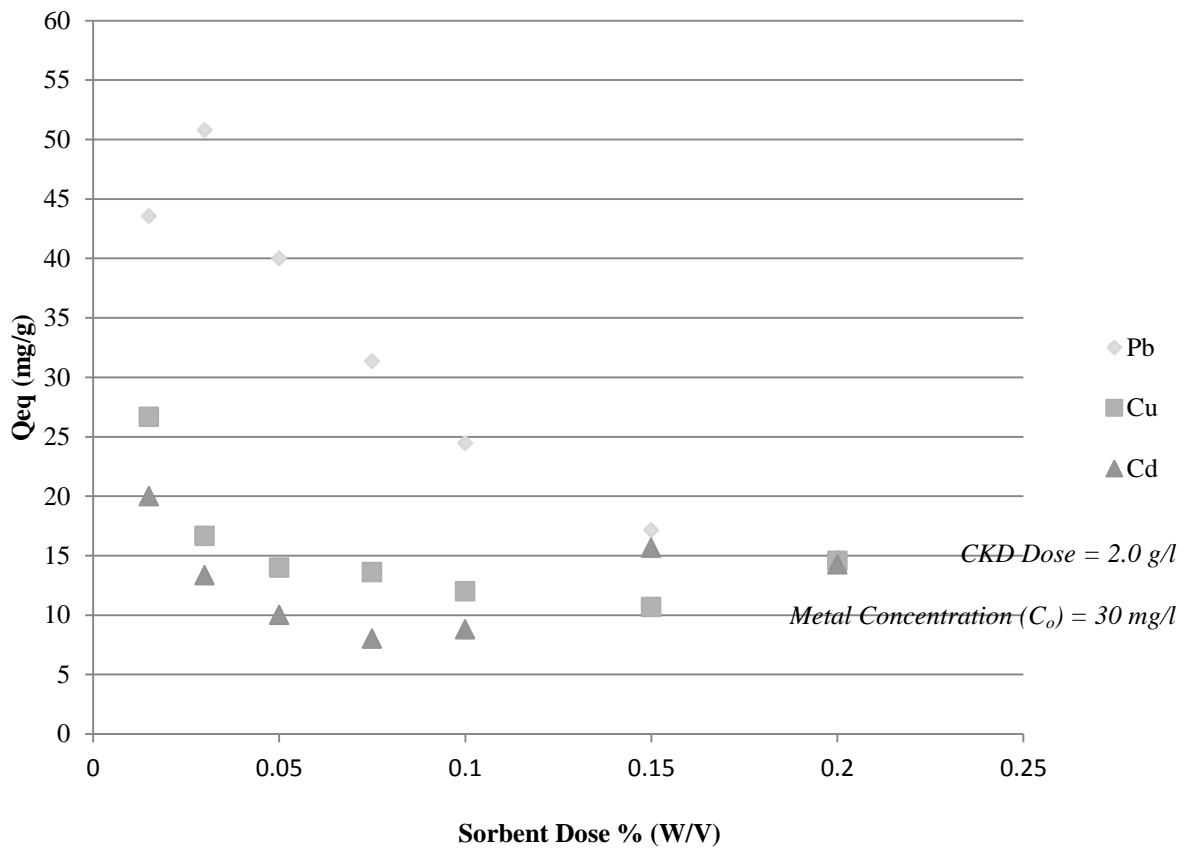


Figure 23: Effect of CKD Doses on Heavy Metal Adsorption at pH 5.5 for 4 hrs Contact Time– Specific Uptake

The following table (Table 13) shows the results of the experimental runs that were conducted to investigate the effect of different CKD doses on the heavy metal uptake at pH 5.5 and 4 hrs contact time. The initial metal concentration for the three target heavy metals was 30 ppm.

Table 13: Effect of CKD Dose on the Heavy Metal Adsorption

CKD Dose (g/l)	Sorbent Dose % (W/V)	Pb Removal		Cu Removal		Cd Removal	
		% Removal	$Q_{eq}$ (mg/g)	% Removal	$Q_{eq}$ (mg/g)	% Removal	$Q_{eq}$ (mg/g)
0.15	0.015	21.8	43.56	13.3	26.67	10.0	20
0.3	0.03	50.8	50.79	16.7	16.67	13.3	13.33
0.5	0.05	66.7	40	23.3	14	16.7	10
0.75	0.075	78.4	31.37	34.0	13.6	20.0	8
1	0.1	81.6	24.47	40.0	12	29.3	8.8
1.5	0.15	85.7	17.13	53.3	10.67	78.3	15.67
2	0.2	99.0	14.85	97.0	14.55	95.0	14.25

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#### 4.4.1.4 *Effect of Initial Metal Concentration*

Like the sorption dose concentration, the initial metal concentration is a significant factor because it has an effect on the sorbent/ sorbate ratio in the system which results in affecting efficiency and sorption capacity.

In order to identify the impact of the initial metal concentration on the adsorption mechanism, the batch equilibrium experiment runs were performed using different metal concentrations: 10, 30, 50, 70, 100, 150, and 200 mg/l, with a CKD dose of 2.0 g/l. The obtained optimum pH and contact time from the previous equilibrium experiments were applied as well.

Figure 24 shows the influence of the initial metal concentration on the adsorption capacity of the CKD. Figure 25 depict also the specific uptake. It is obvious from both figures that the adsorption uptake efficiency together with the sorption capacity ( $Q_{eq}$ ) are affected by sorbent (CKD) to sorbate (metal) ratio as concluded from the previous experiment runs for the sorbent dose effect. The removal efficiency (% removal) is inversely proportional to the initial metal concentration. More increasing of metal ions leads to decrease in the removal efficiency while the specific uptake was increased as long as binding sites were available. From this experiment and the previous experiment presented in section 4.4.1.3: Effect of Sorbent Dose, we can say that:

**If  $X \gg C_o$** , the removal efficiency might increase and the specific uptake will decrease.

**If  $C_o \gg X$** , the removal efficiency will decrease while the specific uptake might increase

Where:  $X$  is the sorbent concentration, and  $C_o$  is the initial metal concentration.

Table 14 shows the initial metal concentration effect on the adsorption mechanism of the CKD.

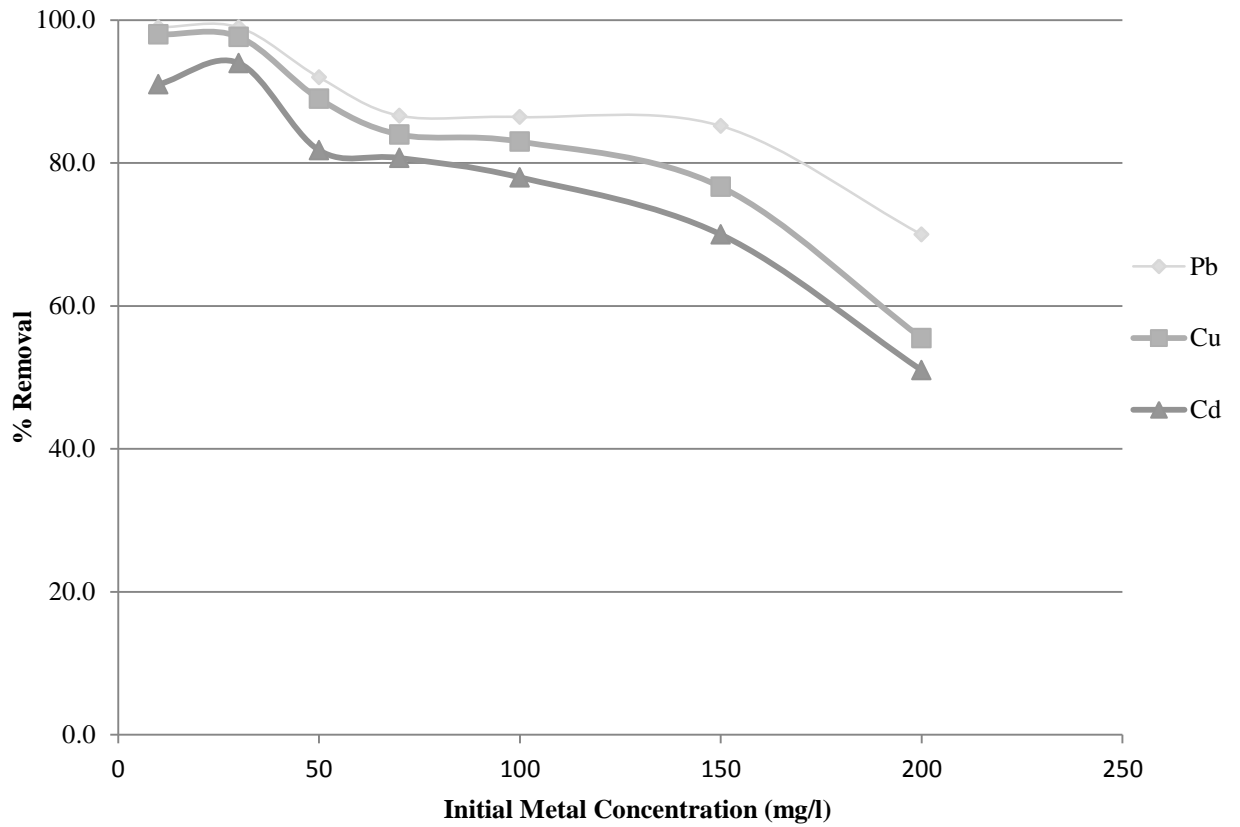


Figure 24: Initial Metal Concentration Uptake

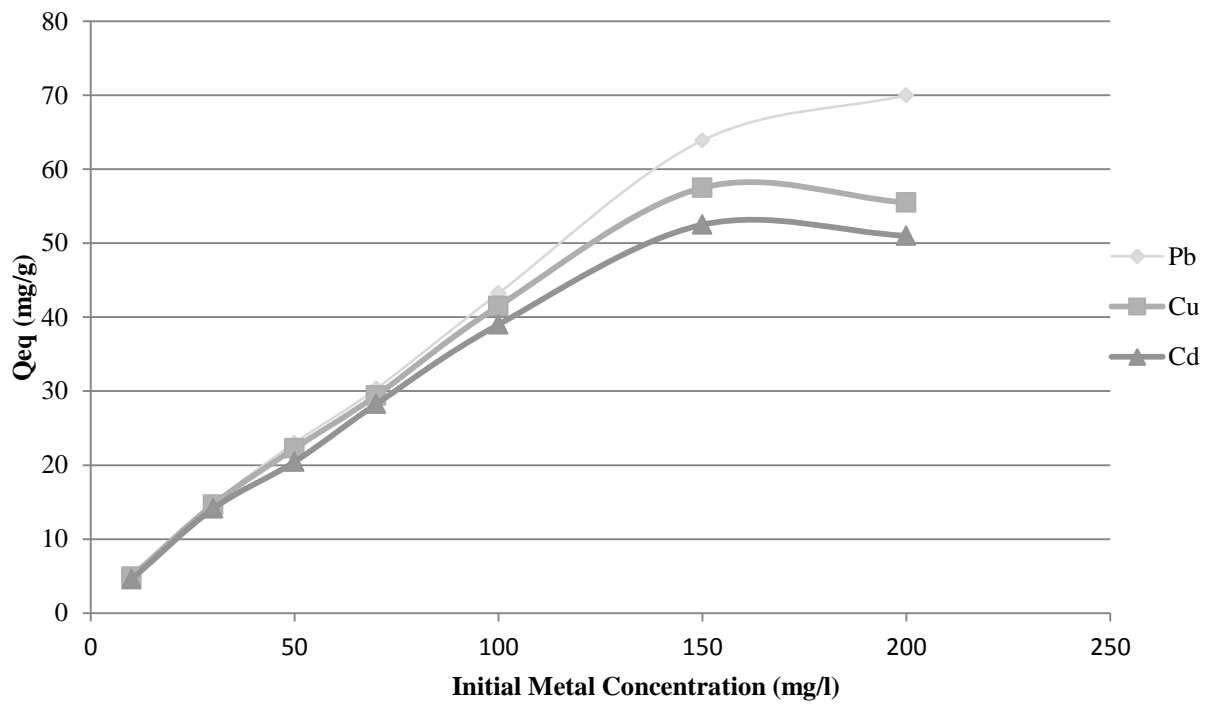


Figure 25: Initial Metal Concentration Specific Uptake

**Table 14: Initial Metal Concentration Effect on the Adsorption Mechanism of CKD**

Metal Conc.	Pb Removal		Cu Removal		Cd Removal	
	% Removal	Q (mg/gm)	% Removal	Q (mg/gm)	% Removal	Q (mg/gm)
10	99	4.95	98	4.9	91.0	4.55
30	90.9	13.64	97.7	14.65	94.0	14.1
50	88.0	21.99	89.0	22.25	81.8	20.45
70	86.6	30.33	84.0	29.4	80.7	28.25
100	86.4	43.22	83.0	41.5	78.0	39
150	87.0	65.21	76.7	57.5	70.0	52.5
200	70.0	69.995	55.5	55.5	51.0	51

## 4.5 Column Experiment

### 4.5.1 Lead

In order to have a meaningful comparison, the effluent concentrations should be compared with the bed volumes rather than run time. This is because of the variable flow rates and run times. The bed volume is calculated as follows:

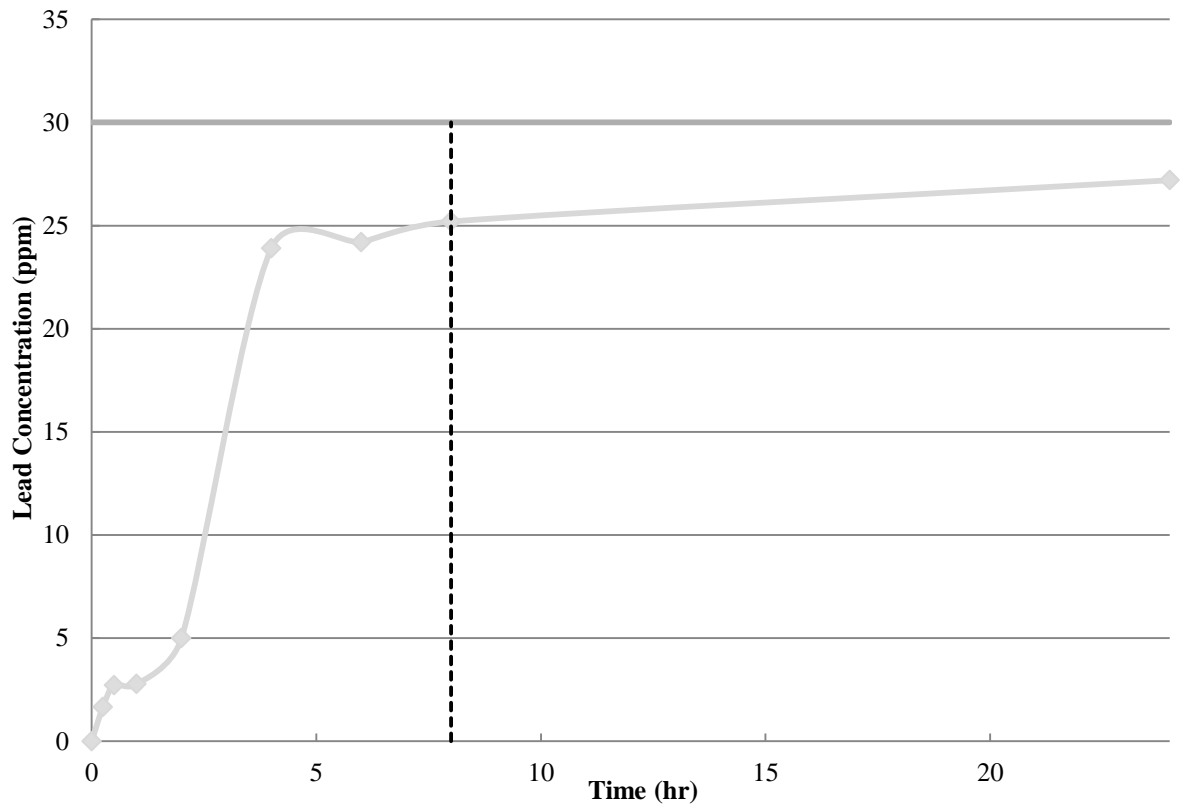
$$\text{Bed Volumes} = \frac{\text{Volume treated}}{\text{Volume of Packed CKD}} = \frac{\text{flowrate}(ml / \text{min}) * \text{time}(\text{min})}{\text{Volume of packed Column}}$$

Table 15 shows the effluent lead concentrations at different times and bed volumes. The bed volume is a measure of the volume of water passed through the packed column of CKD.

**Table 15: Effluent Lead Data for Column Experiment**

Time (hr)	Bed Volumes	C <sub>eff</sub> (ppm)	C <sub>eff</sub> /C <sub>0</sub>
0	0	0	0
0.25	77.99298	1.656	0.0552
0.5	155.986	2.713	0.0904
1	311.9719	2.773	0.0924
2	623.9438	5	0.167
4	1247.888	23.9	0.7967
6	1871.832	24.2	0.8067
8	2495.775	25.2	0.84
24	7487.326	27.2	0.9067

Figure 26 and Figure 27 show the breakthrough of lead versus time. It is obvious that C<sub>eff</sub> reaches almost 80% of the value of C<sub>0</sub> after just 4 hours.



**Figure 26: Influent versus Effluent Pb Concentration**

The breakthrough curve as a function of  $C_{eff}/C_o$  versus CKD bed volumes is shown in Figure 28. It is observed that the maximum breakthrough occurs beyond 2,496 bed volumes where  $C_{eff}/C_o$  was on the increase until the end of the experiment. Calculation of surface concentration at the termination of the run was performed as follows:

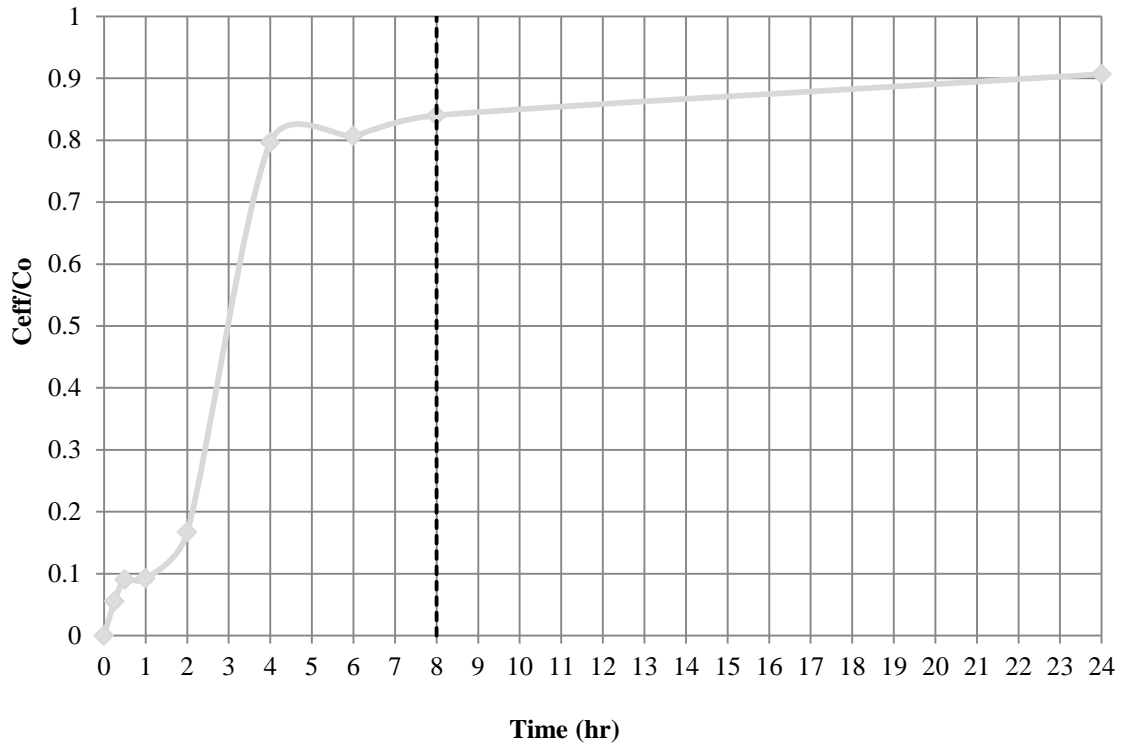


Figure 27: Effluent Pb Concentration versus Time

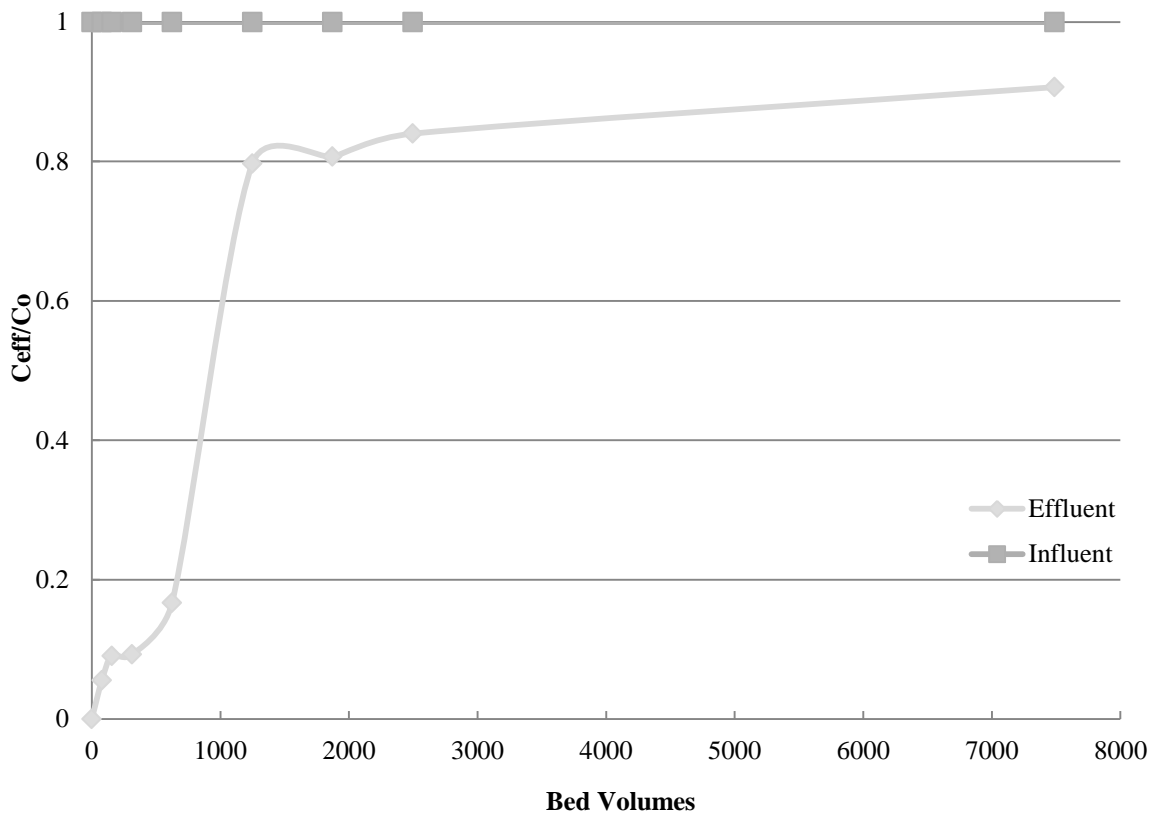


Figure 28: Breakthrough Curve of Pb versus Bed volumes

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$$M_{\text{passing}} = (F \times t_f \times 60 \times C_0) = 0.006 \times 8 \times 60 \times 30 = 86.4 \text{ mg}$$

$$\frac{M_{\text{ads}}}{M_{\text{passing}}} = \frac{A}{A + B} = 35/(35+44)=0.44$$

$$M_{\text{ads}} = \frac{A}{A + B} \times M_{\text{passing}} = 38.8 \text{ mg}$$

Surface concentration at exhaustion =

$$\frac{M_{\text{ads}}}{\text{Mass of CKD in Column}} = 38.8/0.78 = 49 \text{ mg/g}$$

and in molar basis= 240 mM/g

Where:  $M_{\text{passing}}$ = Mass of lead passing through the column

$M_{\text{ads}}$ = Mass of lead adsorbed by the CKD

$F$ = Volumetric Pb solution flow rate through the column (L/min)

$t_f$ = Total time of the column run (hr) until exhaustion

$C_0$ = Influent Concentration of Pb (mg/l)

$A$ = Area representing the adsorbed portion

$B$ =Area representing the un-adsorbed portion

Area A and area B were calculated using a grid method to know the area under the curve in  $\text{cm}^2$ .

The EBCT is a measure of how much time a parcel of fluid spends in the column, on the basis that the column contains no packing. Therefore, the EBCT is simply the column volume (mL) divided by the volumetric flow rate of the liquid (mL/min).



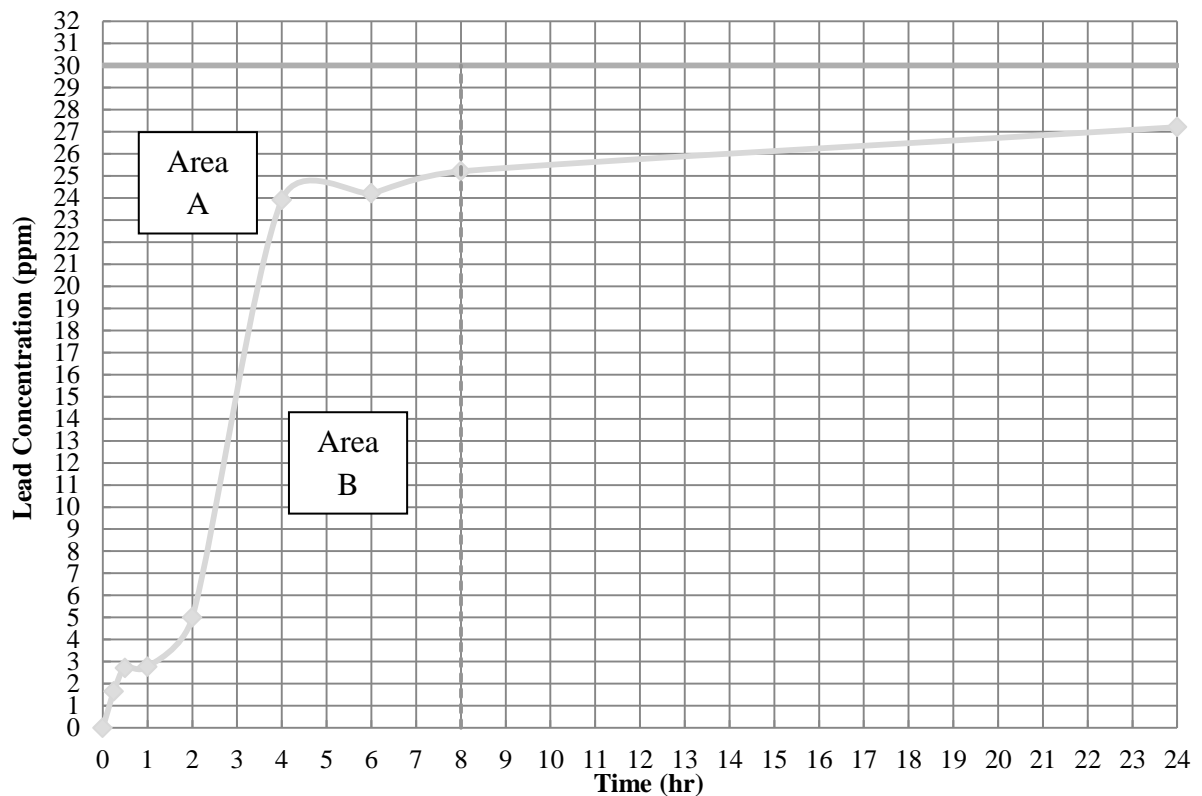


Figure 29: Breakthrough Curve with Designation of Areas for Calculation of Mass of Lead Adsorbed

The EBCT depends on the column bed height. The longer is the bed height the longer is the EBCT (Sun, 2014). Practically, designers often like to work with hydraulic loading rate which is the liquid flow rates expressed in terms of the hydraulic loading (H) in  $L^3/t.L^2$  or  $L/t$ . This is because it based on the cross sectional area of the column.

