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THE AMERICAN UNIVERSITY IN CAIRO

SCHOOL OF SCIENCES AND ENGINEERING

REMOVAL OF LEAD FROM INDUSTRIAL WASTEWATER USING A LOW COST WASTE MATERIAL

BY

Hayam Ahmed Talaat Amer

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science in Environmental Engineering

Under the supervision of:

Dr. Salah El-Haggar

Professor and Chair, Department of Mechanical Engineering

The American University in Cairo

Dr. Ahmed El-Gendy

Associate Professor and Director of the Environmental Engineering Program, Department of Construction and Architectural Engineering

The American University in Cairo

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ABSTRACT

Several industries utilize heavy metals in their industrial processes, eventually discharging them in their wastewater. Water contamination by heavy metals is a major environmental problem due to their acute toxicity and their accumulation in food chains. Therefore, intensive research work has been carried out lately on the feasibility of various low cost materials for the removal of heavy metals from wastewater.

The main objective of the current research was to examine the potential of a low cost material for the removal of Pb^{2+} from a synthetic lead solution. The research work was divided into three core phases. Phase I was a preliminary comparative study among various agricultural wastes; sugarcane bagasse, rice straw and rice husk, two industrial wastes, namely cement kiln dust (CKD) and marble powder, and a natural material; lime.

In Phase II the research was taken to a deeper level as the feasibility of utilizing rice straw for biosorption of Pb^{2+} was profoundly investigated using batch equilibrium experiments. The effect of several operating parameters on the uptake of Pb^{2+} was tested, which are the pH of the solution, contact time, rice straw dose, particle size, initial Pb^{2+} concentration and pre-treatment of rice straw. The percent removal of Pb^{2+} increased with increasing the pH, contact time, and rice straw dose up to the point of equilibrium; however, it decreased with the increase in the particle size. The pre-treatment of rice straw did not yield a considerable increase in the percent uptake of Pb^{2+}. Langmuir and Freundlich isotherm models were used for the evaluation of the equilibrium experimental data; the correlation coefficients were 0.989 and 0.959, respectively. The maximum adsorption capacity of raw rice straw was calculated using Langmuir isotherm; 42.55 mg/g, which is higher than several adsorption capacities of rice straw reported in the literature.

Phase III was conducting fixed-bed column experiments using rice straw. The service time of the columns and the treated volume of wastewater to breakthrough (C_e= 1mg/l) and to exhaustion ($C_e \approx$ 95% C_0) increased with the increase in the bed depth of the packed rice straw; however, they decreased with the increase in the initial Pb^{2+} concentration and the flow rate of the solution.

Physical and chemical characterization of rice straw was carried out in order to define the BET surface area, pore volume, average pore size, surface functional groups, shape of the cell wall and chemical composition. Biosorption of Pb^{2+} using rice straw was inferred to be due to a complex of physical and chemical mechanisms.

TABLE OF CONTENTS

ACRONYMS

AAS	Atomic absorption spectrometer
b	Langmuir constant (l/mg)
BET	Brunauer, Emmet and Teller isotherm
BV	Bed volumes
C_o	Initial Pb^{2+} ions concentration in a liquid phase (mg/l)
C_e	Pb^{2+} ions concentration after adsorption in a liquid phase (mg/l)
C	Effluent Pb^{2+} concentration in a column test (mg/l)
C_b	Effluent Pb^{2+} concentration at breakthrough of a column (mg/l)
DDW	Deionized distilled water
EBCT	Empty Bed Contact Time (min)
EDX	Energy Dispersive X- Ray
EEAA	Egyptian Environmental Affairs Agency
FAO	Food and Agriculture Organization of the United Nations
FTIR	Fourier Transform Infrared Spectroscopy
K_F	Freundlich capacity factor (mg/g) $(L/mg)^{1/n}$
L	Length of the adsorption column (cm)
M	Mass of the packed biosorbent in a column (g)
m	Mass of the biosorbent in a batch experiment (g)
$m_{ad,tb}$	Mass of metal ions adsorbed in a column at breakthrough (mg)
$m_{ad,te}$	Mass of metal ions adsorbed in a column at exhaustion (mg)