The empty bed contact time (EBCT) and hydraulic rating rate were calculated in order to determine the required time for wastewater recovery based on the bed size and volume. The EBCT is considered an important factor for designing the bed column. The EBCT is considered an important factor for designing the bed column as it has a significant impact on the performance of the packed CKD. In order to produce treated wastewater with acceptable quality, the depth of packed column and its corresponding minimum EBCT should be considered (Louis, 2006). As EBCT increases, the bed life will increase until a

maximum value is reached. Accordingly, longer EBCT is applied for industrial wastewater effluents (Mondal, 2008).

- **Breakthrough Concentration ( $C_B$ )= max. acceptable effluent concentration**
- **Critical depth ( $L_{critical}$ ) = depth that leads to the immediate appearance of an effluent concentration equal to  $C_B$  when the column is started up.**
- **Empty bed contact time (EBCT)**
- **$EBCT_{min} = \frac{L_{critical}}{Q/A}$  ;  $EBCT = \frac{V}{Q} = \frac{L_{bed}}{Q/A} = 1.1540 \text{ (cm}^3\text{)}/6 \text{ (ml/min)} = 0.20 \text{ min.}$**

Where the Volume= the column area x the packed CKD length in the column=

$$\pi r^2 \times L = \pi (0.35)^2 (3) = 1.1540 \text{ cm}^3$$

- **Hydraulic Loading Rate (HLR)= Design Flow /Cross Sectional Area**

$$HLR = 6/0.385 = 15.6 \text{ cm/min}$$

All the results of the column experiment are shown in the following table (Table 16).

**Table 16: Analysis of the Column Experiment for Lead**

<b>Parameter</b>	<b>Unit</b>	<b>Value</b>
Breakthrough Bed Volumes		2,496
Surface Concentration At Exhaustion	mg Pb/g CKD	49
	$\mu\text{M/g}$	240
Hydraulic Loading Rate (HLR)	cm/min	15.6
Empty Bed Contact Time (EBCT)	Min	0.20

By comparing the column results with the batch equilibrium ones, one can find that the Pb uptake in the equilibrium experiment at pH 5.5 (pH of the column run) was 72.4  $\mu\text{M/g}$  compared to the column capacity of 240  $\mu\text{M/g}$ . Therefore, the column adsorber shows higher adsorption than the batch equilibrium for the same metal concentration.

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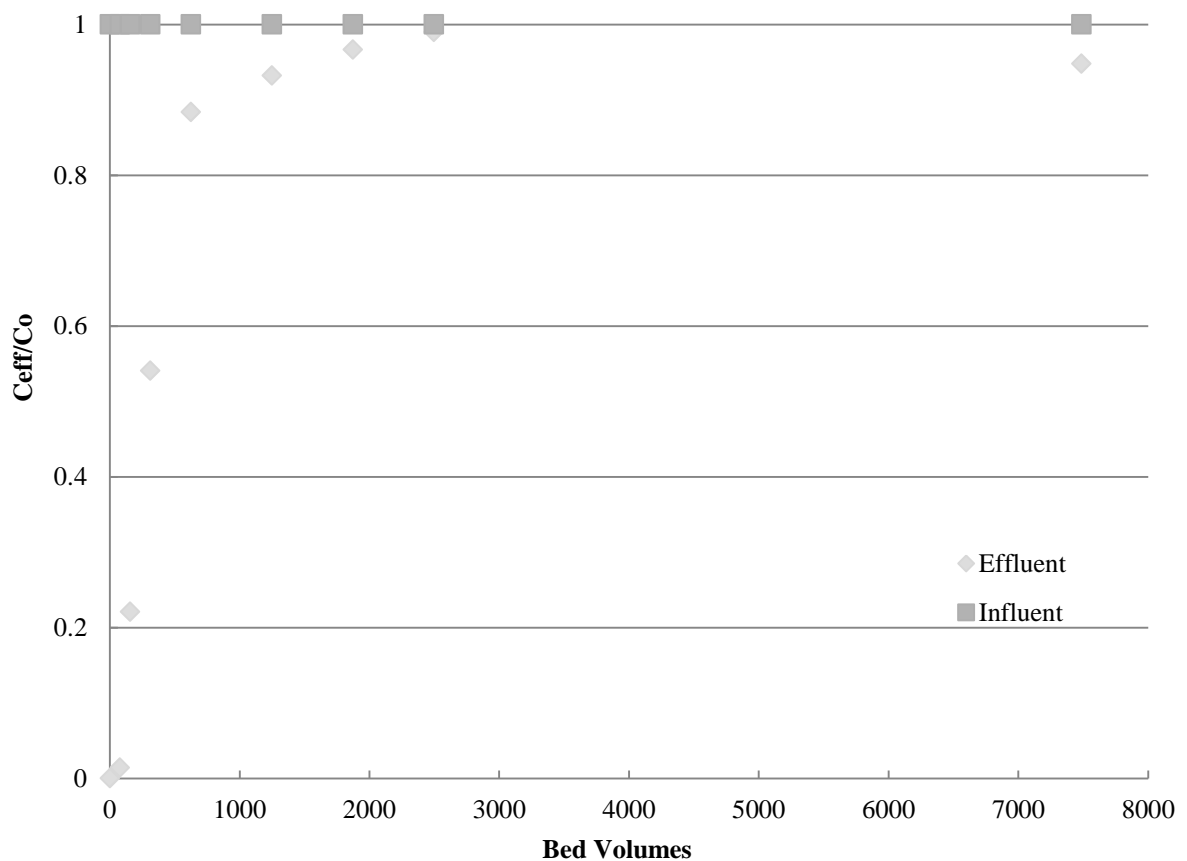
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#### 4.5.2 Copper

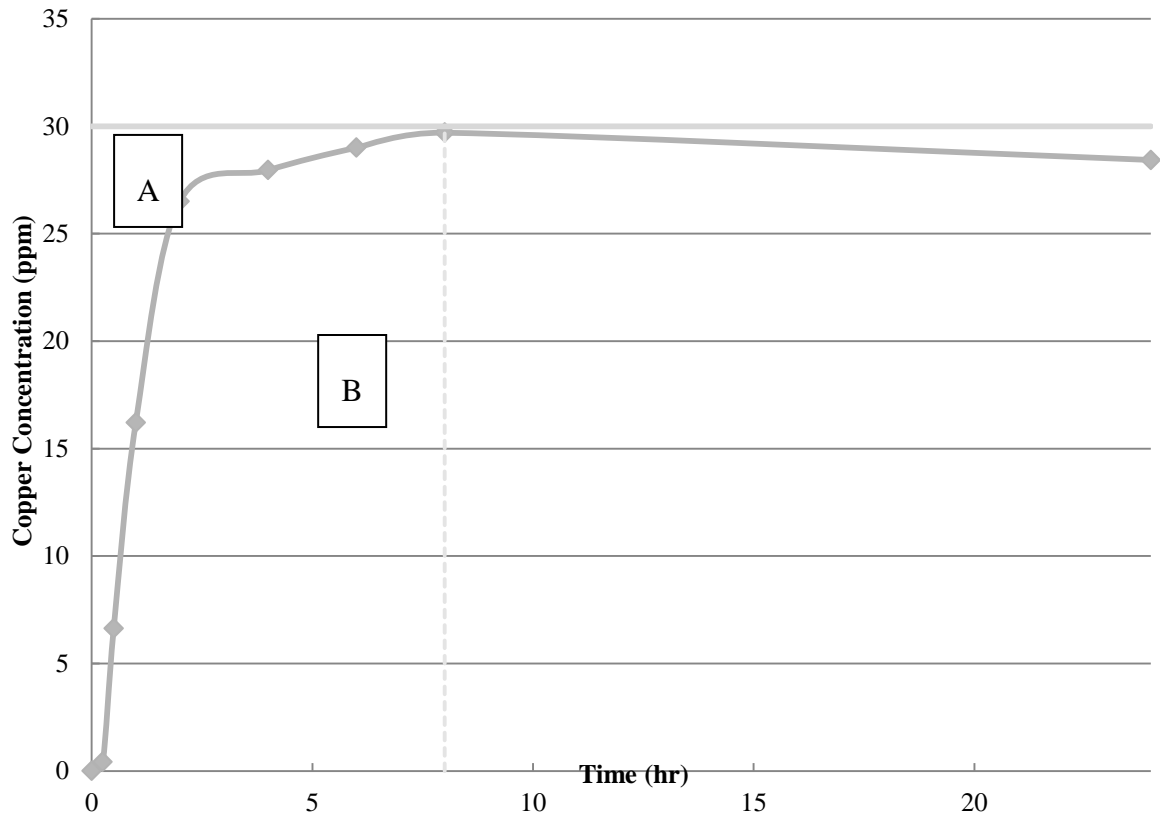
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The experiment was carried out using the same conditions of lead. The flow rate was 6ml/min and the initial metal concentration of Cu was 30 ppm.

Figure 30 and Figure 31 illustrated that, Cu breakthrough is immediate, and that the column approaches exhaustion after 4 hours where  $C_{\text{eff}}/C_o$  reached 93%. This is the same result achieved in the Pb run.



**Figure 30: Breakthrough Curve of Cu versus Bed Volumes**



**Figure 31: Breakthrough Curve with Designation of Areas for Calculation of Mass of Copper Adsorbed**

Calculation of surface concentration was done as mentioned before for lead. Figure 31 summarizes the results of adsorbing copper by CKD in a fixed bed reactor. Table 17 summarizes the design-related calculations.

$$M_{\text{passing}} = (F \times t_f \times 60 \times C_0) = 0.006 \times 8 \times 60 \times 30.0 = 86.4$$

$$\frac{M_{\text{ads}}}{M_{\text{passing}}} = \frac{A}{A+B} = 13 / (13+65) = 0.17$$

$$M_{\text{ads}} = \frac{A}{A+B} \times M_{\text{passing}} = 14.4$$

Surface concentration at exhaustion =

$$\frac{M_{\text{ads}}}{\text{Mass of CKD in Column}} = 14.4 / 0.78 = 18.4 \text{ mg/g and in molar basis} = 290 \mu\text{M/g}$$

$$EBCT = \frac{V}{Q} = \frac{L_{bed}}{Q/A} = 1.5 \text{ (cm}^3\text{)}/6 \text{ (ml/min)} = 0.20 \text{ min.}$$

• **Hydraulic Loading Rate (HLR)= Design Flow /Area**

$$HLR = 6/0.385 = 15.6 \text{ cm/min}$$

**Table 17: Analysis of the Column Experiments for Copper**

Parameter	Unit	Value
Breakthrough Bed Volumes		2,496
Surface Concentration At Exhaustion	mg Cu/g CKD	18.4
	uM/gm	290
Hydraulic Loading Rate (HLR)	cm/min	15.6
Empty Bed Contact Time (EBCT)	min	0.2

Comparing the column results with the batch equilibrium experiment of Cu, the Cu uptake capacity in the equilibrium experiment was 232µM/g compared to the column capacity of 18.4 mg/g (290µM/g). These results confirm that CKD is more efficiently used in column reactors rather than in batch equilibrium experiments.

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#### 4.5.3 Cadmium

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This experiment was conducted at the same condition as the other 2 column experiments and a cadmium solution of 30 mg/l concentration. As seen in Figure 32, Cd breakthrough is immediate and corresponding to ~ 2,500 bed volumes.

Calculation of surface concentration at exhaustion followed the same method as for the previous runs for Pb and Cu:

$$M_{\text{passing}} = (F \times t_f \times C_0) = 0.006 \times 8 \times 60 \times 30 = 86.4$$

$$\frac{M_{\text{ads}}}{M_{\text{passing}}} = \frac{A}{A+B} = 53/(53+27) = 0.66$$

$$M_{\text{ads}} = \frac{A}{A+B} \times M_{\text{passing}} = 57.24$$

$$\text{Surface concentration at exhaustion} = \frac{M_{\text{ads}}}{\text{Mass of CKD in Column}} =$$

57.24/0.78=73 mg/g and in molar basis= 650 $\mu$ M/g

$$\text{EBCT} = \frac{V}{Q} = \frac{L_{\text{bed}}}{Q/A} = 1.5 \text{ (cm}^3\text{)}/6 \text{ (ml/min)} = 0.20 \text{ min.}$$

• **Hydraulic Loading Rate (HLR)= Design Flow /Area**

HLR= 6/0.385=15.6 cm/min

The results of the column experiment for cadmium are summarized in Table 18.

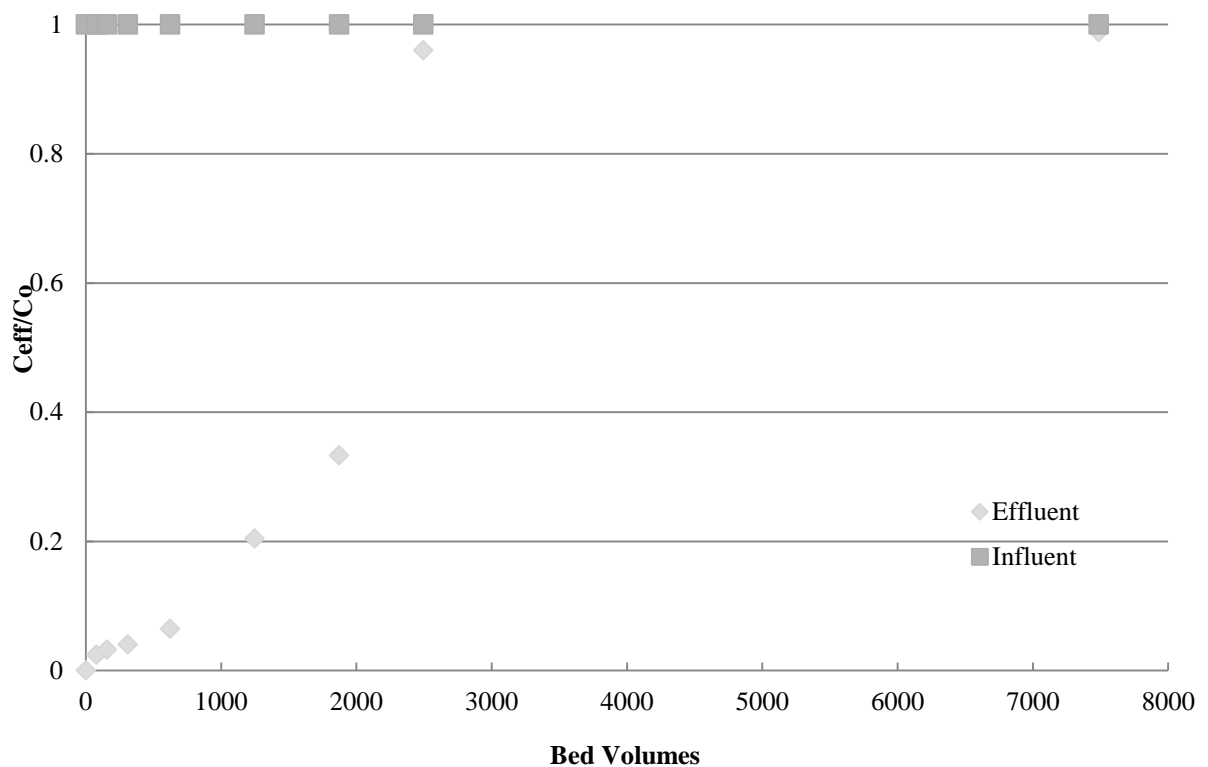


Figure 32: Breakthrough Curve of Cd versus Bed Volumes

Comparing the column results with the batch equilibrium one for Cd, the uptake capacity in the equilibrium experiment was 125 $\mu$ M/g compared to the column capacity of 73 mg/g (650 $\mu$ M/g). Therefore, the column reactors are more effective than batch ones for heavy metal adsorption mechanism.

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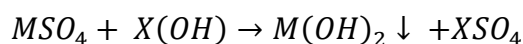
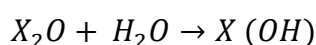
**Table 18: Analysis of the Column Experiment for Cadmium**

<b>Parameter</b>	<b>Unit</b>	<b>Value</b>
Breakthrough Bed Volumes	no.	2500
Surface Concentration At Exhaustion	mg Cd/g CKD	73
	uM/gm	650
Hydraulic Loading Rate (HLR)	cm/min	15.6
Empty Bed Contact Time (EBCT)	Min	0.20

#### **4.6 Adsorption Isotherm**

The adsorption process can result either through the universal Van Der Waals interactions which is known as physical adsorption (physisorption) or by a chemical process (chemical adsorption, chemisorptions). The chemisorptions occur only as monolayer coverage to the adsorbent surface. Also, monlayer surface is formed at energetically homogeneous surface (Dabrowski, 2001). Moreover, it is known that the adsorption of cations on oxide surfaces is mainly affected by the surface hydroxyl groups (Piasecki, 2007). Accordingly, we can conclude that the high alkalinity of the CKD together with the hydroxyl groups is the dominant features of adsorption. Furthermore, the addition of acidic metal ions to strongly alkaline material, such as CKD, would suddenly change the pH of the aqueous solution. Hence, the adsorption of metal ions on the CKD surface might take place either by electrostatic attraction or by complex formation with the surface hydroxyl groups. These complex formations might be attributed to their hydrolysis properties of these metal ions. This adsorption mechanism can be explained as follows (El Awady, 1997):

- 1) Heavy Metals Hydrolysis:

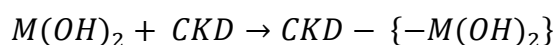


Where; X: Ca, K, Na (major constituents of the CKD)

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M: Pb, Cu, Cd

2) Adsorption of Heavy Metals using CKD:



Accordingly, the adsorption isotherm is very important in order to know the adsorption capacity as well as identifying the significant operating conditions for the system to be as effective as possible. Moreover, the adsorption isotherm could help us to improve the adsorption mechanism. Two isotherm models were hired to perform this work, namely Langmuir Isotherm and Freundlich.

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#### 4.6.1 Langmuir Isotherm

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Langmuir has traditionally been utilized to quantify the performance of different sorbents. This empirical model assumes monolayer adsorption where adsorption can only occur at a finite number of definite localized sites with no lateral interaction (Foo *et al.*, 2010). The isotherm measures the relation between the equilibrium concentration of the element in the solid phase ( $q_e$ , *mg/g*) and the equilibrium concentration of that element in the aqueous phase ( $C_e$ , *mg/l*). The Langmuir equation is as shown:

$$\frac{1}{q_e} = \frac{1}{b} + \frac{1}{abC_e}$$

Where;  $q_e$  mass of heavy metal adsorbed per gram of adsorbent

$C_e$  equilibrium heavy metal concentration in liquid phase, mg of heavy metal/liter

**a** Langmuir constant, liter/mg of heavy metal

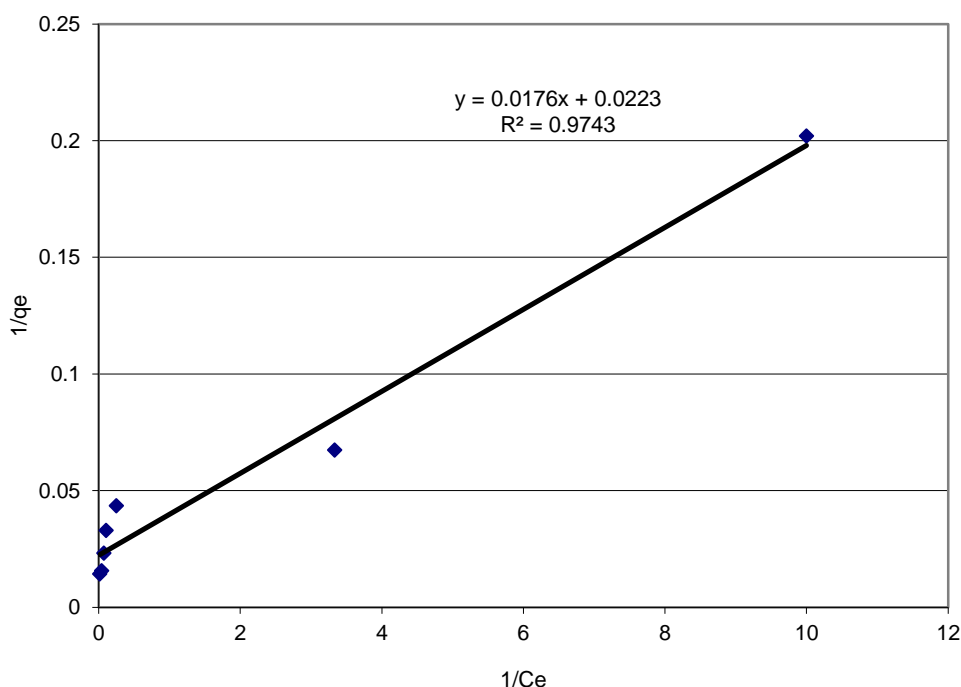
**b** Monolayer coverage, mg of heavy metal/gm of adsorbent



The equilibrium data resulted from the batch equilibrium experiment runs were fitted with Langmuir Isotherm model. The Langmuir adsorption of heavy metals parameters are shown in Table 19 to Table 21. Also, Figure 33 through Figure 35 depicts the linear plot of Langmuir equation and the adsorption parameters are summarized in Table 22. As shown in Table 22, the removal rate and the strength of adsorption is in the order Pb> Cu>Cd.

**Table 19: Langmuir Isotherm for Pb(II) ion using CKD**

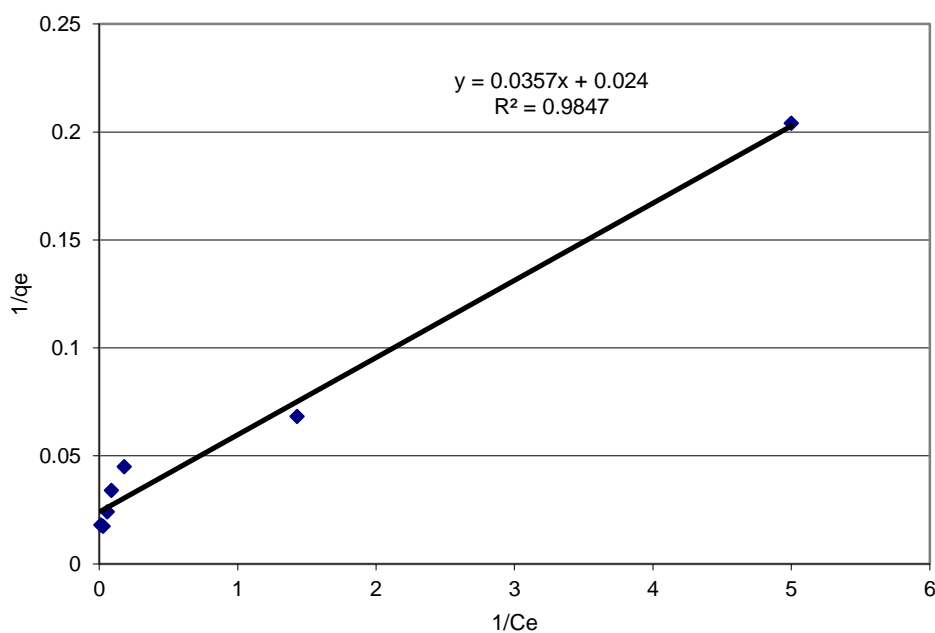
Mass (gm)	Initial Conc. (C <sub>i</sub> ) (mg/l)	Final Conc. (C <sub>e</sub> ) (mg/l)	Volume (L)	q <sub>e</sub> (mg/gm)	1/C <sub>e</sub>	1/Q <sub>e</sub>	C <sub>e</sub> /q <sub>e</sub> (gm/l)
0.1	10	0.1	0.05	4.95	10	0.20202	0.02
0.1	30	0.3	0.05	14.85	3.333333	0.06734	0.02
0.1	50	4	0.05	23	0.25	0.043478	0.17
0.1	70	9.35	0.05	30.325	0.106952	0.032976	0.31
0.1	100	13.553	0.05	43.2235	0.073784	0.023136	0.31
0.1	150	22.2	0.05	63.9	0.045045	0.015649	0.35
0.1	200	60.01	0.05	69.995	0.016664	0.014287	0.86



**Figure 33: Langmuir Isotherm for the Adsorption of Pb (II) using CKD**

**Table 20: Langmuir Isotherm for CuII ion using CKD**

Mass (gm)	Initial Conc. (C <sub>i</sub> ) (mg/l)	Final Conc. (C <sub>e</sub> ) (mg/l)	Volume (L)	q <sub>e</sub> (mg/gm)	1/C <sub>e</sub>	1/Q <sub>e</sub>	C <sub>e</sub> /q <sub>e</sub> (gm/l)
0.1	10	0.2	0.05	4.9	5	0.204082	0.04
0.1	30	0.7	0.05	14.65	1.428571	0.068259	0.05
0.1	50	5.5	0.05	22.25	0.181818	0.044944	0.25
0.1	70	11.2	0.05	29.4	0.089286	0.034014	0.38
0.1	100	17	0.05	41.5	0.058824	0.024096	0.41
0.1	150	35	0.05	57.5	0.028571	0.017391	0.61
0.1	200	89	0.05	55.5	0.011236	0.018018	1.60



**Figure 34: Langmuir Isotherm for the Adsorption of Cu (II) using CKD**

**Table 21: Langmuir Isotherm for adsorption of Cd (II) ion using CKD**

Mass (gm)	Initial Conc. (C <sub>i</sub> ) (mg/l)	Final Conc. (C <sub>e</sub> ) (mg/l)	Volume (L)	q <sub>e</sub> (mg/gm)	1/C <sub>e</sub>	1/Q <sub>e</sub>	C <sub>e</sub> /q <sub>e</sub> (gm/l)
0.1	10	0.9	0.05	4.55	1.111111	0.21978	0.20
0.1	30	1.8	0.05	14.1	0.555556	0.070922	0.13
0.1	50	9.1	0.05	20.45	0.10989	0.0489	0.44
0.1	70	13.5	0.05	28.25	0.074074	0.035398	0.48
0.1	100	22	0.05	39	0.045455	0.025641	0.56
0.1	150	45	0.05	52.5	0.022222	0.019048	0.86
0.1	200	98	0.05	51	0.010204	0.019608	1.92

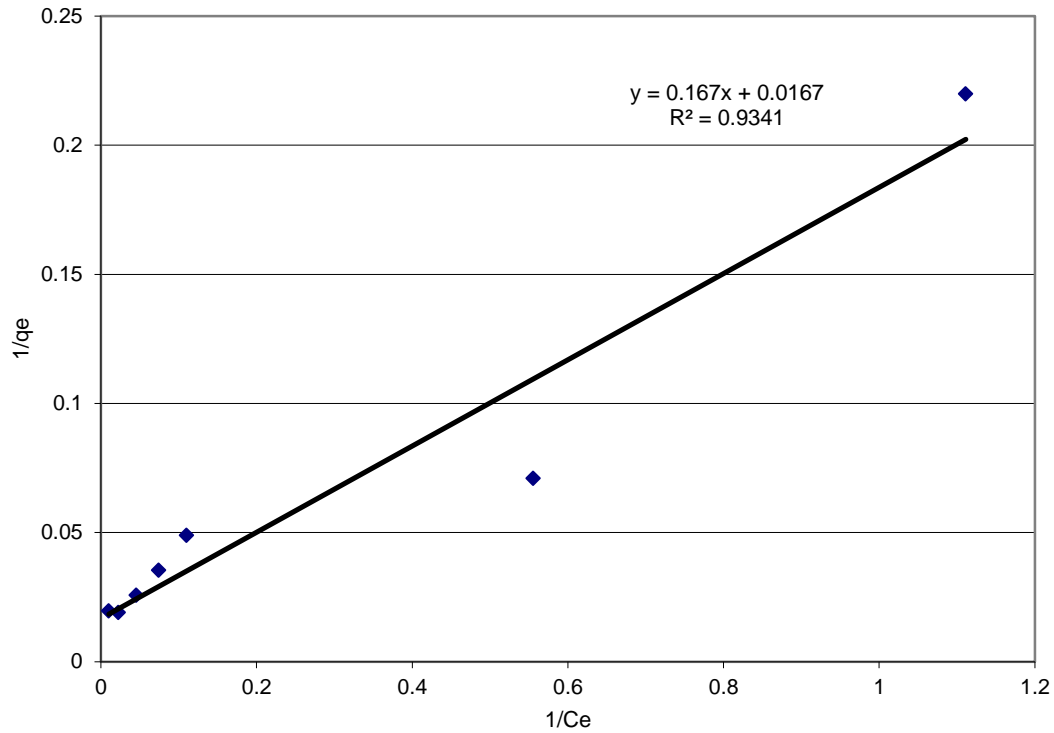


Figure 35: Langmuir Isotherm for the Adsorption of Cd (II) using CKD

Table 22: Langmuir Isotherm Parameters for Heavy Metal Adsorption by CKD

Heavy Metal	1/b	1/ab	R <sup>2</sup>
Lead (Pb II)	0.022	0.017	0.974
Copper (Cu II)	0.024	0.035	0.984
Cadmium (Cd II)	0.016	0.167	0.934

#### 4.6.2 Freundlich Isotherm

Freundlich Isotherm is the best known and most utilized isotherm for the adsorption of a solute from an aqueous phase (Ho, 2004). The Freundlich equation is as follows:

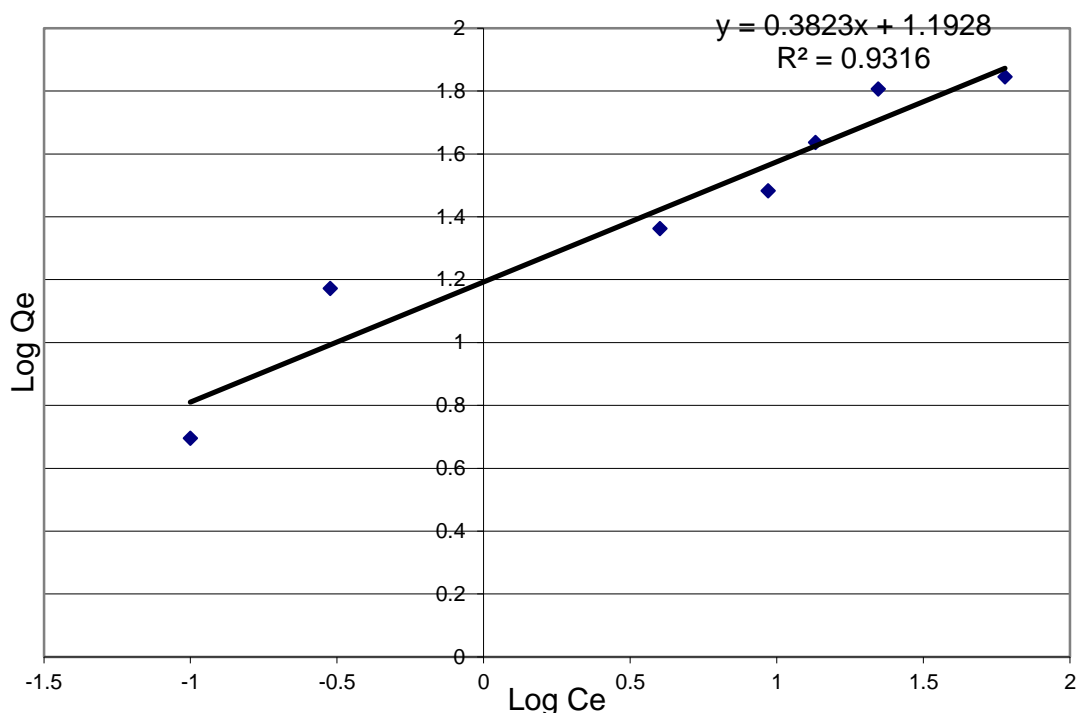
$$\text{Log } q_e = \text{Log } K_f + \frac{1}{n} \text{Log } C_e$$

Where  $K_f$  and  $n$  are Freundlich constants which integrate all factors affecting the adsorption process, such as adsorption capacity and intensity of adsorption

The equilibrium data resulted from the batch equilibrium experiment runs were fitted with Freundlich Isotherm model. The Freundlich adsorption isotherm of heavy metals ions using CKD are shown in Table 23 to Table 25. Figure 36 through Figure 38 show the linear plot of Freundlich equation and the adsorption parameters calculated from these figures are summarized in Table 26. Since  $K_f$  and  $1/n$  are measurements for the adsorption rate and strength, it is concluded that the removal strength of adsorption is in the order  $Pb > Cu > Cd$ .

**Table 23: Freundlich Adsorption Isotherm of Pb (II) Ion using CKD**

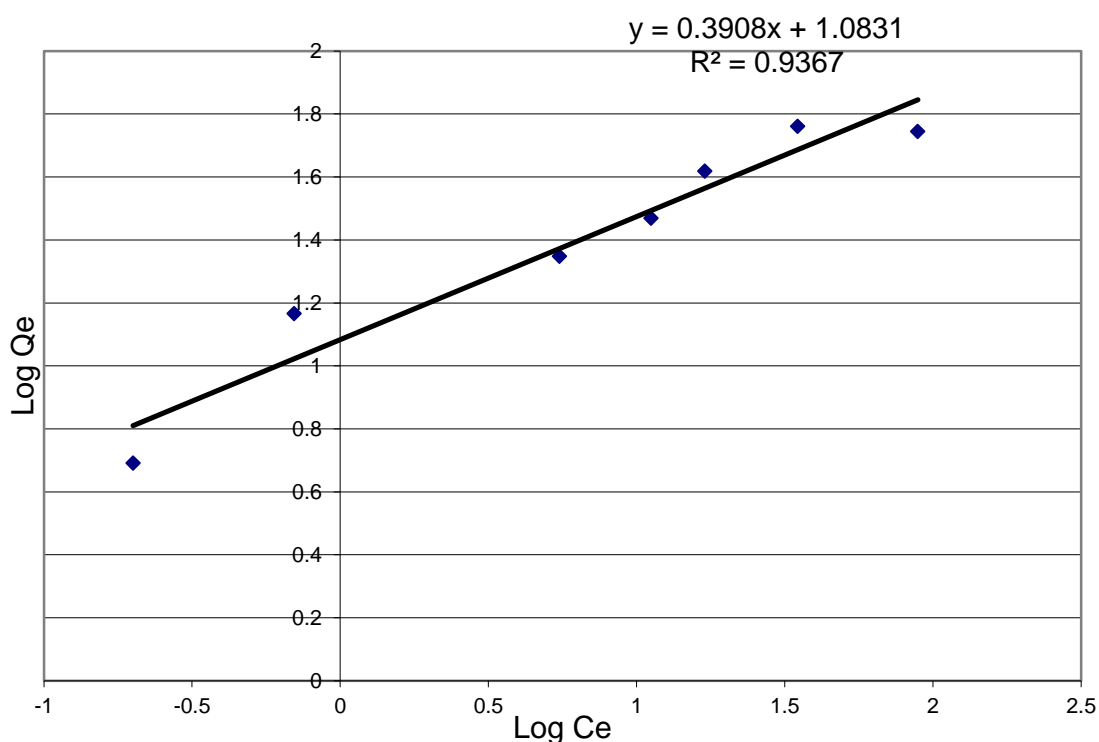
Mass (gm)	Initial Conc. (C <sub>i</sub> ) (mg/l)	Final Conc. (C <sub>e</sub> ) (mg/l)	Volume (L)	Q <sub>e</sub> (mg/gm)	Log C <sub>e</sub>	Log Q <sub>e</sub>
0.1	10	0.1	0.05	4.95	-1	0.694605
0.1	30	0.3	0.05	14.85	-0.52288	1.171726
0.1	50	4	0.05	23	0.60206	1.361728
0.1	70	9.35	0.05	30.325	0.970812	1.481801
0.1	100	13.553	0.05	43.2235	1.132035	1.63572
0.1	150	22.2	0.05	63.9	1.346353	1.805501
0.1	200	60.01	0.05	69.995	1.778224	1.845067



**Figure 36: Freundlich Adsorption Isotherm for Pb(II) Ion Adsorption**

**Table 24: Freundlich Adsorption Isotherm of Cu (II) Ion using CKD**

Mass (gm)	Initial Conc. (C <sub>i</sub> ) (mg/l)	Final Conc. (C <sub>e</sub> ) (mg/l)	Volume (L)	Q <sub>e</sub> (mg/gm)	Log C <sub>e</sub>	Log Q <sub>e</sub>
0.1	10	0.2	0.05	4.9	-0.69897	0.690196
0.1	30	0.7	0.05	14.65	-0.1549	1.165838
0.1	50	5.5	0.05	22.25	0.740363	1.34733
0.1	70	11.2	0.05	29.4	1.049218	1.468347
0.1	100	17	0.05	41.5	1.230449	1.618048
0.1	150	35	0.05	57.5	1.544068	1.759668
0.1	200	89	0.05	55.5	1.94939	1.744293



**Figure 37: Freundlich Adsorption Isotherm for Cu (II) Ion Adsorption**

**Table 25: Freundlich Adsorption Isotherm of Cd (II) Ion using CKD**

Mass (gm)	Initial Conc. (C <sub>i</sub> ) (mg/l)	Final Conc. (C <sub>e</sub> ) (mg/l)	Volume (L)	Q <sub>e</sub> (mg/gm)	Log C <sub>e</sub>	Log Q <sub>e</sub>
0.1	10	0.9	0.05	4.55	-0.04576	0.658011
0.1	30	1.8	0.05	14.1	0.255273	1.149219
0.1	50	9.1	0.05	20.45	0.959041	1.310693
0.1	70	13.5	0.05	28.25	1.130334	1.451018
0.1	100	22	0.05	39	1.342423	1.591065
0.1	150	45	0.05	52.5	1.653213	1.720159
0.1	200	98	0.05	51	1.991226	1.70757

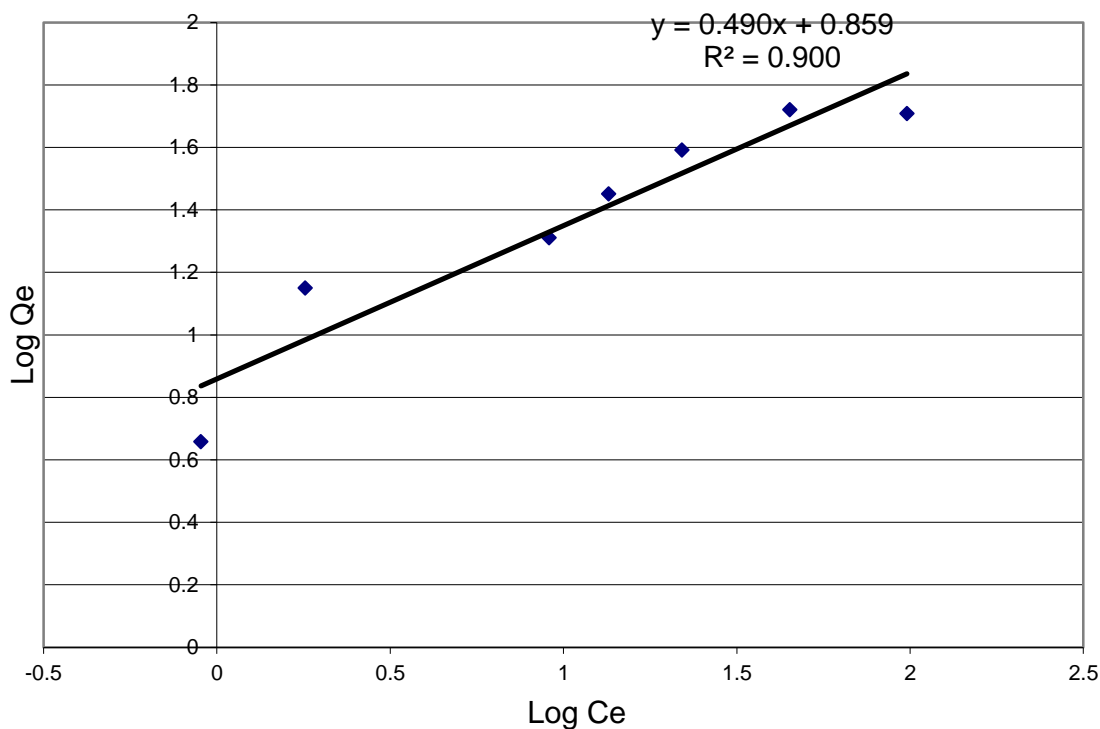


Figure 38: Freundlich Adsorption Isotherm for Cd (II) Ion Adsorption

Table 26: Freundlich Adsorption Parameters using CKD

Heavy Metal	Log $K_f$	1/n	$R^2$
Lead (Pb II)	1.192	0.382	0.931
Copper (Cu II)	1.083	0.39	0.936
Cadmium (Cd II)	0.859	0.49	0.900

#### 4.7 Computational Modeling

The surface titration data was used in the triple-layer surface complexation model (TL-SCM) in order to determine the equilibrium constants of CKD. These constants were used further to identify the adsorption equilibrium constants for the different heavy metals. The main objective of the computational model is to determine the adsorption capacity and behavior of the CKD in order to be used in designing full scale model units. The simulation of the adsorption mechanism is important to verify the performance of CKD and to facilitate the design of adsorption units. The computational model was conducted using FITEQL 4.0 software package. FITEQL 4.0 is a non-linear least-squares

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optimization model developed by John C. Westall of the Oregon State University (Herbelin and Westall, 1999). FITEQL is used to determine chemical equilibrium constants from experimental data and it mainly contains of the Diffuse Layer model, the Stern model and the Triple Layer Model. The former offers the advantage of accounting for ionic strength effects on aqueous-surface interactions in addition to both chemical and electrostatic interactions (Chen and Lin, 2004). The TLM can consider inner layer ( $\alpha$ -plane) and outer layer ( $\beta$ -plane) surface complexes with adsorbable and electrolyte species in addition to diffuse layer interactions as in conventional double-layer theory (Hizal, 2006). Mathematical depiction of the TLM includes mass balances, charge balances, and surface equilibrium equations as follows:

- Mass balances for the electrolyte species, assuming  $\text{NaNO}_3$  background as in experimental runs, are:

$$C_{T, \text{NO}_3^-} = [\text{NO}_3^-] + [>\text{SOH}_2^+ - \text{NO}_3^-]$$

$$C_{T, \text{Na}^+} = [\text{Na}^+] + [>\text{SO}^- - \text{Na}^+]$$

- Surface site balance, considering an inner layer, the surface complex for an adsorbed divalent metal species,  $\text{Me}^{2+}$ , is:

$$C_{T, \text{SO}^-} = [>\text{SOH}_2^+] + [>\text{SOH}] + [>\text{SO}^-] + [>\text{SO}^- - \text{Na}^+] + [>\text{SOH}_2^+ - \text{NO}_3^-] + [>\text{SOMe}^+]$$

- Total soluble  $\text{Me(II)}$  mass balance for the equilibrium condition is:

$$C_{T, \text{Me(II)(sol)}} = [\text{Me}^{2+}] + [\text{MeOH}^+] + [\text{Me(OH)}_2^0] + [\text{Me(OH)}_3^-] + \dots$$

- The inner layer charge balance equates total adsorbed concentrations in the inner layer with the total charges in the  $\alpha$ -plane. For inner layer adsorbed complex:

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$$[> \text{SOH}_2^+] + [> \text{SOH}_2^+ - \text{NO}_3^-] + [> \text{SOMe}^+] - [> \text{SO}^-] - [> \text{SO}^- - \text{Na}^+] = \frac{S_C S_A}{F} C_1 (\psi_o - \psi_\beta)$$

Where;  $S_C$  is the concentration of solid (g/L),  $S_A$  is surface area of the adsorbent,  $F$  = Faraday constant (coulombs/mole),  $C_1$  is inner-layer capacitance (F/m<sup>2</sup>), and  $\psi_i$  = the average electrostatic potential (volt) at the  $o$ - and  $\beta$ -plane, respectively (Sreejalekshmi *et al.*, 2009).

- The analogous outer layer charge balance is:

$$[> \text{SO}^- - \text{Na}^+] - [> \text{SOH}_2^+ - \text{NO}_3^-] = \frac{S_C S_A}{F} [C_1 (\psi_\beta - \psi_o) + C_2 (\psi_\beta - \psi_d)]$$

Where;  $C_2$  is outer-layer capacitance (F/m<sup>2</sup>), and  $\psi_d$  = the average electrostatic potential (volt) in the diffuse layer.

- The charge balance for the diffuse layer is:

$$C_2 (\psi_d - \psi_\beta) = 0.1174 \sqrt{I} \sinh\left(\frac{F \psi_d}{2RT}\right)$$

Where;  $R$  = universal gas constant (cal/°K·mole),  $T$  = absolute temperature (°K), and  $I$  = ionic strength (mol/L)

- The metal-hydrolysis mass law expressions:

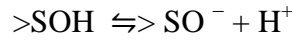
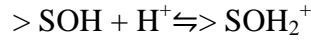
$$K_{n, \text{hydrolysis}} = \frac{[\text{Me}(\text{OH})_n^{2-n}][\text{H}^+]}{[\text{Me}^{2+}]}$$

- Metal ion adsorption from aqueous solution is assumed to occur at functional group sites on the surface of cement kiln dust. The predominant adsorption sites



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for this case are assumed to be  $>\text{SOH}_2^+$ ,  $>\text{SOH}$ , and  $>\text{SO}^-$ . The following protolysis reactions describe the acid-base chemistry of the surface:



Where; the surface species  $>\text{SOH}_2^+$ ,  $>\text{SOH}$ , and  $>\text{SO}^-$  can acquire protons in solution.

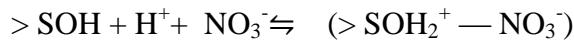
- TL-SCM expressions for the equilibrium constants are:

$$K_{s1} = \frac{[>\text{SOH}_2^+]}{[>\text{SOH}][\text{H}^+]} \exp(F\psi_0 / RT)$$

$$K_{s2} = \frac{[>\text{SO}^-][\text{H}^+]}{[>\text{SOH}]} \exp(-F\psi_0 / RT)$$

Where;  $K_{s1}$  and  $K_{s2}$  are equilibrium constants for the respective surface protolysis reactions, and  $F$ ,  $R$ ,  $T$ , and  $\psi_0$  are as defined previously (Sreejalekshmi *et al.*, 2009).

- Interactions of electrolyte ions with the surface species are according to the following reactions in correspondence to the equilibrium expressions:



$$K_{E1} = \frac{[>\text{SOH}_2^+ - \text{NO}_3^-]}{[>\text{SOH}][\text{H}^+][\text{NO}_3^-]} \exp[-F(\psi_\beta - \psi_0) / RT]$$

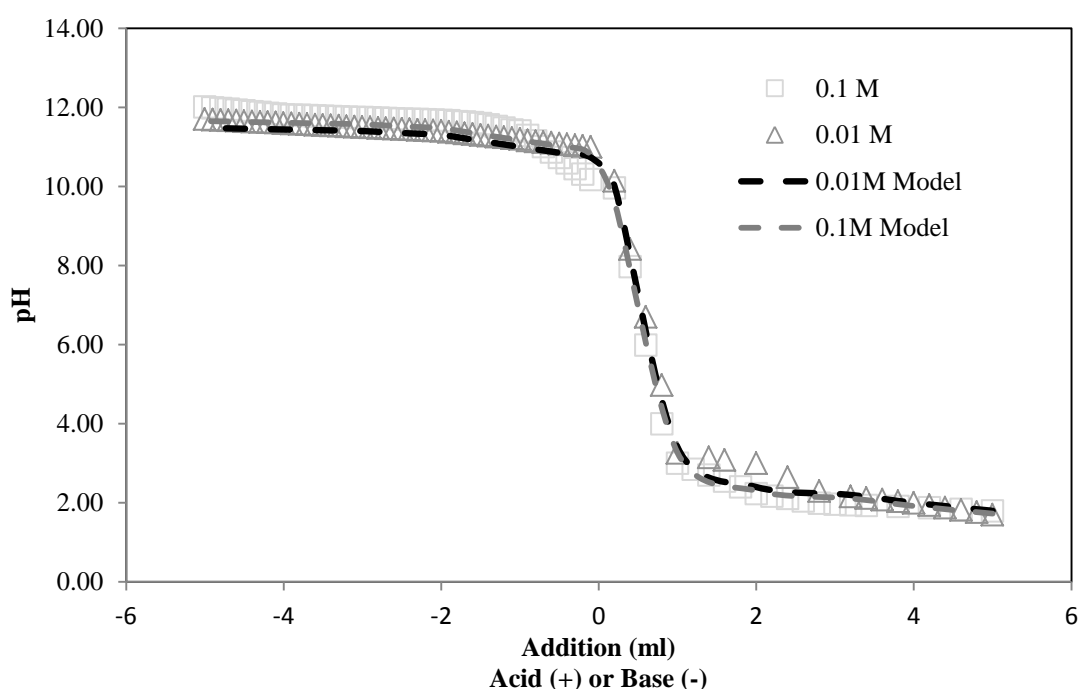


$$K_{E2} = \frac{[>\text{SO}^- - \text{Na}^+][\text{H}^+]}{[>\text{SOH}][\text{Na}^+]} \exp[-F(\psi_0 - \psi_\beta) / RT]$$

Where;  $\psi_\beta$  = the average potential (volt) of the outer, or  $\beta$ , plane. Model calculations also required the surface area of the sorbent ( $\text{m}^2/\text{g}$ ), surface site density ( $\text{sites}/\text{nm}^2$ ) and linear charge potential ( $\text{F}/\text{m}^2$ ).

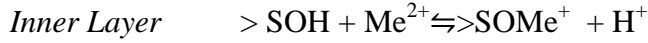
Figure 39 shows the potentiometric data plot at two ionic strengths compared to the TL-SCM simulations. The pH of zero charge is  $\sim 10.0$ . The  $\log K_i$  values are:

$$\text{Log } K_{S1} = 1.6 \quad \log K_{S2} = -2.8 \quad \log K_{E1} = 3.50 \quad \log K_{E2} = -5.30$$

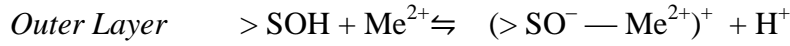


**Figure 39: Potentiometric Titration Data and TL-SCM Simulation for Cement Kiln Dust using FITEQL 3.1**

For heavy metals adsorption, the hydrolysis and precipitation of  $\text{Me}(\text{II})$  hydroxides should be included in the analysis. It was obvious that significant lead precipitation occurs at pH as low as 6-7, while for copper from pH 7 to 8 and cadmium is at pH  $\sim 8$ . Therefore, the adsorption mechanism will take place at pH values less than the precipitation values. For all three target metals, the predominant aqueous species is  $\text{Me}^{2+}$  at these lower pH values. Therefore, the most likely adsorption reactions used in the TLM-SCM of adsorption equilibria were inner- and outer-layer complexes of  $\text{Me}^{2+}$  as follows:



$$K_{\text{ads},1} = \frac{[>\text{SOMe}^+][\text{H}^+]}{[>\text{SOH}][\text{Me}^{2+}]} \exp(F\phi_0 / RT)$$



$$K_{\text{ads},2} = \frac{[(>\text{SO}^- - \text{Me}^{2+})^+][\text{H}^+]}{[>\text{SOH}][\text{Me}^{2+}]} \exp[-F(\phi_0 - 2\phi_\beta) / RT]$$

Batch equilibrium pH adsorption edges are presented in Figure 40 to Figure 42 for Pb, Cu, and Cd respectively. Data are presented for CKD of 0 g/L and 2.0 g/L. The dashed curve (with associated precipitation data) in each figure represents the model calculation for metal hydroxide precipitation. Figure 40 to Figure 42 also indicate that substantial adsorption occurred at pH values less than those of precipitation. The adsorption equilibrium constants were determined by using the obtained  $\log K_{Si}$  and  $\log K_{Ei}$  constants. Adsorption equilibrium constants as well as those for metal hydrolysis and metal-hydroxide precipitation are listed in the following table (Table 27).

The adsorption obviously took place by electrostatic attraction of  $\text{Me}^{2+}$  cations to the CKD surface for  $\text{pH} < \text{pH}_{\text{zpc}}$  (10.0) where the sorbent surface charge is negative. However, for all three target metals there were notable removal of metal at approximately pH 5.5, indicating that surface complexation reactions are also important. It is difficult to determine whether heavy metal uptake at higher pH values is dominated by adsorption, precipitation, or a complex surface interaction. It is likely a combination of several processes that might occur simultaneously.