$m_{in,t}$	Influent mass of metal ions to the column at time t (mg)
$m_{out,t}$	Effluent mass of un-adsorbed metal ions at time t (mg)
MTZ	Mass Transfer Zone (cm)
1/n	Freundlich intensity parameter
NILE	New Center for Integrated Studies of Land & Environment
N-SB	NaOH treated sugarcane bagasse
Q	Solution flow rate (ml/min)
q	Adsorption capacity (mg/g)
q_b	Adsorption capacity at breakthrough (mg/g)
q_e	Adsorption capacity at exhaustion (mg/g)
q_{max}	Maximum adsorption capacity (mg/g)
Raw-RH	Raw rice husk
Raw-RS	Raw rice straw
Raw-SB	Raw sugarcane bagasse
SEM	Scanning Electron Microscope
t_b	Breakthrough time of a column (h)
t_e	Exhaustion time of a column (h)
TA-N-RH	Tartaric acid and NaOH modified rice husk
TA-N-SB	Tartaric acid and NaOH modified sugarcane bagasse
TA-RS	Tartaric acid modified Rice Straw
TA-SB	Tartaric acid modified sugarcane bagasse

UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
V	Volume of the Pb^{2+} synthetic solution (l)
WHO	World Health Organization

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1 : INTRODUCTION

1.1 Sustainable Development

1.1.1 Definition and Background

The notion of sustainable development (SD) has developed since it was first brought up at the biosphere conference in Paris in 1968. In 1987, the United Nations World Commission on Environment and Development issued a report named ‘Our Common Future’, commonly known as the Brundtland report, where the classic definition of sustainable development according to this report is: “development that meets the needs of the present without compromising the ability of future generations to meet their own needs” (Bolcárová and Kološta 2015). Sustainable development was also defined as “sustainable development in terms of optimal economic growth accompanied with positive development of other sustainable development indicators from social, economic and environmental fields” (Bolcárová and Kološta 2015).

Sustainable development integrates three complementary areas of development, which are the economic, social and environmental areas, as shown in Figure 1. According to Soubbotina (2004), achieving sustainability in the three domains cannot be achieved without first ensuring equity and balance. The term ‘Sustainable’ could be replaced by the terms ‘equitable and balanced’, in other words, the core of sustainable development should be based on balancing the needs and interests of the different sectors of a society within the same generation, and among the future generations, all together in the three correlated areas: economic, social and environmental (Soubbotina 2004). The main target of the EU Sustainable Development Strategy (SDS), issued by The European Council in Gothenburg in 2001 and revised in Brussels in June 2006, was to ensure continuous enhancement of the quality of life for the current and coming generations (Bolcárová and Kološta 2015).