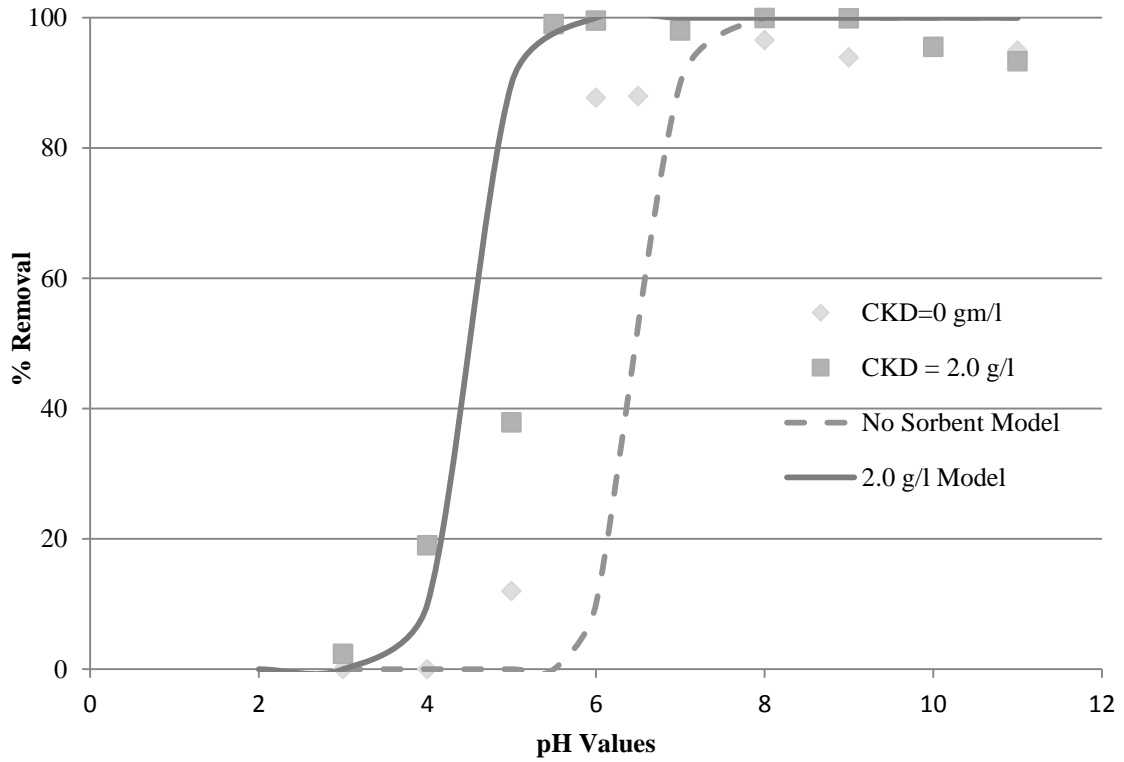


Figure 40: Pb(II) adsorption edges with TL-SCM

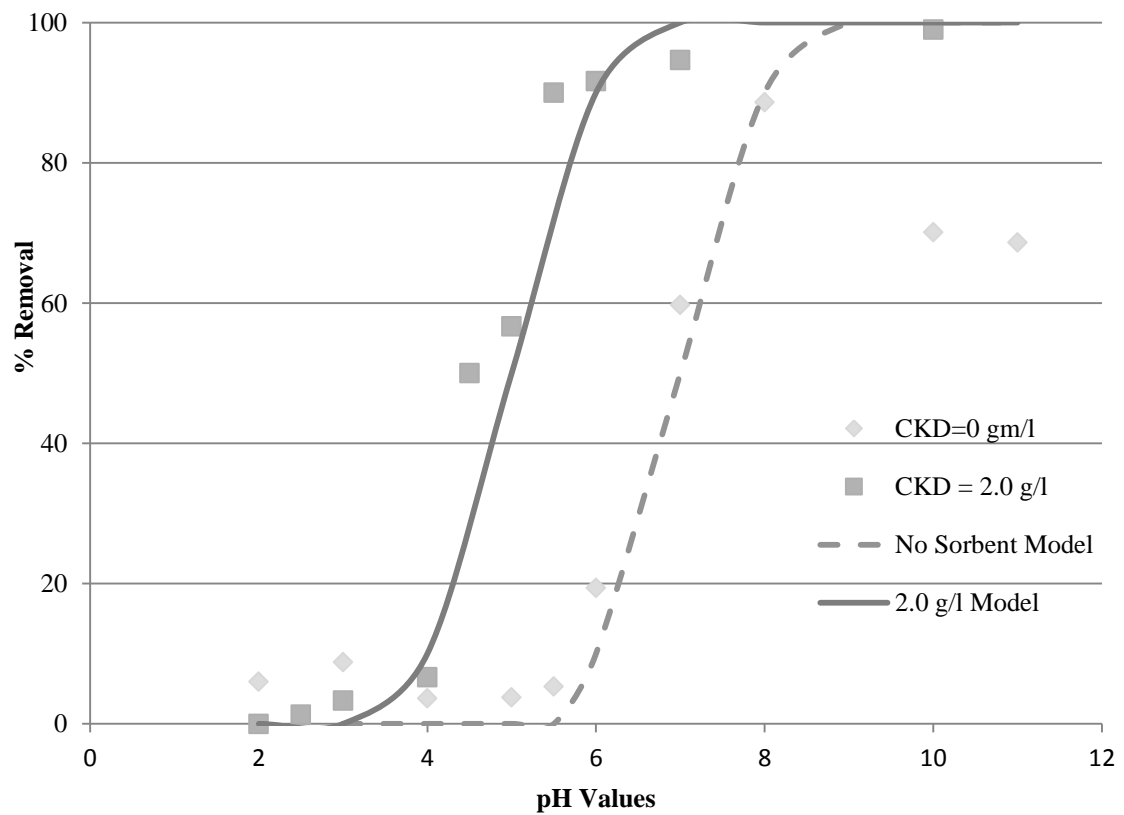


Figure 41: Cu (II) adsorption edges with TL-SCM

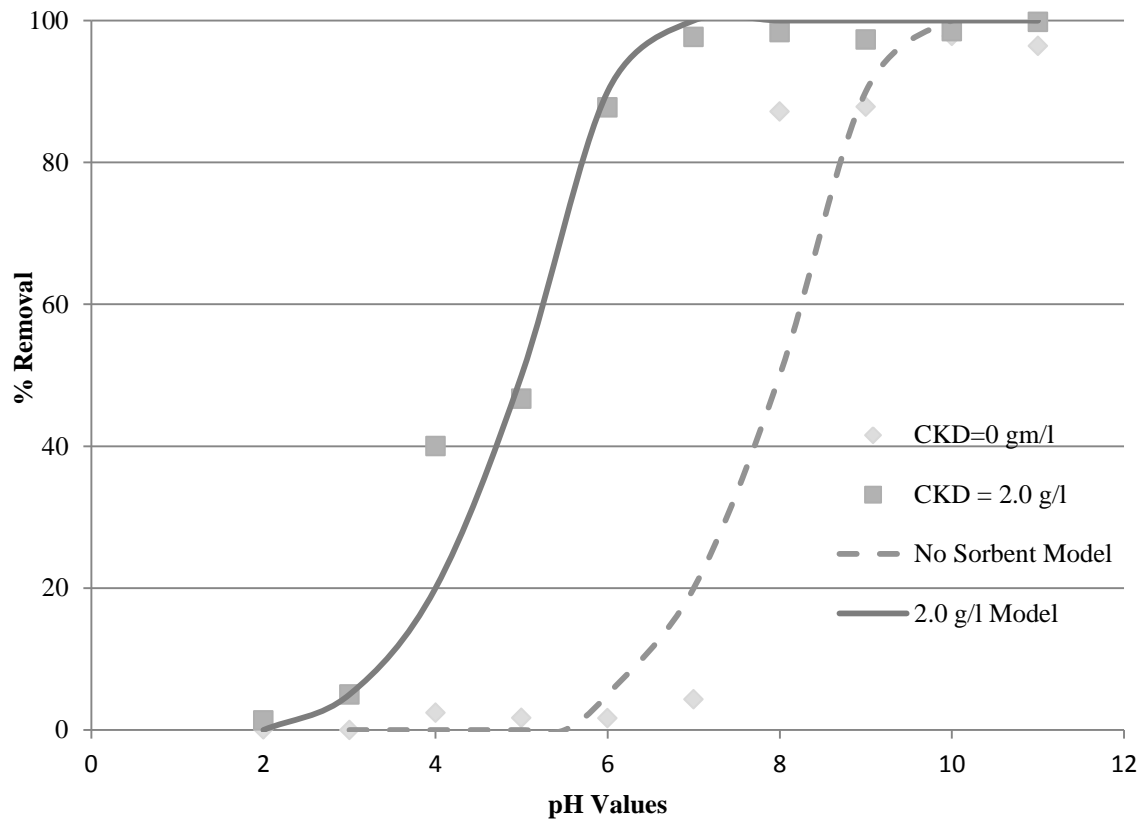


Figure 42: Cd (II) adsorption edges with TL-SCM

In terms of adsorption capacity in  $\mu\text{M/g}$  at given pH values between 5 and 6, the uptake capacity followed the trend of  $\text{Pb} > \text{Cu} > \text{Cd}$ , which is consistent with the electronegativity of these metals (1.854, 1.85, and 1.52 respectively).

Table 27: Equilibrium Constants for TL-SCM of Adsorption Edges

Reaction		Log K
<b>Lead</b>		
Hydrolysis:	$\text{Pb}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{PbOH}^+ + \text{H}^+$	-7.71
	$\text{Pb}^{2+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_2 + 2 \text{H}^+$	-17.12
	$\text{Pb}^{2+} + 3 \text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_3^- + 3 \text{H}^+$	-28.06
Solubility:	$\text{Pb}^{2+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_{2(\text{s})} + 2 \text{H}^+$	-12.80
Layer SC:	$> \text{SOH} + \text{Pb}^{2+} \rightleftharpoons > \text{SOPb}^+ + \text{H}^+$	<b>-1.80</b>
<b>Copper</b>		
Hydrolysis:	$\text{Cu}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CuOH}^+ + \text{H}^+$	-5.80

	$\text{Cu}^{2+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_2 + 2 \text{H}^+$	-14.80
	$\text{Cu}^{2+} + 3 \text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_3^- + 3 \text{H}^+$	-26.20
Solubility:	$\text{Cu}^{2+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_{2(\text{s})} + 2 \text{H}^+$	-12.70
Layer SC:	$> \text{SOH} + \text{Cu}^{2+} \rightleftharpoons (> \text{SO}^- - \text{Cu}^{2+})^+ + \text{H}^+$	<b>-1.88</b>
<b><i>Cadmium</i></b>		
Hydrolysis:	$\text{Cd}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CdOH}^+ + \text{H}^+$	-10.03
	$\text{Cd}^{2+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_2 + 2 \text{H}^+$	-20.35
	$\text{Cd}^{2+} + 3 \text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_3^- + 3 \text{H}^+$	-33.30
Solubility:	$\text{Cd}^{2+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_{2(\text{s})} + 2 \text{H}^+$	-18.60
Layer SC:	$> \text{SOH} + \text{Cd}^{2+} \rightleftharpoons (> \text{SO}^- - \text{Cd}^{2+})^+ + \text{H}^+$	<b>-3.20</b>

#### 4.8 Fourier Transform Infrared Spectroscopy (FTIR):

The FTIR experiment was conducted in order to determine the chemical bonds between the target heavy metals and the sorbent (CKD) by obtaining an infrared absorption spectrum before and after the metal adsorption. The chemical bonds in a molecule can be determined by interpreting the infrared absorption spectrum. As shown in Figure 43 to Figure 45, the FTIR analysis indicated that there is a difference in the band intensity and frequency of the main functional groups on the surface of the CKD. The outcome data was compared with the absorption peaks of known types of atomic bonds that are listed in the FTIR correlation tables. Table 28: The Type and Intensity of the Observed Chemical Bonds.

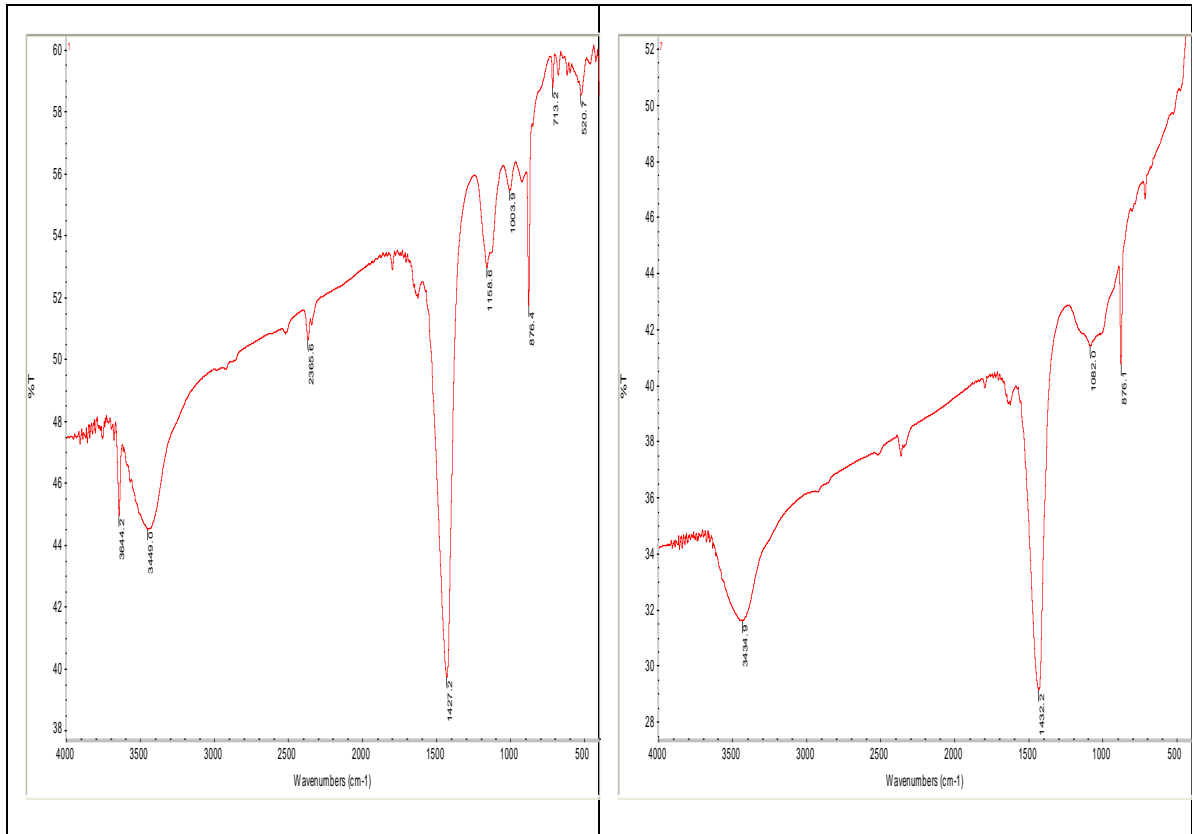


Figure 43: Comparison between CKD before and after Pb removal

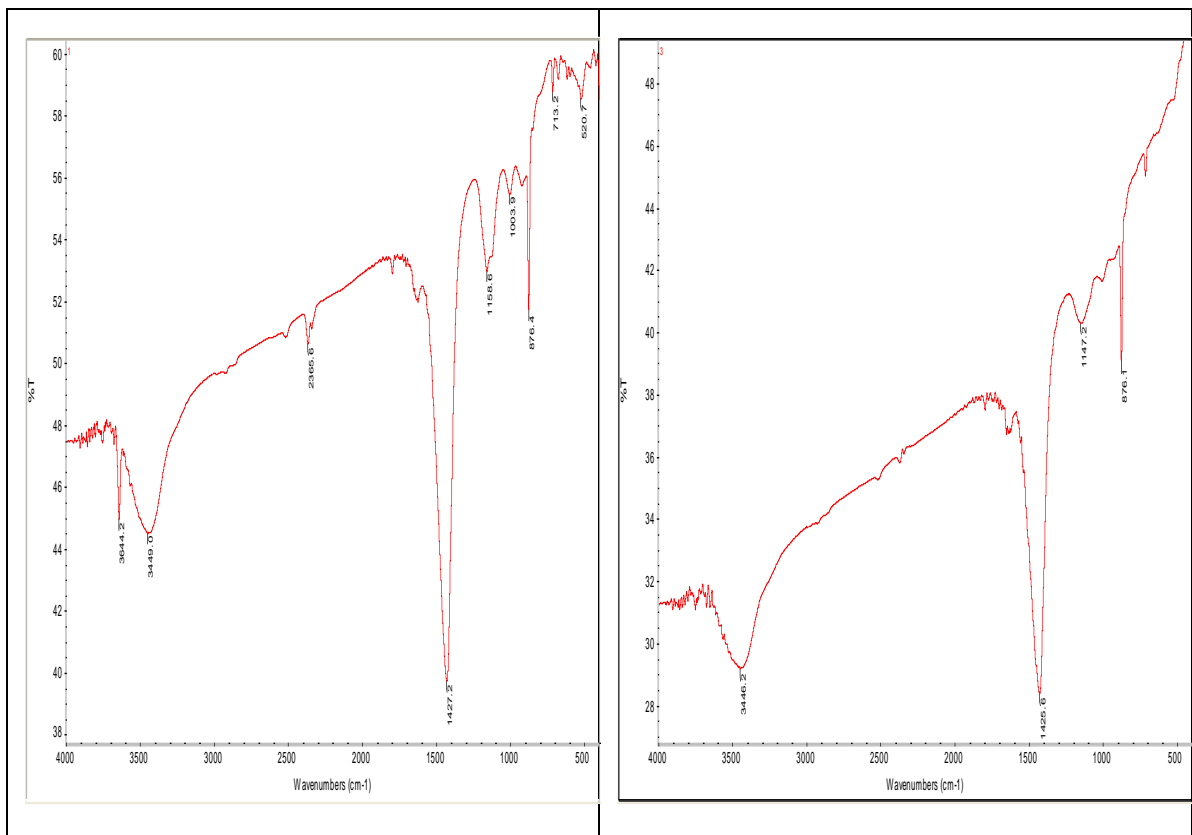


Figure 44: Comparison between CKD before and after Cu Removal

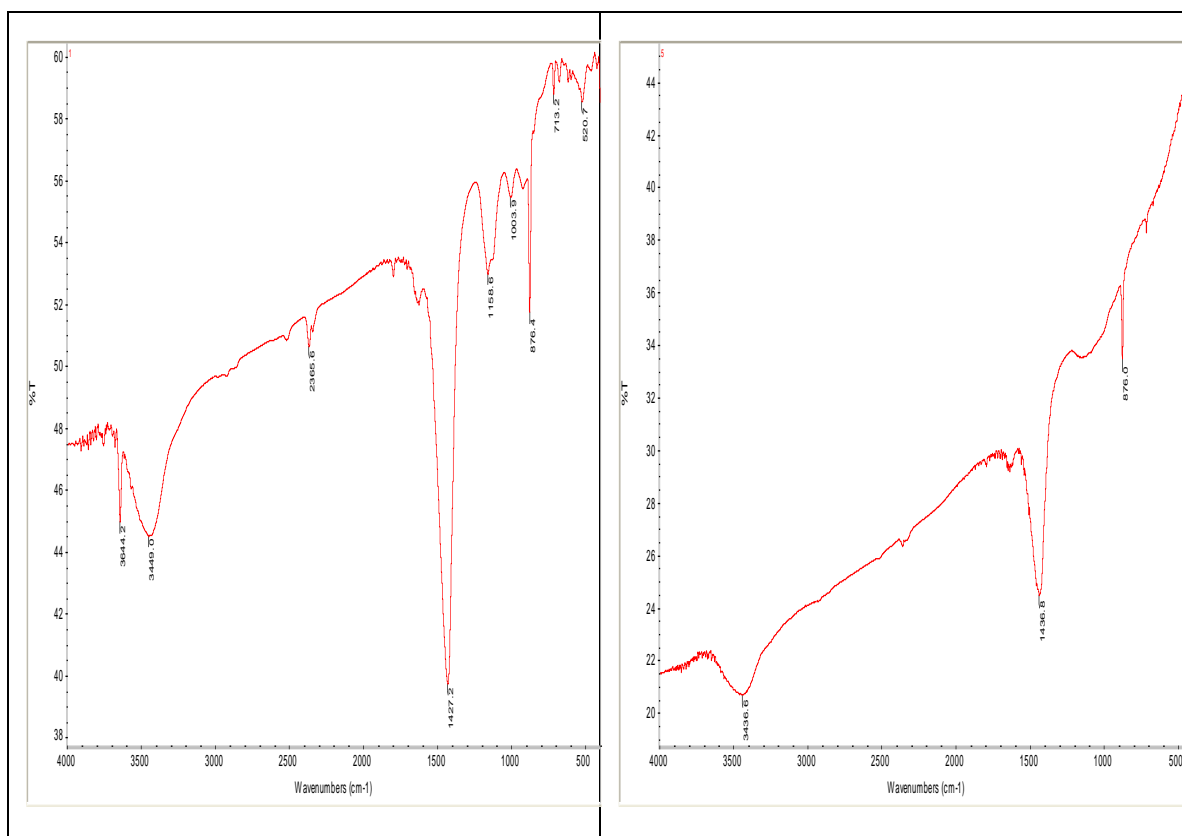


Figure 45: Comparison between CKD before and after Cd removal

Table 28: The Type and Intensity of the Observed Chemical Bonds

Characteristic Adsorption (Cm <sup>-1</sup> )	Bond	Type of Bond	Specific Type of Bond	Intensity
3434.9 (raw+all)	N-H	Primary Amines	Any	Strong
		Secondary Amines	Any	Weak to medium
3449.0	O-H	Carboxylic Acids	Low Concentration	-
	N-H	Primary Amines	Any	Strong
2365.6	N-H	Ammonium ions	Any	Multiple broad peaks
1432.2 (raw+all)	C-H	Alkyl	Methylene	Strong
1158.6	C-O	Alcohols	Tertiary	Medium
		Esters	Any	Two bands (distinct from ketones, which do not possess a C-O bond)
	C-N	Aliphatic Amines	Any	Often Overlapped



	C-X	Fluoroalkanes	Trifluoromethyl	Two strong, board bands
1003.9	C-X	Fluroalkanes	Ordinary	-
1082.0 (raw+all)	C-N	Aliphatic Amines	Any	Often Overlapped
	C-X	Fluoroalkanes	Ordinary	-
876.1(raw+all)	C-H	Aromatic	Meta-disub-benzene	Strong
713.2	C-H	Aromatic	Monosubstututed Benzene	Strong
520.7	C-X	Bromoalkanes	Any	Medium to Strong

#### 4.9 Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX)

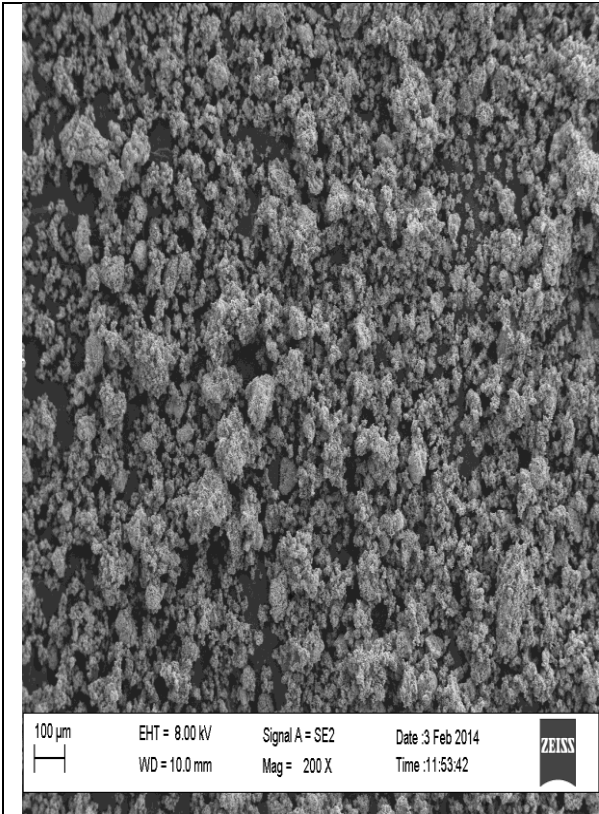
Electron micrographs with different magnifications were taken from Scanning Electron Microscope (SEM) to make a comparison between the cell wall appearance before and after heavy metals uptake. Figure 46 to Figure 50 represent the SEM photo – micrographs with different magnifications (from 200X up to 10.0 KX) of the native CKD and the CKD after 30 mg/l metal adsorption for the three target heavy metals, namely lead, copper, and cadmium. The micrograph of native CKD (raw CKD) indicates the presence of net of pores on its surface layer, and there was no defined metal ion in these pores. This was also investigated by the Energy Dispersive X-Ray (EDX) microanalysis. On the other hand, the electron dens spots (white spots) throughout the CKD wall were observed in micrograph of the sorbent after metal adsorption at the same magnification. This indicates that there is likely co-precipitation of the metals that have formed and attached at the outer surface pores. This was also investigated by the EDX analysis. This result indicated that, the physical adsorption mechanism is one of the possible mechanisms that could happen in metal adsorption by CKD. This hypothesis was confirmed through the good fitting of Langmuir adsorption isotherm model which proves that the adsorption of metal ion by CKD could be characterized as a monolayer.

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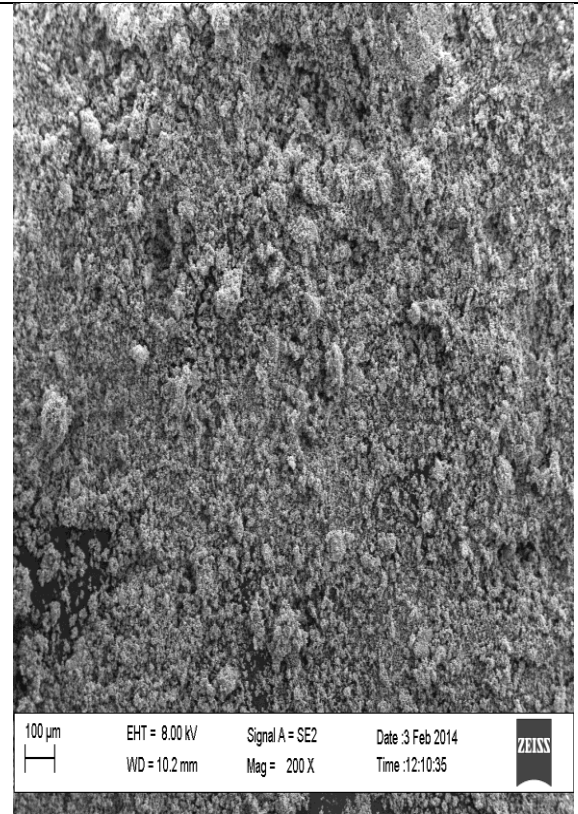
The Energy dispersive X-ray microanalysis (EDX) is useful for the study of the chemical and elemental characteristics of the adsorbent. It was reported that metal ions in adsorption systems are divided into two classes; the first class consists of ions such as  $K^+$ ,  $Na^+$ ,  $Mg^{+2}$ , and  $Ca^{+2}$ , which are found in relatively high concentrations in the CKD. These ions are important in maintaining the structure of proteins by neutralizing the negative charges of hydroxyl chains, and in controlling the function of cell membranes which selectively pass certain molecules (Saad, 2008).

The CKD was subjected to EDX analysis before and after metal adsorption. The EDX spectra of raw CKD is shown in Figure 51 and for lead, copper, cadmium exposed CKD are shown in Figure 52, Figure 53, and Figure 54 respectively.

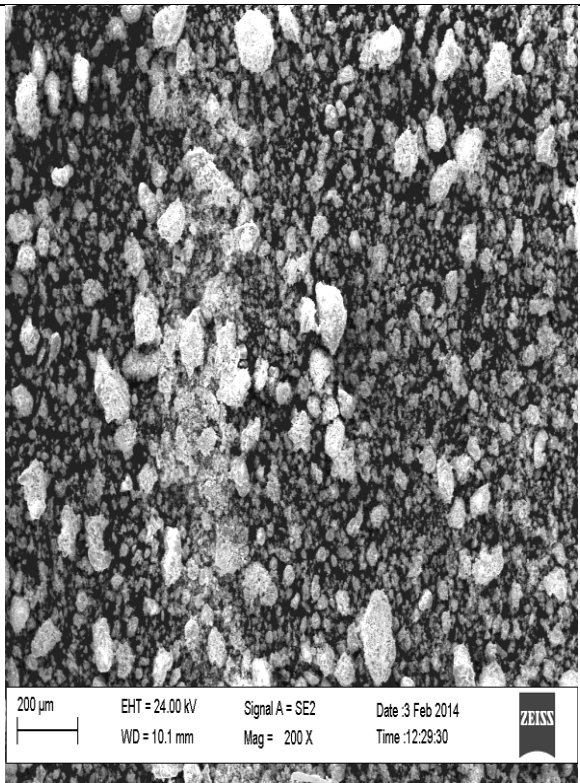
As shown in Figure 51 the EDX spectrum of the raw CKD showed peaks of  $Na^+$ ,  $Al^{+2}$ ,  $Si^{+4}$ ,  $Cl^+$ ,  $K^+$ ,  $Ca^{+2}$ ,  $Fe^{+3}$ , and  $Mo^+$  with different ratios. After lead adsorption, lead peak was observed on the spectrum, while  $Al^{+2}$ ,  $Si^{+4}$ ,  $Cl^+$ ,  $K^+$ ,  $Fe^{+3}$  and  $Mo^+$  peaks disappeared as shown in Figure 52. This indicates that lead ions replaced these elements on the cell wall of CKD. The same phenomenon was observed for both copper and cadmium adsorption, but with different metal ions replacements as shown in Figure 53 and Figure 54 respectively. This result indicated that, the ion exchange mechanism is one of the possible mechanisms that could happen in metal adsorption.



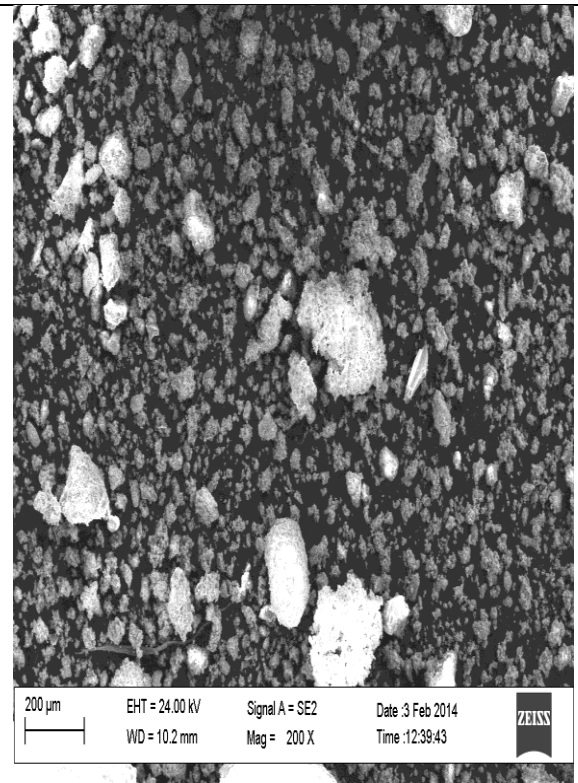
(Raw)



(After Lead)

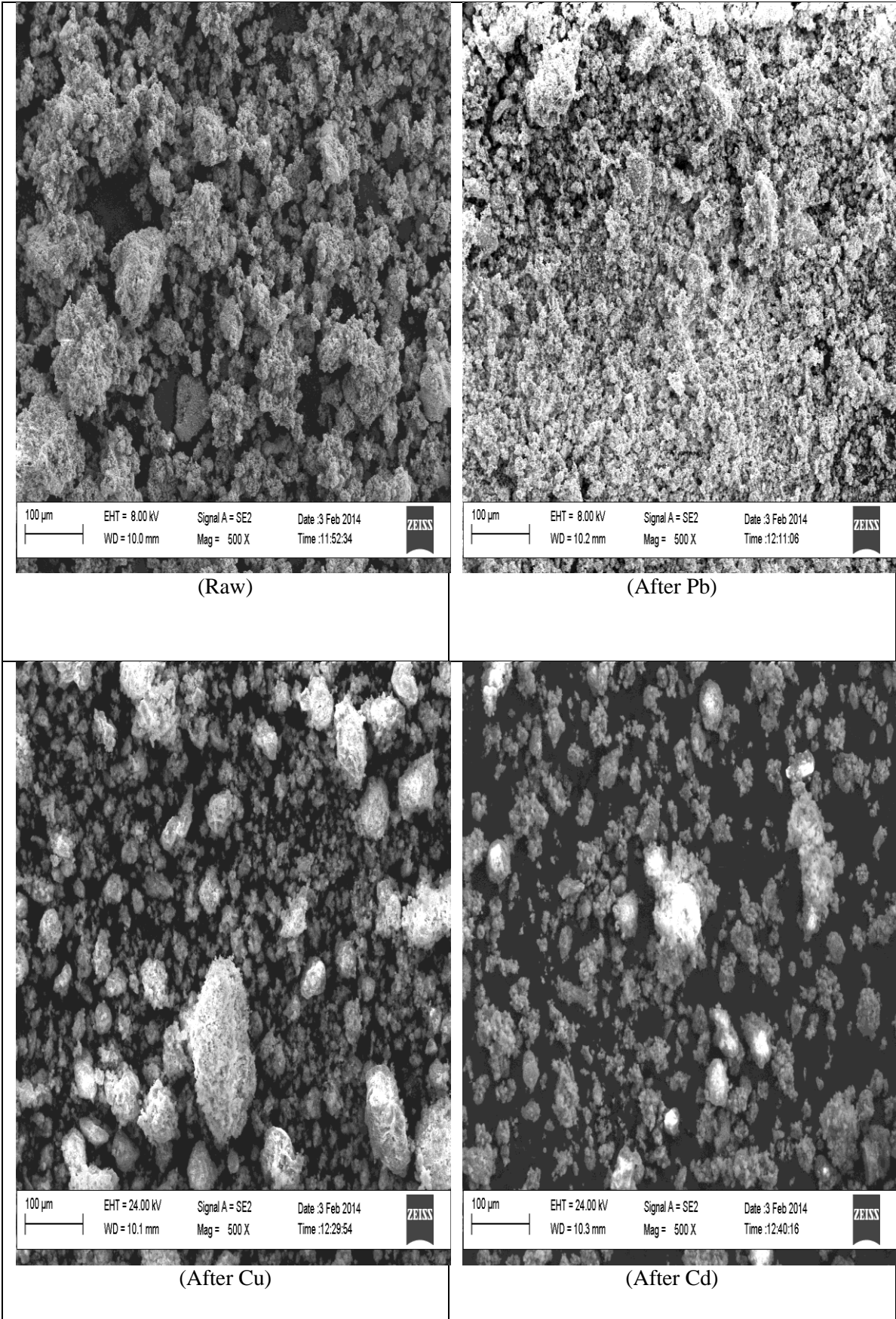


(After Cu)

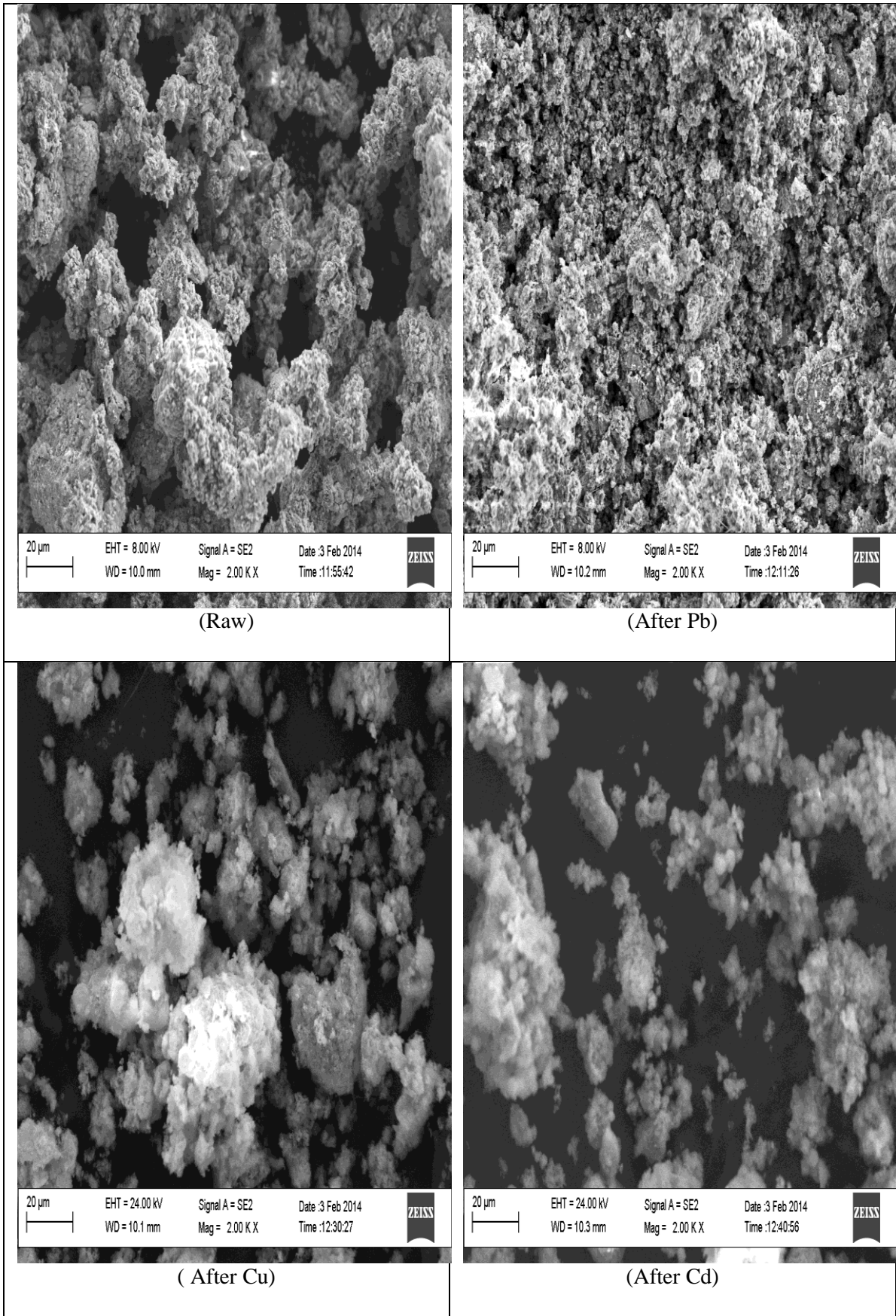


(After Cd)

Figure 46: Comparison between Native CKD and after Metal Adsorption at 200X Magnification

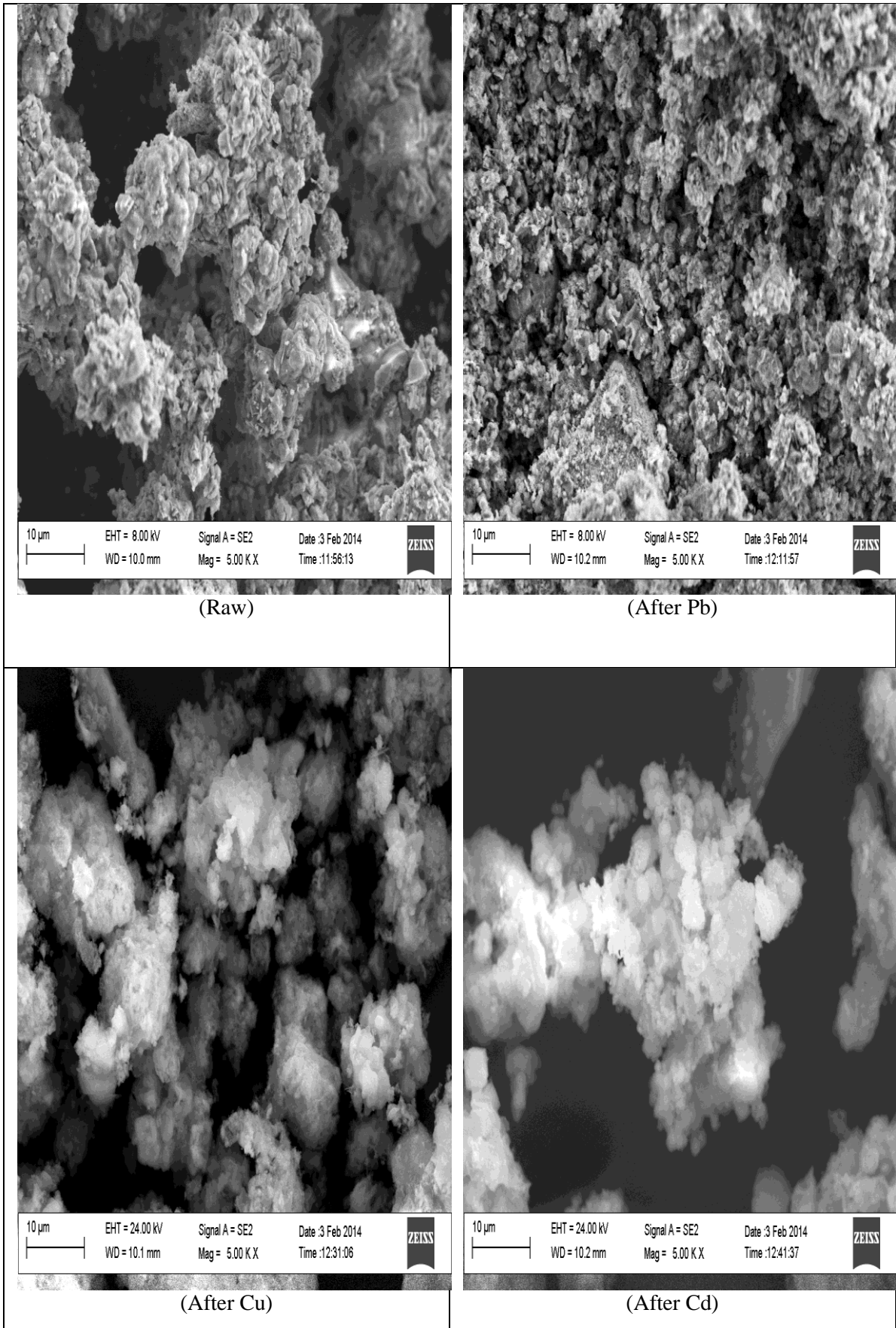


**Figure 47: Comparison between Native CKD and after Metal Adsorption at 500 X Magnification**

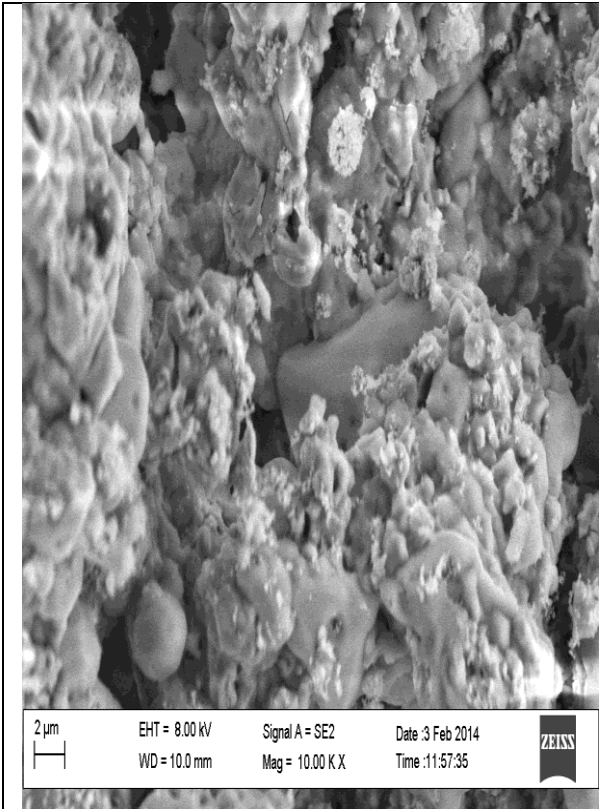


**Figure 48: Comparison between Native CKD and after Metal Adsorption at 2.00 KX Magnification**

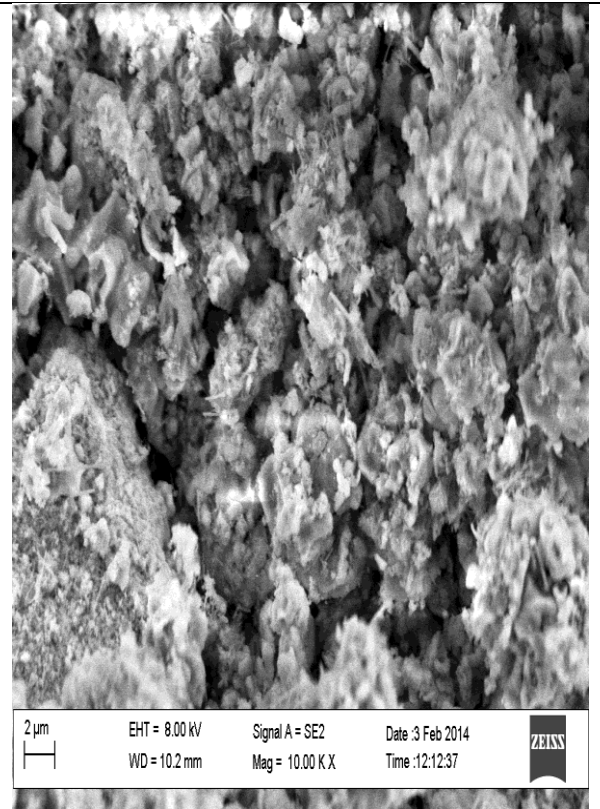




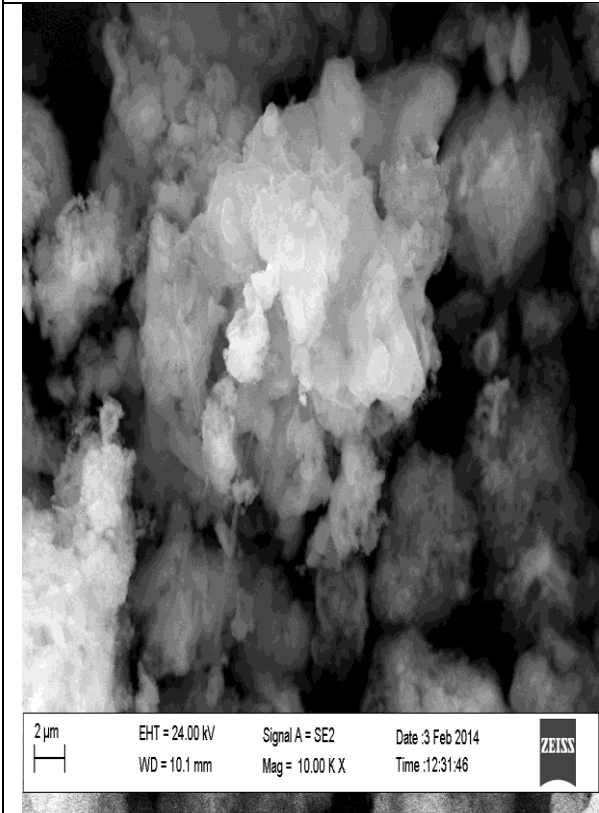
**Figure 49: Comparison between Native CKD and after Metal Adsorption at 5.00 X Magnification**



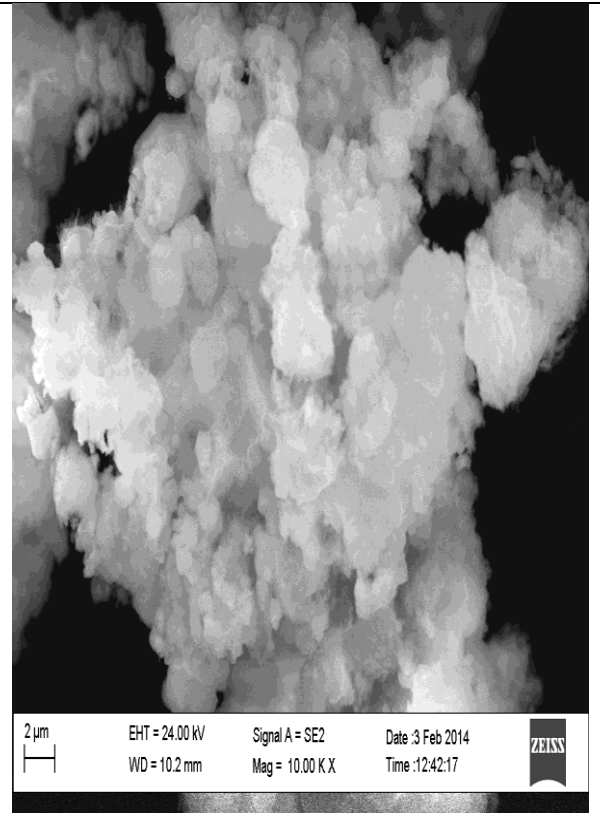
(Raw)



(After Pb)



(After Cu)



(After Cd)

**Figure 50: Comparison between Native CKD and after Metal Adsorption at 10.0 kX Magnification**

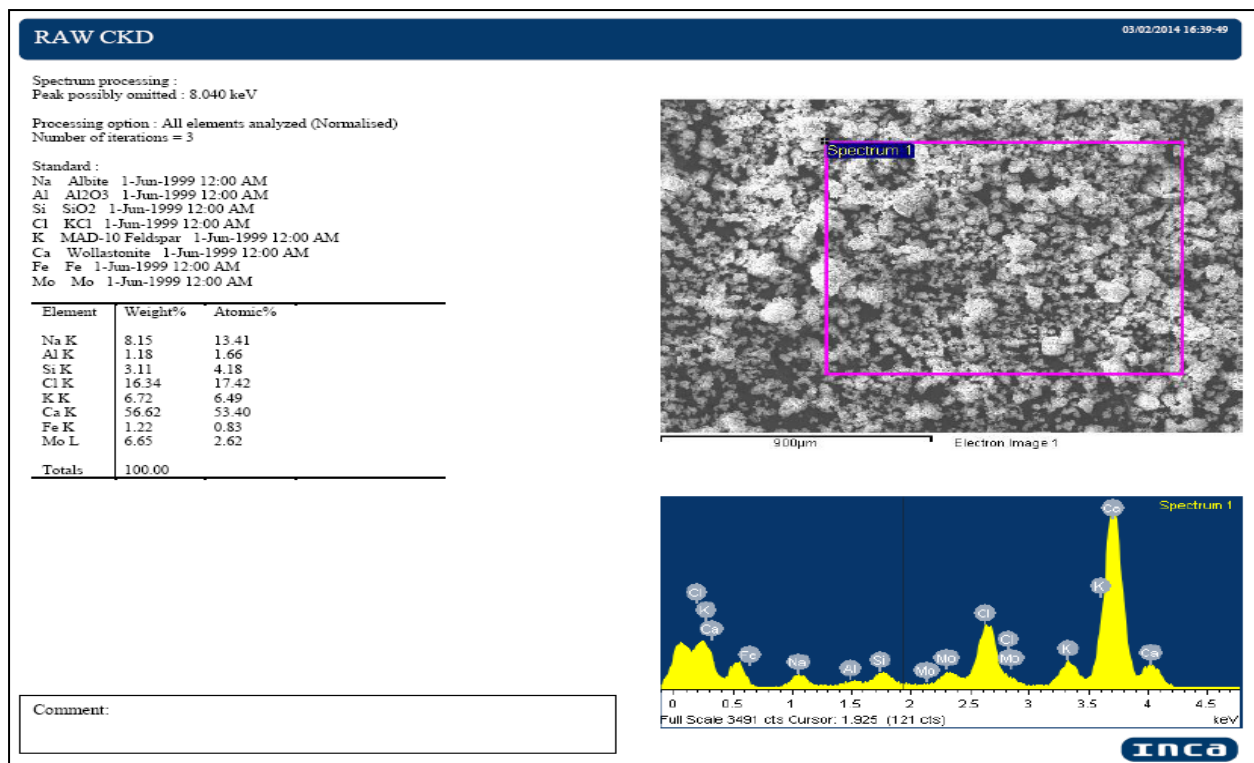


Figure 51: EDX Analysis for Raw CKD

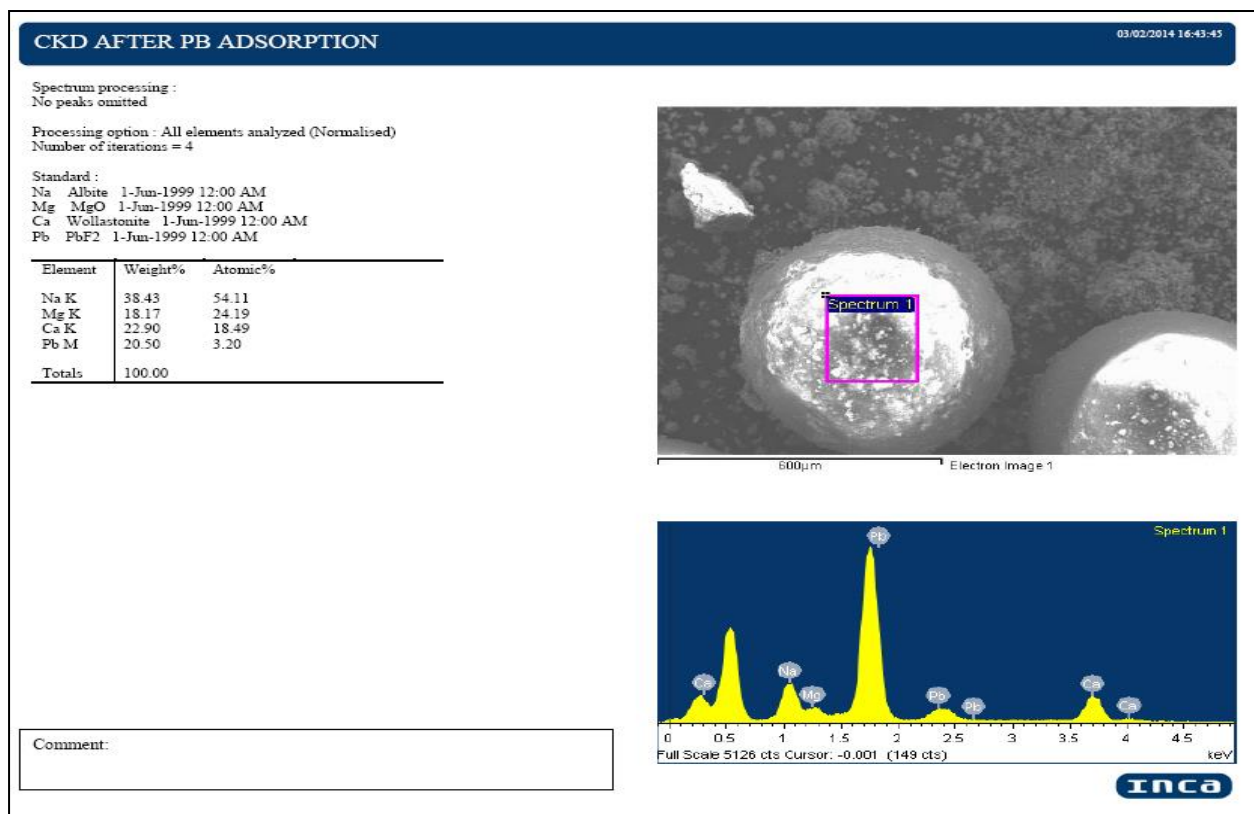


Figure 52: EDX Analysis for CKD after Pb Adsorption



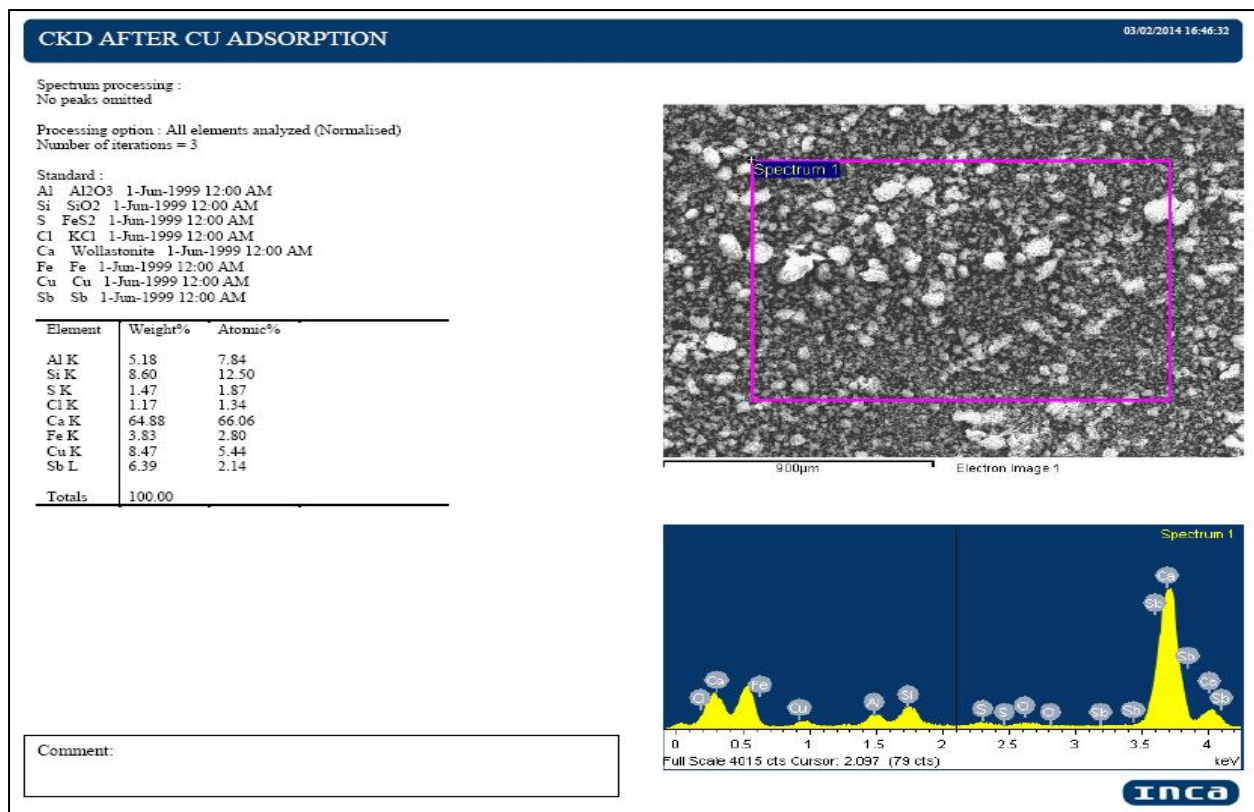


Figure 53: EDX Analysis for CKD after CU Adsorption

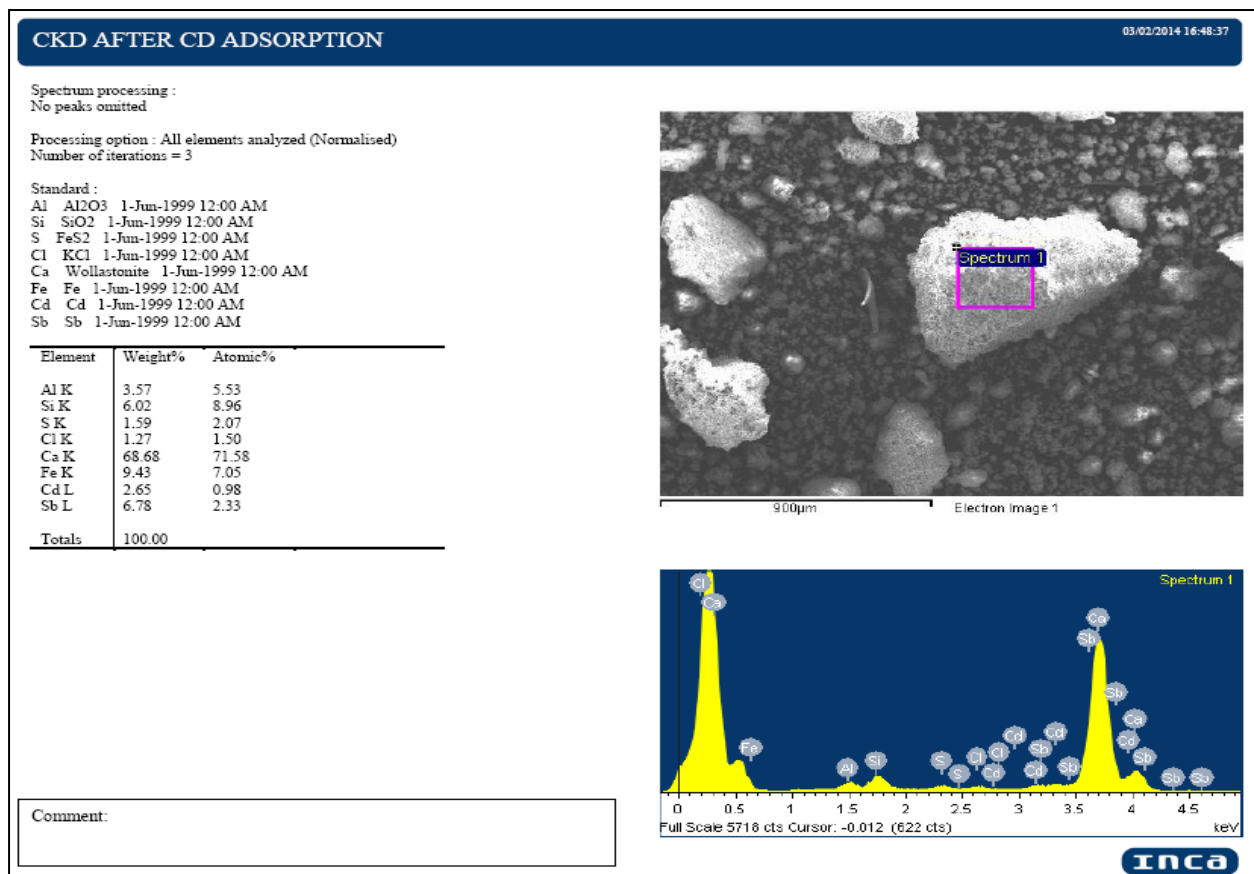


Figure 54: EDX Analysis for CKD after CD Adsorption

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#### 4.10 Effect of CKD on Physio-chemical and Biological Characteristics of Wastewater

In addition to the effect of the CKD on the heavy metal removal, it was also important to know whether the CKD will remediate any other constituents in wastewater or not. In order to investigate the impact of the CKD on the physico-chemical and microbiological properties of wastewater, three different raw wastewater samples were examined. The samples were collected from municipal, domestic, wastewater plants in order to focus on the physico-chemical and microbiological properties only without the influence of any heavy metal. Wastewater samples were taken from three treatment plants, namely Abu Rawash, New Cairo and City Center.

Coagulation studies conducted in completely mixed batch reactors showed the ability of CKD to reduce the organic material concentrations and to remove pathogens and suspended solids from raw wastewater with high uptake capacity. Analyses of all samples were carried out at room temperature and according to the standard methods as mentioned in Chapter 3: Methodology. The results show that the organic substances (COD and BOD) removal efficiency could reach 77% while for suspended solids; the uptake capacity fluctuates between 30 to 60%. The pathogenic material has been minimized by > 50%. The results of the treated effluents by the CKD are in compliance with the Egyptian standards (Law 93/1962 and its amendments in 2000) for the reuse of the biologically treated effluent for irrigation. Consequently, the potential of using cement kiln dust as a coagulant in wastewater treatment is very promising.

Figure 55 shows the removal of organic load (BOD) after adding CKD, compared to nominal load of different wastewater sources. The organic load was significantly affected by the presence of the CKD. The removal efficiency amazingly reached > 70% for all samples. The COD loads before and after adding the CKD are shown in Figure 56. The

removal efficiency reached more than 70% after adding the CKD. The BOD and COD values resulted after adding the CKD for most samples are in compliance with the national standards set for secondary treated wastewater to be used for irrigation. According to the national standards, the primary treated wastewater could be used to irrigate forests while the secondary treated one could be used in landscaping.

The suspended solids removal efficiency fluctuates between 50 and 80 %. Figure 57 shows the removal of total suspended solid (TSS) after adding CKD, compared to nominal load of different wastewater sources. The TSS reached the allowable limits by the national standards for secondary treated wastewater after adding the CKD as well.

Table 29 shows the values of E-Coli after treatment with CKD, compared to nominal load of different wastewater sources. This experiment has shown that the E-Coli removal barely reaches 13% at  $\text{pH} \leq 7.5$  for Abu Rawash while it reaches 50% at  $\text{pH} \geq 8.0$  for the other samples. This indicates that E-Coli removal is most probably affected by the pH. The *E-Coli* effluent concentrations are still high compared to the national standards where the standard allowable limit is 1000 Cell/100 ml. This is a common issue in the conventional and advanced wastewater treatment applications. As such, disinfection is always required at the final stage.

**Table 29: The removal of E-coli compared to nominal load of different wastewater samples**

Sample	E-coli (No./100ml)		
	AbuRawash WWTP	New Cairo WWTP	CityCenter WW Pumping station
Raw Wastewater	$7.5 \times 10^7$	$8 \times 10^7$	$10 \times 10^7$
Treated wastewater with CKD	$6.5 \times 10^7$	$4 \times 10^7$	$5 \times 10^7$
Removal efficiency	13%	50%	50%

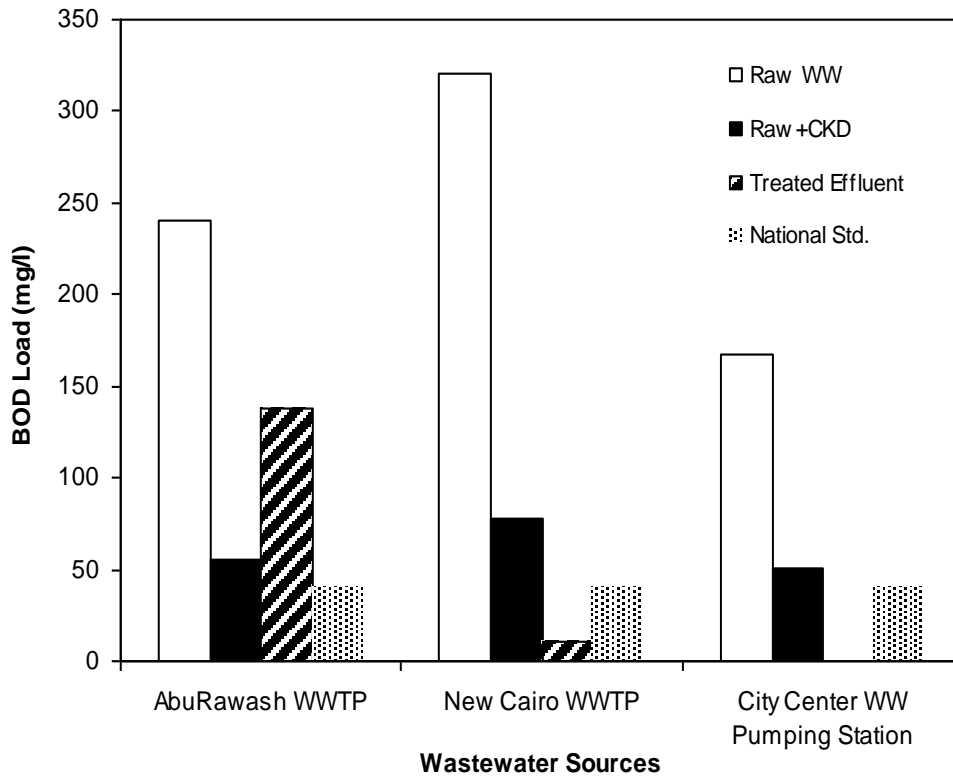


Figure 55: Effect of CKD to the three wastewater samples on BOD

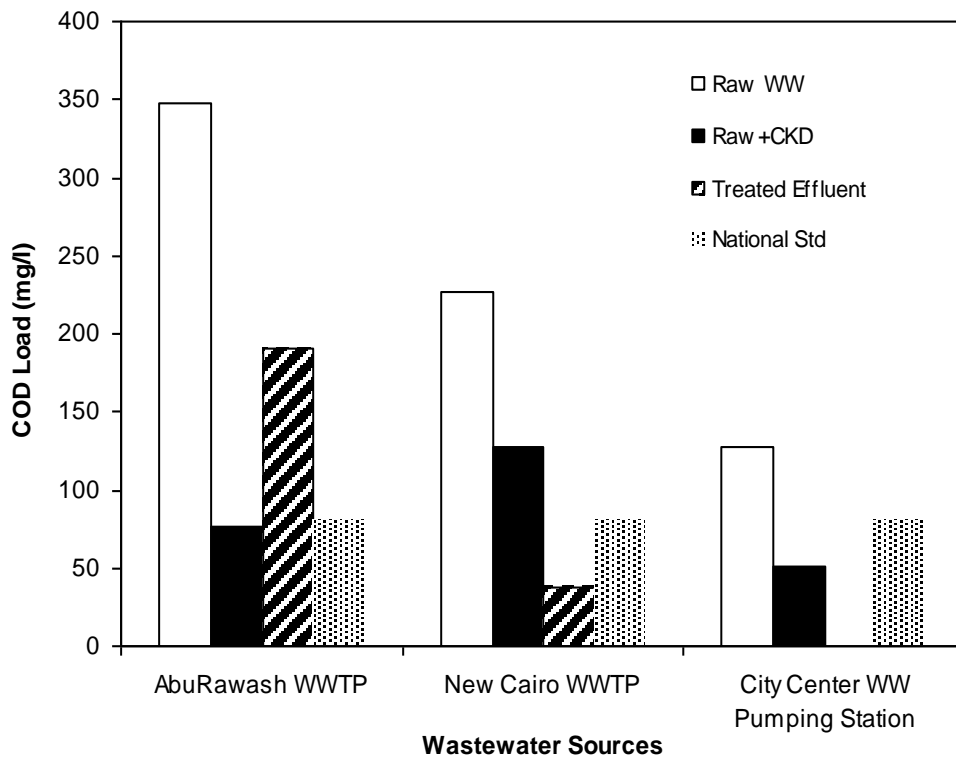


Figure 56: Effect of CKD to the three wastewater samples on COD

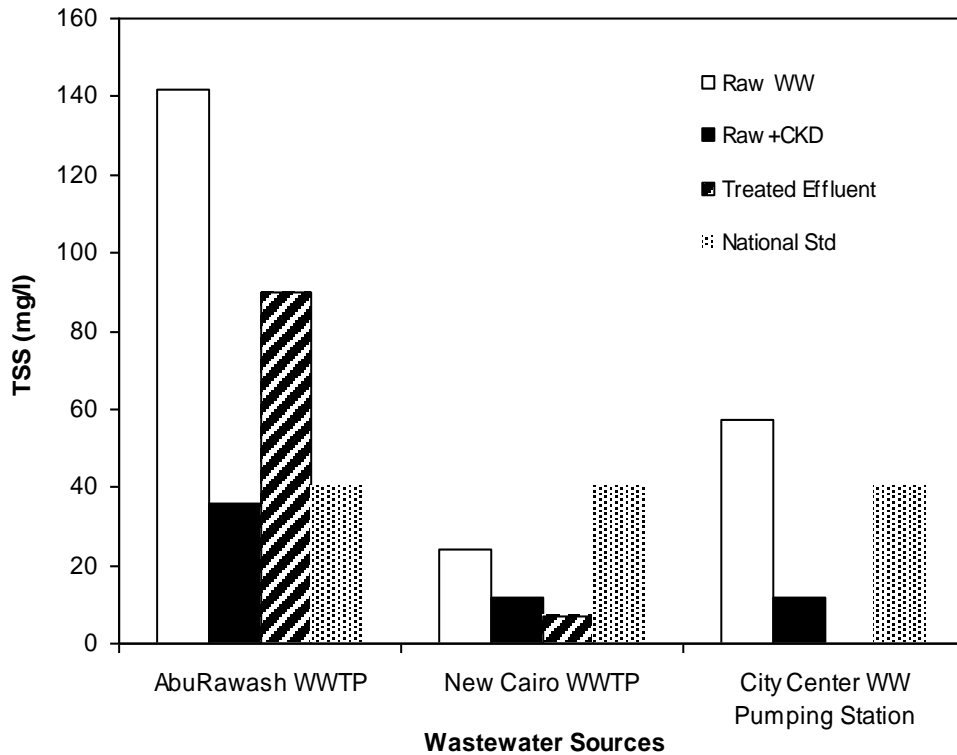


Figure 57: Effect of CKD to the three Wastewater Samples on TSS

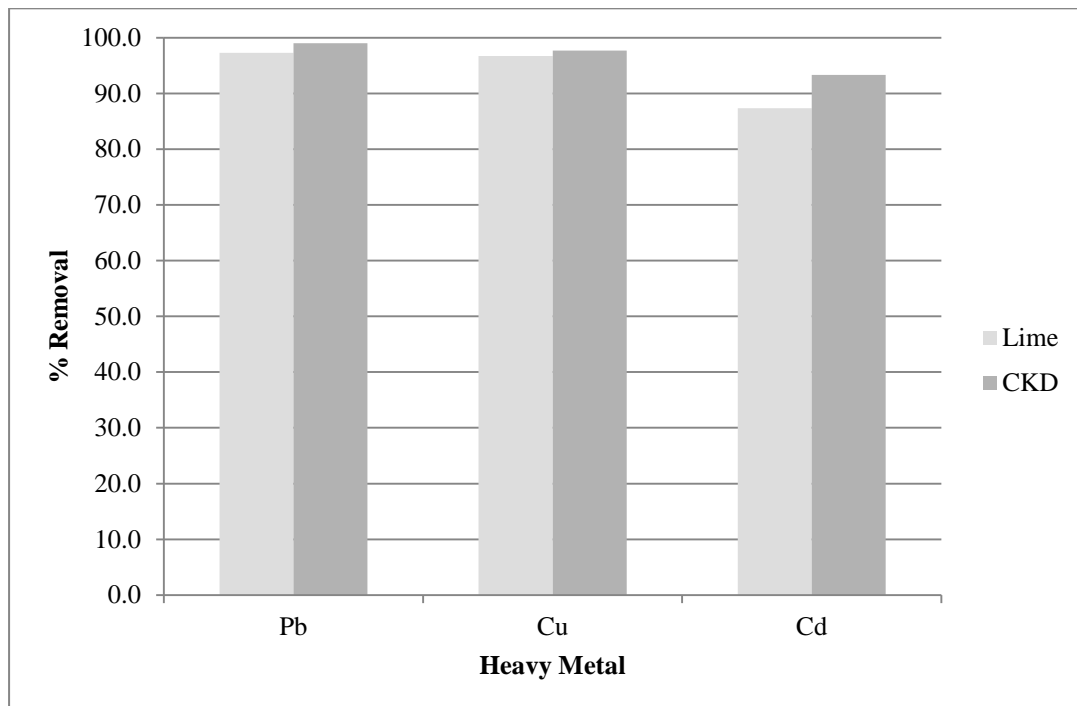
## 4.11 Comparison between CKD and Hydrated Lime on Wastewater Treatment

### 4.11.1 Effect of Hydrated Lime on Heavy Metals Recovery Compared to CKD

The effect of hydrated lime on heavy metals uptake was investigated. The hydrated lime as a prime source of CaO was examined and compared to CKD in heavy metals removal. This is to determine the effect of other chemical compositions present in the CKD. Heavy metal uptake from synthetic solutions were examined and compared with CKD at the same optimum conditions derived from the batch equilibrium experiments for CKD. 2.0 g/l of hydrated lime was added to 30ppm synthetic solution of the target heavy metals of study and agitated for 4 hours. The results, shown in Figure 58, show that the hydrated lime has the same effect on the removal of heavy metals. Accordingly, the CaO as a major constituent on both sorbents, hydrated lime and CKD, plays the significant role on the adsorption process regardless the effect of any other chemical compositions. This

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might be attributed to the complex chemical reactions and functional groups between the oxides and the heavy metals.



**Figure 58: Comparison between Lime and CKD on Heavy Metals Uptake**

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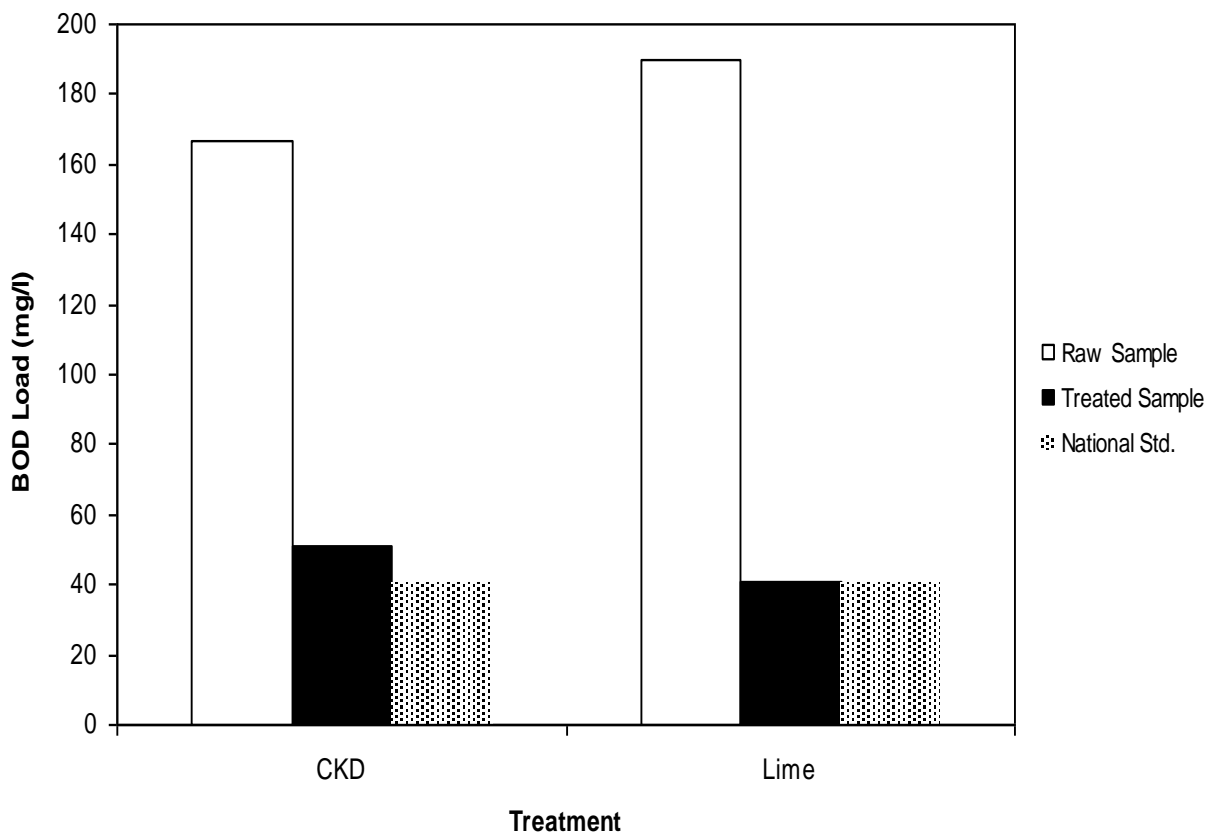
#### 4.11.2 Effect of Hydrated Lime on Physio-chemical and Biological Enhancement Compared to CKD

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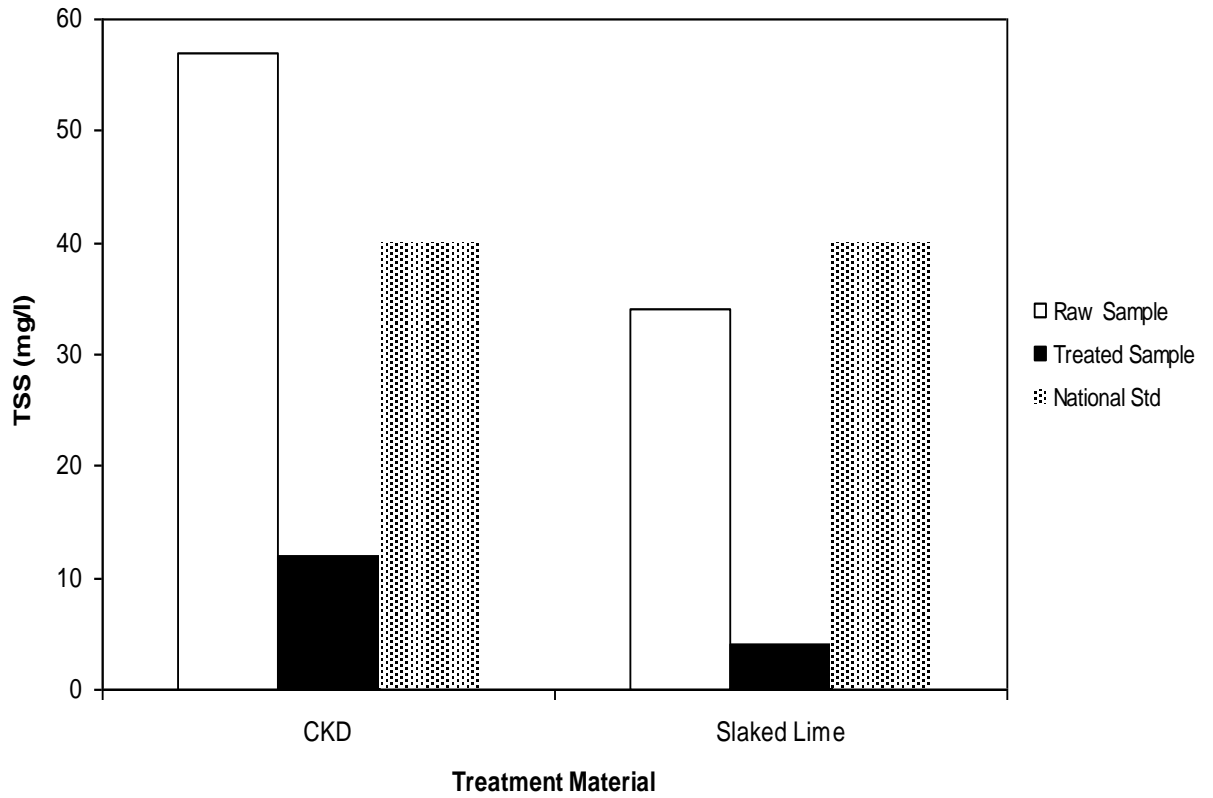
The experimental studies conducted in completely mixed batch reactors on domestic wastewater showed the ability of CKD and hydrated lime to reduce the organic material concentrations in terms of BOD by 69% and 78%; respectively. TSS removal efficiency reached 89%. A significant enhancement in pathogens removal has been observed by the addition of hydrated lime. The high calcium content in both substances; 55% for CKD and 85% for lime, favors their use in wastewater treatment applications.

Both CKD and hydrated lime demonstrated potential to treat raw domestic wastewater in batch equilibrium studies in terms of physico-chemical analysis. Figure 59 shows that the removal efficiency of BOD can reach 69% by adding CKD while it can reach 78% by using the hydrated lime. The Lime shows higher affinity than CKD in reducing the TSS where the removal

efficiency reached 88% and 79% respectively as shown in Figure 60. Regarding microbiological analysis, the hydrated lime reveals distinctive results in combating pathogens and bacteria. Table 30: E-Coli count after Wastewater Treatment with CKD and Hydrated Lime. The final concentrations of the physico-chemical and microbiological analysis make the use of either CKD, hydrated lime, or probably a combination of both in wastewater treatment applications very promising.



**Figure 59: Effect of CKD and Hydrated Lime Addition to Wastewater on BOD Removal in Comparison to the National Regulations**



**Figure 60: Effect of CKD and Hydrated Lime Addition to Raw Wastewater on TSS Removal**

**Table 30: E-Coli count after Wastewater Treatment with CKD and Hydrated Lime**

Sample	E-coli (No./100ml)	
	CKD	Hydrated Lime
Raw Wastewater	$10 \times 10^7$	$4 \times 10^5$
Treated wastewater	$5 \times 10^7$	$4.60 \times 10^4$
Removal efficiency	50%	89%



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## CHAPTER 5: PILOT SCALE

A pilot scale simulating the treatment of raw industrial wastewater using CKD with 20 to 25 L/hr capacity was designed and fabricated to test the capability of CKD in removing heavy metals cations and improving the wastewater characteristics. The design was based on the optimum operating conditions resulted from the bench scale experiments and isotherm modeling, including cement kiln dust (CKD) dose, retention time, and equilibrium constants.

### 5.1 Pilot Scale Unit Description

The pilot scale unit consists of a full wastewater treatment plant (WWTP), i.e primary, secondary, and tertiary treatment as follows:

1- Primary Treatment Units:

- a. Coagulation Tank
- b. Flocculation Tank
- c. Settling Tank
- d. Sand Filtration

2- Secondary Treatment Unit:

- a. Heavy Metals and Wastewater Treatment Tanks using CKD

3- Tertiary Treatment Unit:

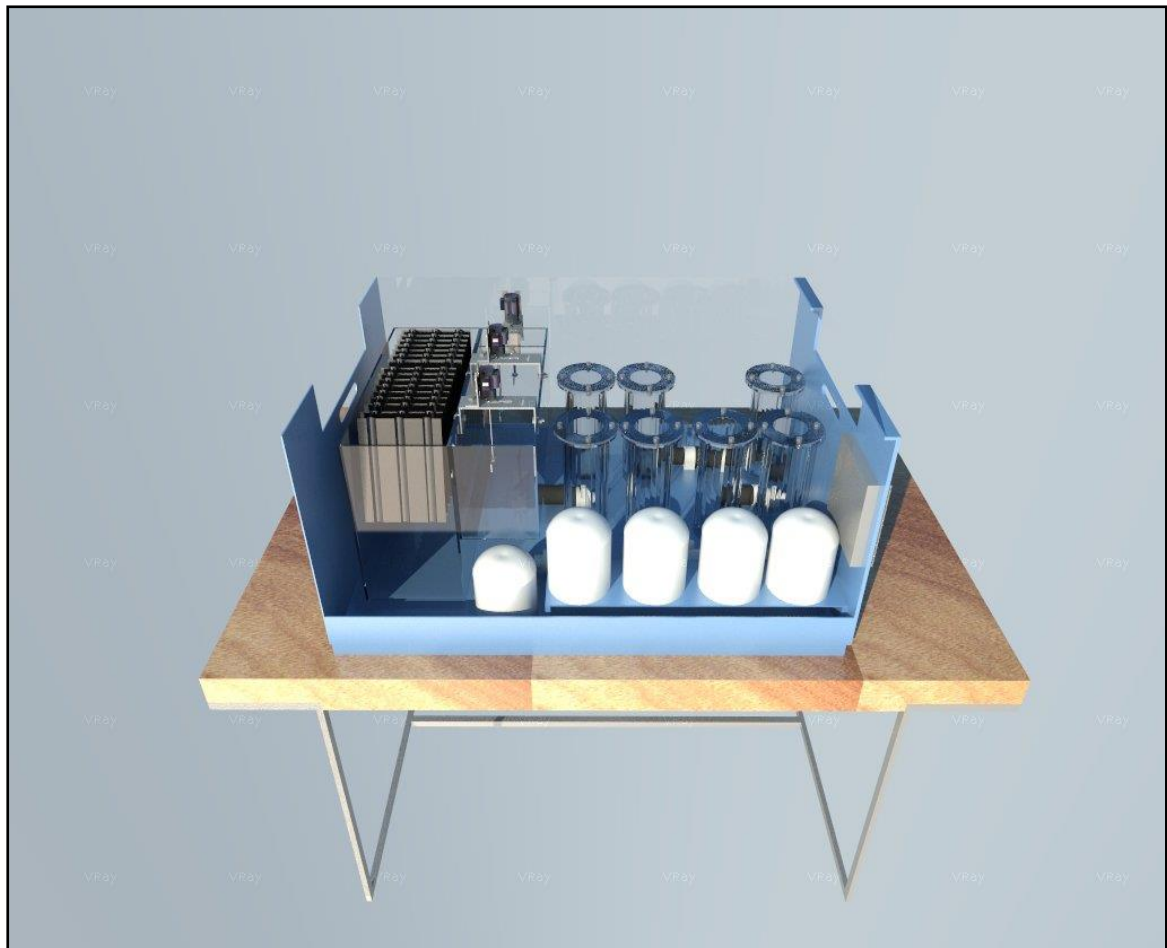
- a. Final Sand Filtration together with Activated Carbon
- b. Ultra Violet (UV) Unit

Moreover, the unit is equipped with the following:

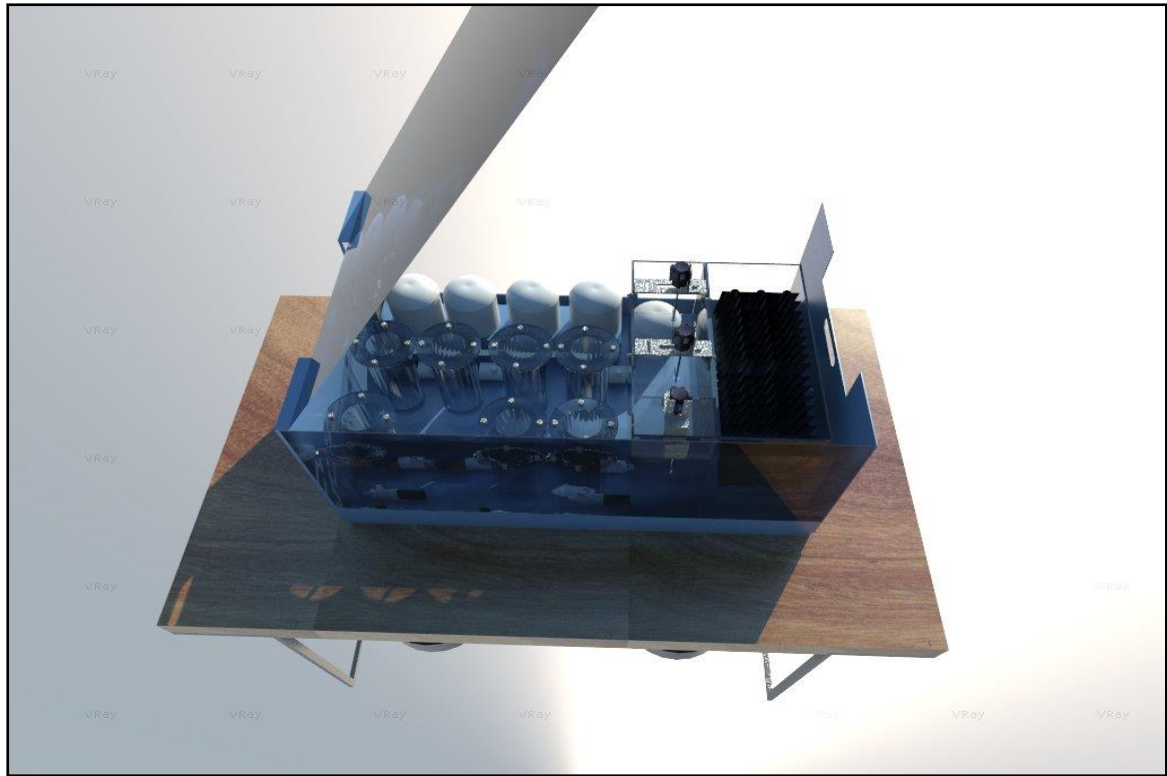
- 1- Feeding Tank

- 
- 2- Effluent Storage Tank
  - 3- Collection Sampling Tanks for each Treatment Stage
  - 4- Displacement Pumps and Mixers
  - 5- Electrical Control Panel
  - 6- Pipes, Valves ...etc.

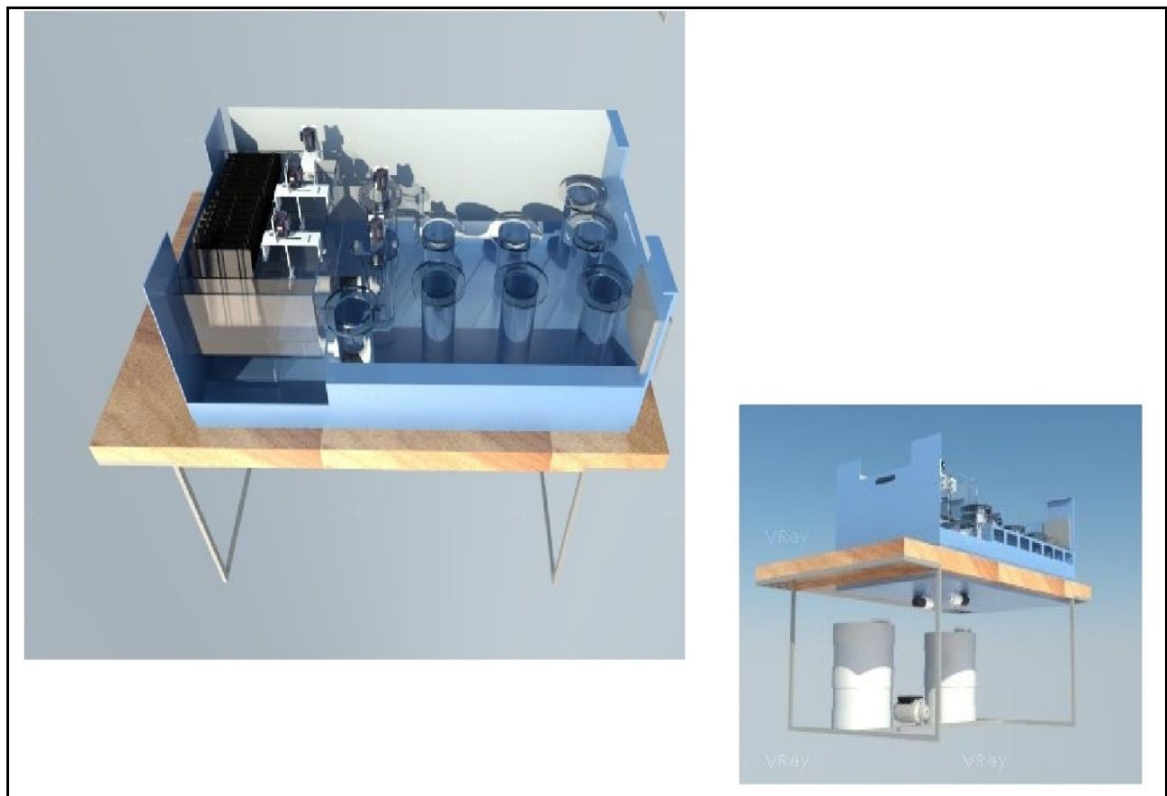
Figure 61 to Figure 63 show the design isometric layouts of the pilot scale WWTP with different orientations and views.



**Figure 61: Layout of a Pilot Scale WWTP - Front View**



**Figure 62: Layout of a Pilot Scale WWTP- Top View**



**Figure 63: Layout of a Pilot Scale WTP – 3D Images**

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The unit is fabricated from transparent poly acrylic material to better monitor and to observe the treatment processes. The following equations were used to identify the dimension of the different treatment units.

*I – Primary Treatment Process:*

1- Coagulation Tank Design Equations:

$$V = Q T$$

Where,  $V$  is volume in liters (L)

$Q$  is flow rate in liters per hour (L/hr)

$T$  is the detention time in hours (hr)

Given the fact that the used paddle is a vertical-shaft paddle mixer, the detention time can be typically assumed to be between 10 to 30 minutes (Mihelcic, 2010).

Since  $Q = 20$  L/hr and  $T = 10$  minutes (0.17hr) (assumed)

Therefore  $V = 3.4$  L; round it up to 3.75 L.

Check detention time:  $T = Q/V = 3.75/20 = 0.19$  hr > 0.17hr [Ok].

$$V = L * W * H$$

Assuming  $W = 1.5$  L and  $H = 2.5$  L

Therefore:  $L = 10$  cm,  $W = 15$  cm,  $H = 25$  cm

2- Flocculator design Equations:

A conventional vertical shaft turbine flocculation system was used. The same as the coagulation tank, the volume of the flocculation tank can be determined as follow:

$$V = Q T$$

In the flocculation tank, more detention time is required compared to the coagulation tank to ensure more settling time. Therefore, the detention time was assumed to be 0.5 hrs.

Therefore  $V = 20$  (l/hr) \* 0.5 (hr) = 10 L.

The volume of the flocculation tank was increased to 15 L to ensure better mixing.

---

Check detention time:  $T = Q/V = 15/20 = 0.75 \text{ hr} > 0.5 \text{ hr}$  [Ok].

Therefore:  $L = 15 \text{ cm}$ ,  $W = 40 \text{ cm}$ ,  $H = 25 \text{ cm}$ .

### 3- Settling Tank Design Equations:

$$V = QT$$

Assuming the  $V = 35 \text{ L}$  ( $20 \text{ cm} \times 50 \text{ cm} \times 35 \text{ cm}$ )

Therefore,  $T = 35 \text{ (L)} / 20 \text{ (L/hr)} = 1.75 \text{ hrs}$

Determining the critical particle settling velocity:

$$V_c = \frac{Q}{A}$$

Therefore,  $V_c = 0.02 \text{ (m}^3\text{/hr)} / 0.1 \text{ (m}^2\text{)} = 0.002 \text{ m/hr} = 0.2 \text{ cm/hr}$ . This means that any particle with a settling velocity greater than the critical velocity ( $V_c$ ) will be removed.

Also, the settling tank was equipped with five lamella settlers to enhance the removal of the suspended solids and colloids.

Figure 64 shows the primary treatment tanks dimensions.

### 4- Filter Design Equations:

$$A = Q/F$$

Where,  $A$  is the area in  $\text{m}^2$

$Q$  is the flow rate  $\text{m}^3\text{/hr}$

$F$  is the filtration rate  $\text{m}^3 / \text{m}^2 \cdot \text{hr}$ ;

Filtration is used for removing small flocs or precipitated particles. The filtration process is used as primary turbidity removal process. Rapid sand filtration gravity type was employed due to its simplicity and low energy requirement. The influent wastewater is driven by gravity force downward. The advantages of the rapid sand filter are that it requires relatively small foot print, is less sensitive to raw wastewater quality, does not require large quantity of sand, and can be regenerated by backwashing.

Assuming  $F = 3 \text{ m}^3 / \text{m}^2 \cdot \text{hr}$  and  $Q = 20 \text{ L/hr}$  ( $0.02 \text{ m}^3\text{/hr}$ ). Therefore, the  $A = 0.007 \text{ m}^2$

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Therefore  $D = 0.092$  m (9.2 cm) rounded up to 10 cm.

Assuming  $L = 3 D = 30$  cm.

The Filter media was uniform in size to allow the filter to operate properly. Also, the sand was washed prior the treatment process starts. The uniformity coefficient (UC)  $[d_{60}/d_{10}]$  was approximately 1.5.

### *II- Secondary Treatment Process (Heavy Metals Removal Tanks):*

Two types of tanks were used for heavy metals removal. The first type was cylindrical tanks with stirrer (batch type) and the second one fixed bed cylindrical columns. Each type consists of two tanks, one in duty and one standby in case of CKD exhaustion or tanks maintenance. The capacity of each tank is approximately 2.5 L. The tank is 10 cm in diameter and 30 cm height.

### *III- Tertiary Treatment Unit:*

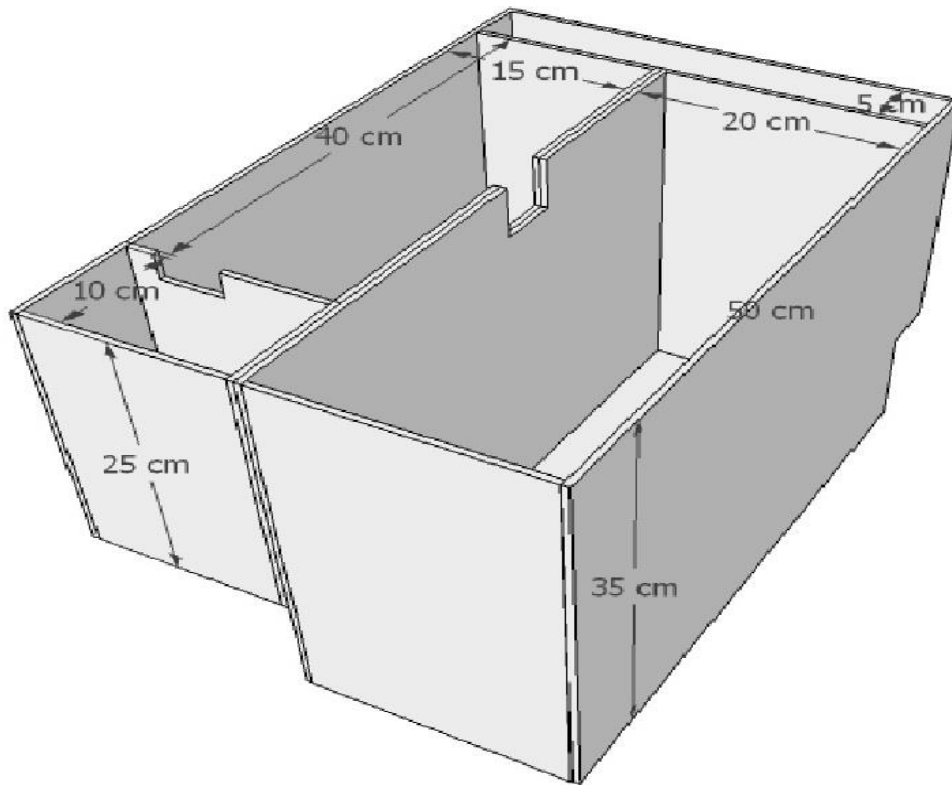
#### 1- Sand Filtration

The same as the primary filtration, sand filtration tank equipped with granular activated carbon (GAC) was used. The GAC was used to treat any color or odor nuisance. The tank has a cylindrical shape with 10 cm diameter and 30 cm height.

#### 2- Ultraviolet Lamp

The ultraviolet (UV) is an electromagnetic radiation having a wavelength between 100 and 400 nm. The UV photons can recover the wastewater from any existing bacteria, protozoa, or microorganisms. It reacts directly with the nucleic acid in the form of deoxyribo-nucleic acid (DNA) and damages it.

Figure 65 to Figure 67 show the pilot scale unit before and after installation.



**Figure 64: The Primary Treatment Process Tanks Dimensions**



**Figure 65: The Pilot Scale Unit before Installation**





**Figure 66: The Pilot Scale after Installation**



**Figure 67: The Pilot Scale after Installation (Side View)**



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## 5.2 Process Description

Raw industrial wastewater sample (80 L) from a glass industry was collected and tested in the proposed wastewater treatment pilot scale unit.

In glass manufacturing, lead oxide, potash, zinc oxide, and other metal oxides are used as coloring or de-coloring agents. Accordingly, liquid effluents resulted from grinding, polishing, coating and electroplating processes include suspended solids, heavy metals (i.e., lead), and variations in pH (USEPA, 2013; IFC, 2007).

The following steps describe the operation steps of the pilot scale. Also, Figure 68 shows the treatment processes block diagram and Figure 69 shows the process flow chart.

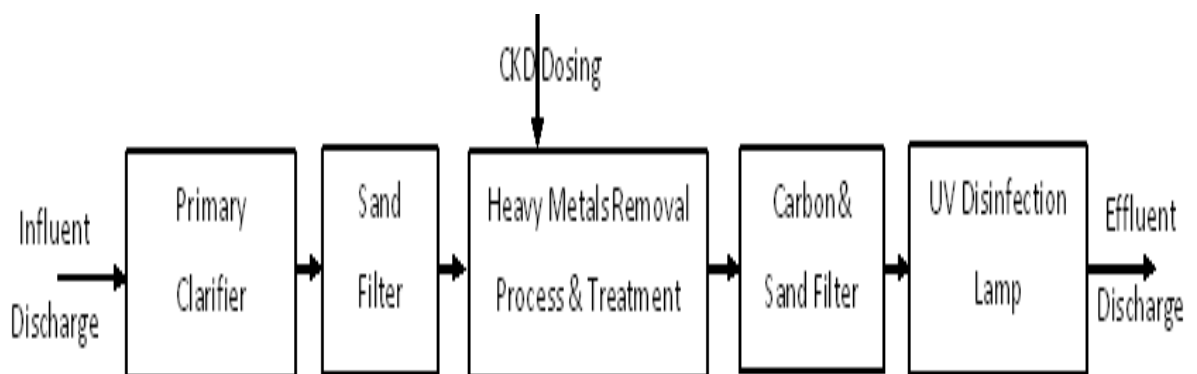
- 1- The feeding tank was filled with collected industrial wastewater.
- 2- Wastewater was then pumped to the primary settling unit. The primary settling tanks equipped with lamella were used to remove suspended particles and colloids. Figure 71 shows the lamella with the suspended colloids and suspended particles after the primary treatment process has been carried out. No chemicals or coagulants (i.e., alum, ferric chloride, or potassium permanganate) were added in the experimental runs.
- 3- Effluent from settling tanks flows by gravity to an equalization tank. The equalization tank is used to maintain a steady flow to the further treatment processes.
- 4- The flow then passes through a sand filter column to remove any remaining colloids or suspended solids.
- 5- The filtrate is then fed to the heavy metals' removal tanks. Two types of tanks were used alternatively in each run. The first type is a fixed bed bioreactor, while the second one is a stirrer tanks (batch equilibrium tanks). Each type has a standby

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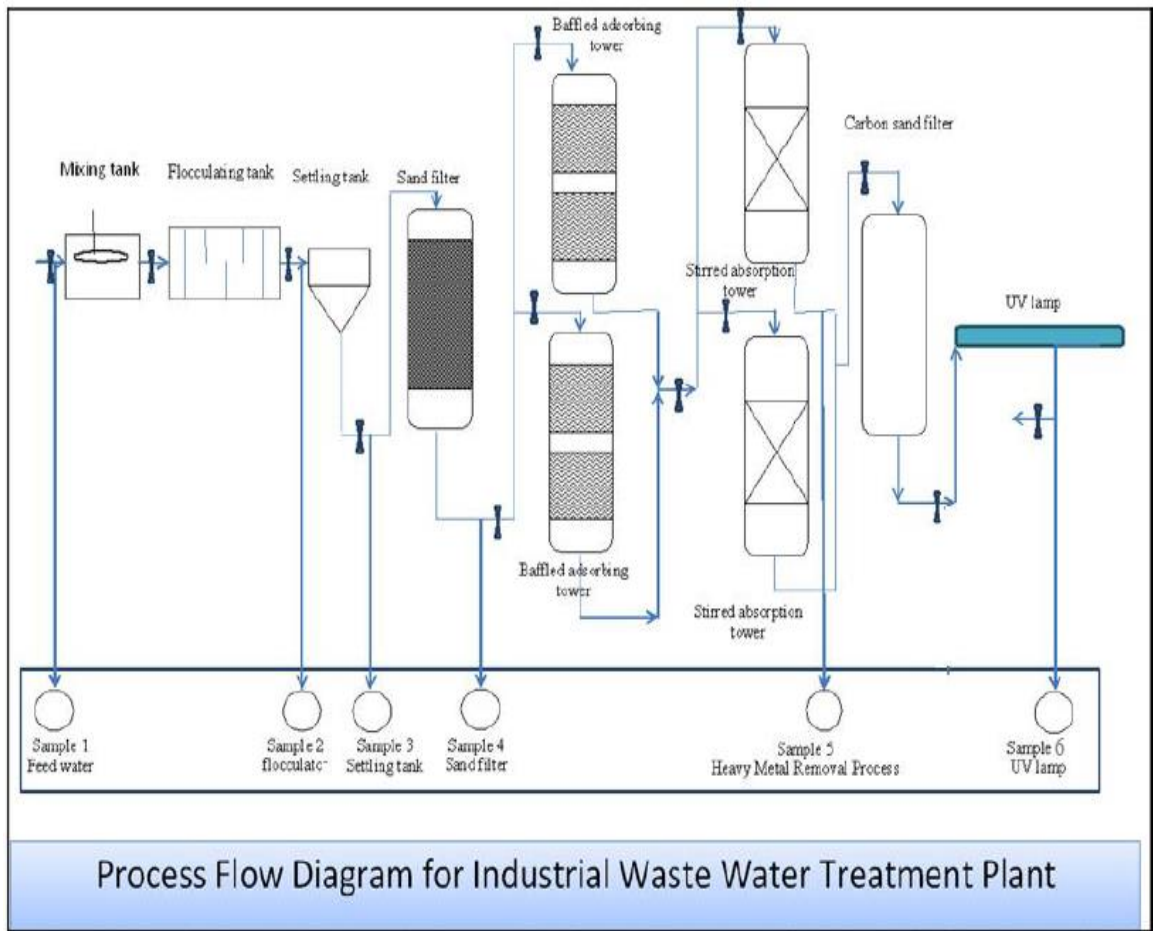
tank that can be used in case of the exhaustion of the CKD or due to maintenance. In the fixed bed reactor, approximately 500 gm was poured in the reactor. In the batch tanks, 2 gm/l of CKD was added during the experimental runs and mixed at high stirrer speeds.

- 6- The flow after then passes through a carbon sand filter where some of the suspended CKD particulate can be removed. The activated carbon was used to remove any odor nuisance from the industrial water samples. Also, the carbon sand filter was used as a final bleaching stage.
- 7- The treated industrial wastewater then passed through an UV lamp unit and then to storage tanks. The UV lamp was used in order to destroy any pathogens or bacteria that could be found in the treated wastewater.
- 8- A sample was collected after each treatment step and analyzed in order to understand the efficiency of each treatment process.
- 9- All pumps and the stirrer of the mixer tanks were controlled through an electrical control panel as shown in Figure 72.

Figure 70 shows the pilot scale during operation.



**Figure 68: Treatment Processes Block Diagram**



Process Flow Diagram for Industrial Waste Water Treatment Plant

Figure 69: Treatment Process Flow Chart



Figure 70: A Photo for the Pilot Scale during Operation



**Figure 71: The Lamella with the Accumulated Colloids**



**Figure 72: Pumps and Mixer Control Panel**

### 5.3 Pilot Scale Unit Output and Results

The designed pilot scale was used to treat industrial wastewater resulting from glass manufacturing. The influent and effluent samples were analyzed not only for heavy

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metals, such as lead, cadmium, copper, zinc, cobalt, and chromium, but also for all other physiochemical parameters (COD, BOD, TSS, and TDS). The effluent results were compared to the allowable limits by the Egyptian regulations (decree 44/2000) for treated wastewater reuse in irrigation purposes. The Egyptian decree number 44/2000 has categorized the treated wastewater into three groups in correspondence to its degree of treatment, primarily, secondary, and tertiary. The treated industrial wastewater results were amazingly equivalent to the secondary treatment category, and hence it could be used for landscape irrigation for instance. Table 31 shows the sampling and results of the pilot scale experimental runs. Also, Figure 73 shows a visual (physical) comparison between the raw industrial wastewater and the treated samples. It was found that the designed system is able to significantly recover heavy metals from industrial wastewater as well as reduce the solids and organic content of wastewater (i.e., TSS, COD, and BOD). The only drawback of this system that was observed is a slight increase in the pH of the wastewater especially after passing through the heavy metal removal unit. This is attributed to the alkalinity of the cement kiln dust.



**Figure 73: A visual comparison between the raw industrial sample and the treated effluents**

**Table 31: Pilot Scale Sampling and Analyses**

Parameter	Unit	Raw Sample	After Settling Tank	After CKD Reactor	After Sand Filtration +UV	Egyptian All. Limits (Decree 44/2000)	International Standards*	Final % Removal	
<b>pH</b>	-	8.42	8.42	9.6	9.96	6-10	6-9	-	
<b>TDS</b>	mg/l	320	290	283	201	2000	2000	37%	
<b>TSS</b>	mg/l	442	154	44	24	40	50	95%	
<b>COD</b>	mg/l	127		76	79	80	150	38%	
<b>BOD</b>	mg/l	99		25.7	28	40	50	72%	
<b>Ammonia (NH<sub>3</sub>)</b>	mg/l	0.963		0.50	0.451	NA	15	53%	
<b>Turbidity</b>	FTU	482	140	1	~1	NA	NA	100%	
<b>Color</b>	PtCobalt	1505	915	74	39	NA	NA	97%	
<b>Heavy Metals</b>	<b>Pb</b>	mg/l	31.5	30.1	1.0	0.242	5	5	99%
	<b>Cu</b>	mg/l	0.566	0.464	0.094	0.074	0.2	0.2	87%
	<b>Cd</b>	mg/l	ND	ND	ND	ND	0.01	0.01	-
	<b>Cr</b>	mg/l	0.139	0.121	0.082	0.074	ND**	0.1	47%
	<b>Co</b>	mg/l	0.125	0.118	0.048	0.01	0.05	10	92%
	<b>Ni</b>	mg/l	0.70	0.653	0.057	0.039	0.2	0.2	94%
	<b>Fe</b>	mg/l	0.586	0.553	0.88	0.115	5	5	80%
	<b>Zn</b>	mg/l	1.152	1.137	0.038	0.012	2	2	99%
* Food and Agricultural Organization of the United Nations (FAO), 1985									
**ND: Not Determined									

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## CHAPTER 6: ECONOMIC VIABILITY

### 6.1 Back Ground

One of the main positive impact of implementing the proposed project is the disposal of large quantities of cement kiln dust (CKD) in an economically and sustainable manners. This chapter evaluates the economic viability of treating industrial wastewater using CKD in Egypt. The experimental data obtained from the pilot scale explained in details in Chapter five were scaled up and used to perform the economic viability. As discussed in Chapter 5, the pilot scale reactor was fed by 80 liters of industrial wastewater from glass manufacturing with high lead concentrations (30 ppm) and Chemical Oxygen Demand (COD) of around ~130 ppm. The TDS and TSS in raw industrial wastewater samples were 320 ppm and 442 ppm; respectively. It was found that, the reactor is capable of treating industrial wastewater with 30 ppm lead concentration and other heavy metals traces. Moreover, it was obvious that the reactor has high efficiency to recover the industrial wastewater from all other physiochemical constituents (i.e., COD, TDS, and TSS).

The economic viability of a project extends beyond the initial financial analysis. It entails analyzing the data using shadow prices as to eliminate price distortions, analyzing the indirect costs and benefits of the project, and looking at the overall effect of the project on the economy. The economic indicators are based on the net economic present value (NEPV) and economic rate of return (ERR) which results from the industrial wastewater application. Based on the economic evaluation, the Egyptian government can determine the projects of benefit to the economy and can formulate their policies.



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## 6.2 INTRODUCTION

The most voluminous by-product generated from cement manufacturing processes is cement kiln dust (CKD). CKD results from blending and clinkering process of raw materials. Although a small amount of CKD can be recycled in the cement manufacturing, huge amounts of CKD need to be disposed of (Hawkins et al., 2003). Accordingly, appropriate disposal of the CKD is a challenging problem in the cement industry due to environmental concerns.

In this study, CKD showed very high potential and promising results in treating industrial wastewater from heavy metals and other physiochemical constituents. The outcome of the bench and pilot scale experimental runs has obviously shown that the CKD can tackle the contemporary challenges of treating industrial wastewater in sustainable as well as environmentally manner.

In Egypt, industrial wastewater influent is around 1.3 BCM/yr (Egypt 2<sup>nd</sup> National Communication, 2010). According to the EEAA, 91 plants in Egypt were discharging their industrial wastewater resulting in the release of huge amounts of heavy metals contaminant into fresh water bodies (EEAA, 2007). This poses a threat to both rural and urban communities. Improper discharge of industrial wastewater may lead to the destruction of the water bodies in addition to the destruction of aquifers and in turn precious underground water. Moreover, some of these industries could be allocated within residential areas, such as electroplating, metal finishing, and leather tanning. Industrial wastewater constitutes 39% of the environmental problems of the industrial sector (Egypt Second National Communication, 2010). On the other hand and according to the dramatic increase on the population, the water expenditure per capita is on the decrease. This explains that in the coming few years we need to well manage our usage of



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water and to investigate new efficient solutions to reserve our water budget. One of the most viable solutions is to treat wastewater and reuses it for irrigation purposes. This should form a part of the water budget in Egypt.

The proposed industrial wastewater treatment unit can treat industrial influents, currently disposed of in an unsustainable way. Furthermore, one of the main significant positive effects relies on improving human wellbeing due to the reduction of pollutants from untreated industrial wastewater and utilizing a harmful industrial waste in the treatment process which is cement kiln dust (CKD).

The aim of this section is to ascertain the economic feasibility in developing a small scale industrial wastewater treatment system for the removal of heavy metals using CKD. The proposed system would treat the industrial wastewater from heavy metals and physiochemical constituents. The treated effluents could be used directly for irrigation purposes in compliance with the Egyptian laws and regulations. The study assesses the socio-economic impacts of the proposed project.

### **6.3 Economic Analysis Methodology**

This section identifies the equations used to perform the economic viability for the proposed project. The economic viability entails analyzing the data using shadow process as to eliminate price distortion, analyze the indirect costs and benefits of the project, and look at the overall effect of the project on the economy. The payback period (PBP), economic rate of return (ERR), and net economic present value (NEPV) are the economic indicators used to evaluate the project. Equation 5 was used to calculate the PBP from an investment. To be used in the study, it is required to estimate the initial capital costs and expected yearly profits.

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**Equation 5: Investment Pay Back Period**

$$\text{Pay Back Period(Years)} = \frac{\text{Initial Capital Cost(USD)}}{\text{Profits(USD/Year)}}$$

The ERR is the discount rate that will equate the NEPV of the economic benefit (EB) and economic cost (EC). NEPV was calculated using Equation 6 as follows:

**Equation 6: Net Economic Present Value Equation**

$$NEPV = -C_o + \sum_{i=1}^T \frac{NCF_i}{(1 + SDR)^i}$$

Where;  $C_o$  is the initial investment which is a negative cash flow,  $NCF_i$  is the net cash flow for year  $i$  while SDR is the social discount rate.

The next step in completing the economic study was to estimate the initial capital cost for the treatment system. The capital cost for any wastewater treatment facility depends on many factors and parameters, such as equipment cost, installation, piping, instrumentation and controls, and engineering. The following table (Table 32) shows the standard capital cost algorithm according to USEPA (USEPA, 2014). The EPA also stated that 4% of the total capital cost is required for annual maintenance.

**Table 32: Standard Capital Cost Algorithm (US.EPA, 2014)**

<b>Factor</b>	<b>Capital Cost</b>
Equipment Cost	Technology – Specific Cost
Installation	25 to 55 percent of Equipment Cost
Piping	31 to 66 percent of Equipment Cost
Instrumentation and Controls	6 to 30 percent of Equipment Cost
<b>Total Construction Cost</b>	<b>Equipment + Installation + Piping Instrumentation and Controls</b>

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Engineering	15 Percent of Total Construction Cost
Contingency	15 Percent of Total Construction Cost
<b>Total Indirect Cost</b>	<b>Engineering + Contingency</b>
<b>Total Capital Cost</b>	<b>Total Construction Cost + Total Indirect Cost</b>

The US EPA guidelines for identifying the cost of the treatment technology were used. The guidelines provide a general description of how EPA developed costs for the different individual treatment technology and the development of costs for each of the wastewater and sludge treatment technologies evaluated. Equation 3 in the EPA guidelines is used to estimate the capital cost for the secondary precipitation system in the model technology for metals.

**Equation 7: Capital Cost Equations for Secondary Chemical Precipitation**

$$\ln(Y1) = 13.829 + 0.544 \ln(X) + 0.00000496(\ln(X))^2$$

Where *Y1* is the capital cost in USD and *X* is the daily flow rate in Million Gallons.

This secondary chemical precipitation equipment consists of a single mixed reaction tank with pumps and a treatment chemical feed system, which is sized for the full daily batch volume. This treatment technology is equivalent to the proposed CKD treatment facility. EPA calculated capital cost estimates for the secondary precipitation treatment systems from vendor quotations.

These costs include the cost of the mixed reaction tanks with pumps and treatment chemical feed systems. The total construction cost estimates include installation, piping and instrumentation, and controls. The total capital cost includes engineering and contingency at a percentage of the total construction cost plus the total construction cost as explained in Table 32.

For the facilities that have at least primary chemical precipitation in-place, EPA assumed that the capital cost for the secondary precipitation treatment system would be

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zero. The in-place primary chemical precipitation systems would serve as secondary precipitation systems after the installation of upstream selective metals precipitation units.

Unlike the financial feasibility studies where the rate of return compared by the weighted average cost of capital (WACC), the ERR is compared with the social discount rate in order to know whether the project is viable or not. The social discount rate is the rate at which the value placed by society on future benefits and costs declines over time. The social discount rate reflects the social opportunity cost of capital, so that it provides the link between costs and benefits occurring at different time. According to the UN-ECLAC (2011), little consensus exists on the choice of an appropriate SDR in developing countries. A significant interest rate variation of 8-15% was reported. Ministry of finance in its info memorandum report for 6th of October Wastewater Treatment Plant (WWTP) in 2009 reported that the central bank of Egypt (CBE) discount rate averaged 10% in 2008, and observed short-term lending and deposit rates were in the range of 12.2% and 6.1% respectively in 2008. Since no risk premium is anticipated in this analysis, 8% interest rate was used as the social discount rate. The estimation of no risk premium was based on that sustainable and environmentally friendly infrastructure projects are social capital projects. Moreover, the proposed project aims at alleviating a health risk issue from both CKD and industrial wastewater.

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## **6.4 WWTP Sizing for Economic Analysis**

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### **6.4.1 WWTP Properties**

In order to complete the economic feasibility study, the pilot scale WWTP was sized so that it would be suitable for treating the industrial wastewater generated from industrial zones in Egypt. To size the plant, certain parameters had to be set in order to define the system. The selected parameters concerning the plant and operation are:

- The pilot plant is designed to treat 20 ~ 25 L/day industrial wastewater.

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- The influent wastewater is obtained from a real glass manufacturing for proper simulation.
  - The influent discharge composes of heavy metals and physiochemical constituents.
  - The sludge quantities can be evaluated to be 3% of the influent wastewater.

It is assumed that the full scale treatment unit will be installed to treat at least 1,000 m<sup>3</sup>/day.

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#### 6.4.2 WWTP Sizing

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From the assumptions outlined in the previous section, the yearly feed loading requirements are calculated. Accordingly, the total input to full scale system is 365,000 m<sup>3</sup>/year. Therefore, the amount of CKD needed to treat this amount of industrial wastewater is 2 tones daily (730 t/year) in case of batch treatment. Much less amounts of CKD can be utilized in case of using column adsorption towers. This depends on the breakthrough of the CKD in treating the industrial waste. From the bench scale experiments, it can be concluded that 250 kg CKD will be required to treat 1,000 m<sup>3</sup>. Therefore, the required amount of CKD in case of using it in column adsorption towers is 0.25 tones daily (91.25 t/year).

### 6.5 Economic Analysis

The economic feasibility study is computed in U.S. Dollars which requires conversion of Egyptian pounds to U.S.Dollars without distortions. In 2012, Hagag identified the shadow exchange rate from 2007 to 2010 using the supply and demand approach which is based on the ratio between capital and goods inflows and outflows. The shadow exchange rate (SER) from 2010 to 2016 has been also anticipated on an annual devaluation value of 3%. The SER varies from 6.7 up to 8.2 EGP. Based on the

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current exchange rate and the SER, using 7.30 EGP is a reasonable value for the current study.

Based on findings shown in the previous section, the treatment system is to treat 1,000 m<sup>3</sup>/day industrial wastewater in order to be re-used for irrigation purposes. The exhausted CKD for the treatment process can be used in other industrial processes, such as ceramics and brick productions (El-Awady, 2000). Therefore, the traded product from the plant is the treated effluents assuming that the generated CKD from the treatment process that could be used in other process facilities has no value as a conservative approach.

Comparing the proposed system to conventional aerobic wastewater treatment systems, the proposed system will save the energy required for aeration. Therefore, the proposed system will have another economic value from an energy savings point of view. The energy savings were calculated based on the shadow price of the national electricity. The electricity tariff depends on the amount of monthly consumption. The national tariff of electricity increases if the rate of consumption increases. The amount of electricity saved from using the proposed system is estimated to be 2.5 kwh/m<sup>3</sup>. This amount is the average required energy for conventional aerobic wastewater process based on personal communication with different national and international designers. Therefore, the annual energy savings is approximately 913 MWh. Accordingly, the equivalent commercial tariff category of 0.58 EGP/ kwh is applied. According to the African Development Bank report “Reforming Energy Subsidies in Egypt”, the subsidy rate of electricity is estimated to be 44% (Hagag, 2012). Another important saving factor is the less need of land area to install the CKD treatment facility units in comparison to the conventionally aerobic treatment units. However, this factor has not been taken into consideration as a conservative approach.

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The average international price of treated effluent wastewater that could be used for irrigation purposes in the Mediterranean is 0.23 Euro/m<sup>3</sup> (Chartzoulakis, 2001). Using the international exchange rate for Euro and U.S. Dollar (XE, 2014), the price of treated wastewater will be 0.32 USD/ m<sup>3</sup>.

The next step in completing the economic study was to estimate the initial capital cost for the treatment system. Equation 7 was used to estimate the initial capital cost. Since the flow rate is 1,000 m<sup>3</sup>/day, it was calculated that the capital cost is 491,000 USD.

## 6.6 Economic Indicators

The economic analysis was performed on a life time period of 10 years. Using the yearly operating costs and income from reusing the treated wastewater effluents as a basis, the estimated yearly profits were calculated. The yearly profits and the initial capital costs were then used to calculate the expected payback period (PBP) using Equation 5. The ERR and the NEPV were computed using Equation 6. Table 33 shows the economic indicators. In addition to the economic indicators, economic contribution or indirect effects of the treatment facility will be measured in terms of value added, employment, and foreign exchange earnings. The value added is a major economic indicator to explain to what extent the project is valuable. By subtracting the transfer abroad from the domestic value added, we can obtain the national value added. The domestic value added is measured as the difference between the gross output (i.e., wages, net benefits...) and the material inputs. The gross output of the treatment system exceeds the material inputs. The domestic value added is equal to the national value added as the transfer abroad is zero. Therefore, the value added is a significant positive value. The project leads to employment generation where more employees will be required to maintain the new project. The new job roles generated by the project will bring about a

more technically savvy pool of laborers. The project is projected to save electricity as one of the important inputs to any treatment facility. In addition, it will produce a tradable product which is clean water for irrigation use.

Comparing the ERR to the selected SDR at 8% as previously discussed in section 3 of this chapter “Economic Analysis Methodology”, it is obvious that the project is economically viable. In addition to the ERR, the NEPV is positive. However, we can conclude that implementing the proposed treatment system in Egypt is economically viable taking into consideration the indirect economic contributions.

**Table 33: Economic Analysis Indicators**

<b>Item</b>	<b>Cost</b>
<b>Outcome(USD/year)</b>	
Initial Capital Cost	491,000
Maintenance	19,640
<b>Income(USD/year)</b>	
Electricity Savings	104,400
Treated Effluents	320
<b>Economic Indicators</b>	
Economic Rate of Return (ERR) (%)	11.5
Pay Back Period (years)	5.7
NEPV (USD)	79,894

## 6.7 Outcomes and Findings

The economic analysis concludes that the project will help contribute to the sustainable development of Egypt through its contribution to the environmental, economic, and social pillars. The high ERR (11.5%) and high positive NEPV are observed by using the treated effluents in irrigation purposes and saving electricity from the new innovative proposed treatment technology. Moreover, using cement kiln dust (CKD) as a harmful industrial waste in the treatment facility improves the indirect economic contribution to the society. The project has also a positive value added and



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creates new jobs. Thus, it would be in the best interests of the economy as a whole for projects like this to be implemented on a greater scale.

The following points have also been concluded:

- The project will help contribute to the sustainable development of Egypt through its contribution to the environmental, economic, and social pillars. The economic analysis showed that the proposed project is economically viable.
- The project has positive value added, and will create job opportunities. Thus, it would be in the best interests of the economy as a whole if projects like this are implemented on a greater scale due to its positive impact on the society.
- The treated effluent will be used directly for irrigation purposes since it meets the national and international requirements for restricted irrigation.
- The proposed technology will save an immense amount of energy and electricity could reach approximately 913 MWh annually for every 1,000 m<sup>3</sup> treated effluent. This might help in solving the energy crises in Egypt. Moreover, it will indirectly help in reducing greenhouse gas emissions such as CO<sub>2</sub> resulted from electricity consumption, which increases the quality of life of society.
- The positive impact of reducing air pollution and enhancing the air quality by using the cement kiln dust as a harmful solid waste in the treatment facility guarantees that the workforce as well as the nearby receptors are no longer affected by the respiratory irritation problems which leads to less incidence of hospitalization due to air pollution.
- Implementing new technology will lead to tech and knowledge transfer. The project showcases an innovative way to use cement kiln dust as an industrial waste in treating wastewater to produce treated effluents.

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- The project also encourages private partnership and government to mitigate industrial wastes and wastewater issues.

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# CHAPTER 7: CONCLUSION AND RECOMMENDATIONS

## 7.1 Conclusion

The adsorption characteristics of cement kiln dust (CKD) were determined from adsorption studies using heavy metals, namely lead, copper, and cadmium. Two common methods of application, completely mixed batch reactors, and continuous flow columns were utilized. Moreover, a pilot scale experiments were run using a treatment unit of a capacity of 20 to 25 L/h. The adsorption performance of the CKD was determined using sorption isotherm models. Based on the outcomes and results of this study, the following conclusion can be drawn:

- Cement Kiln Dust (CKD) is an industrial hazardous waste. The major components of the CKD are alumina, calcium oxide, silica, ferric oxide, and magnesium oxide.
- The experimental runs show that the CKD has a high affinity to adsorb the target heavy metals from the aqueous solutions.
- CKD shows potential to adsorb heavy metals from aqueous solutions at  $\text{pH} \geq 5.5$ . CKD has a negative charge below  $\text{pH} 10.0$  for different ionic backgrounds. Also, the surface titration experiment shows that the zero point of charge for the CKD is at  $\text{pH} 10.0$ .
- Cement Kiln Dust (CKD) demonstrates potential to adsorb heavy metals, even at  $\text{pH}$  values less than the  $\text{pH}_{\text{zpc}}$ . Metal removal is a result of electrostatic interactions in addition to surface complexation.
- A TL-SCM was used to describe surface protonation of the CKD at various ionic strengths assuming  $>\text{SOH}_2^+$ ,  $>\text{SOH}$ , and  $>\text{SO}^-$ -surface species; and the

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equilibrium relationship of Me(II) adsorption as a function of pH and CKD dose. The removal rate and the strength of adsorption is in the order Pb> Cu>Cd as depicted by Langmuir and Freundlich isotherm models as well.

- The adsorption-pH edge indicated that there was a notable removal of Cd before pH 9; the removal reached its peak value at pH 6.0 with an uptake capacity 90%, while the Cd precipitation action took place at pH >9 to reach removal efficiency greater than 90%.
- The adsorption-pH edge indicated that there was a notable removal of Pb before pH 5.5; the removal reached its peak value at pH 5.5 with an uptake capacity 99%.
- The adsorption-pH edge indicated that there was a notable removal of Cu before pH 5; the removal reached its peak value at pH 6.0 with an uptake capacity 91%.
- Heavy metals removal at high pH values is attributed to metal precipitation.
- The column reactors have higher adsorption capacity than the batch ones for the same initial concentration of adsorbate. This is due to the fact that the driving force throughout the column run is higher with respect to the liquid phase concentration of the solute.
- A unit of a capacity of 20 to 25 l/h has been designed. The unit is successfully able to treat an industrial wastewater generated from glass manufacture from any heavy metals or physiochemical constituents. The pilot scale is able to produce treated effluent with high quality in compliance with the international and national guidelines.
- The treated effluent can be used directly for irrigation purposes according to Egyptian regulations (decree 44/2000) and international standards (FAO, 1985).

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- The economic analysis showed that the proposed project is economically viable (ERR 11.5%). Thus, it will help contribute to the sustainable development of Egypt through its contribution to the environmental, economic, and social pillars.
  - The project has positive value added, and will create job opportunities.
  - The project showcases an innovative way to use cement kiln dust as an industrial waste in treating wastewater to produce treated effluents.

## **7.2 Recommendations for Future Work**

Further technical and experimental works are required to investigate the following:

- The CKD adsorption capacity and mechanism on adsorbing heavy metals from multicomponent synthetic solution containing different heavy metals on a bench scale studies should be determined.
- The applicability of using the produced sludge in other processing facilities, such as tiles, ceramics, or bricks needs to be studied. Also, the leachate of the final product manufactured from the produced sludge should be analyzed to determine the release of any heavy metals to the environment.
- The feasibility of using pelletized CKD should be tested and identified.
- Manufacturing CKD cartridges to be used in the adsorption towers should be investigated. This might help to facilitate the handling and transportation of CKD to treatment plants.

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