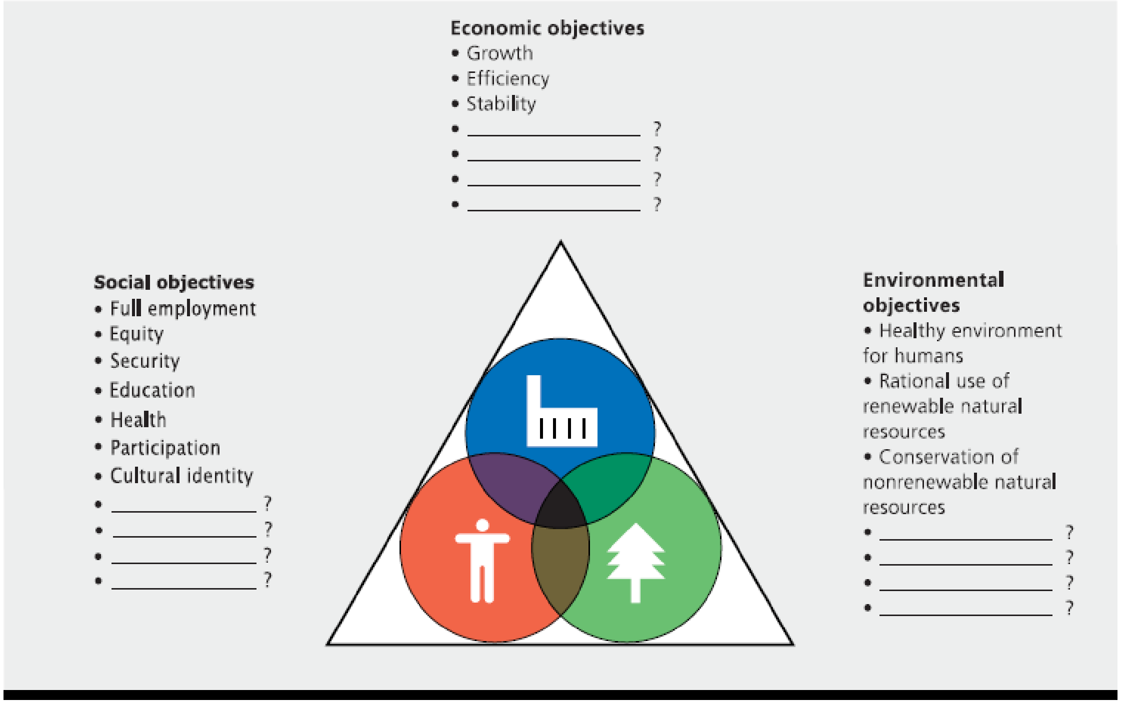


Figure 1: Objectives of Sustainable Development (Soubbotina 2004)

1.1.2 Economic Sustainability

Economic growth in itself does not necessarily lead to economic sustainability; for instance, if economic growth of a country is reflected in a high Gross Domestic Product (GDP); however, people live in poverty due to low salaries and wages, economic growth is not sustainable in this case. Therefore, for an economic growth to be sustainable, the income of a country has to be used to provide the people with satisfying salaries, and wages, a good standard of hospitals, education, food, and housing that can be available for all members of the society without any kind of discrimination. Economic growth is quantitative, in other words it is related to the amount of economic change concerning investment, income, output, and consumption. Conversely, sustainable development is qualitative, as it is related to the quality of life, the economic, social and environmental changes. Finally, combining both concepts attains economic sustainability. Economic growth should not negatively affect the life quality, the environment, or natural resources (Munier 2005).

1.1.3 Social Sustainability

Social sustainability is related to social equity, which is achieved by providing every citizen with his right for housing, food, health care, and jobs (Munier 2005).

1.1.4 Environmental Sustainability

Environmental sustainable development is achieved through conservation of natural resources, prevention of environmental pollution, and compliance to environmental laws and regulations. Conserving natural resources through recycling, reusing, or recovery of material is an achievement of the Cradle- to- Cradle concept, which is a very essential concept because creating new sources of raw material is an expensive, and a difficult task, additionally waste disposal and incineration are either expensive processes, require space for land filling, and can cause contamination of soil, air, and water (El Haggar 2007).

1.2 Industrial Wastewater

Water is a renewable resource, it is naturally renewed within the hydrological cycle; however, once used it gets polluted and of course the extent of pollution is directly correlated to the purpose it was used for (WHO/UNEP 1997). Industrial wastewater is defined as “any wastewater generated from any manufacturing, processing, institutional, commercial, or agricultural operation, or any operation that discharges other than domestic or sanitary wastewater” (Industrial Waste Management Division 1998). Due to the water scarcity problem that Egypt and many other countries all over the world are facing, which is expected to become more serious in the future, wastewater treatment technologies, whether domestic or industrial, are very vital; therefore, more efforts and finance are ought to be assigned for research work in that field. Treating and reusing wastewater will eventually allow conserving fresh water for potable and domestic use, while using lower quality water, treated wastewater, for other uses that does not require high quality of water, such as irrigation, landscaping and industrial re-use. High quality water should not be used for purposes that can bear lower water quality (WHO/UNEP 1997). Figure 2 shows the various uses of domestic and industrial treated wastewater presented by the World Health Organization in 1989. The way out of the global problem of water shortage is creating alternative water sources, simultaneously with more efficient water use and proper control on the water consumption (WHO/UNEP 1997). Hence, treating wastewater to be suitable for re-use or to be complying with the permissible limits for discharge in waterways achieves the sustainable development concept in terms of; reusing wastewater in various purposes, which is an application of the cradle to cradle concept, conserving and sustainably managing the available water resources, and protecting surface water bodies and aquatic life from potential contamination; thus, protecting human health from exposure to heavy metals.

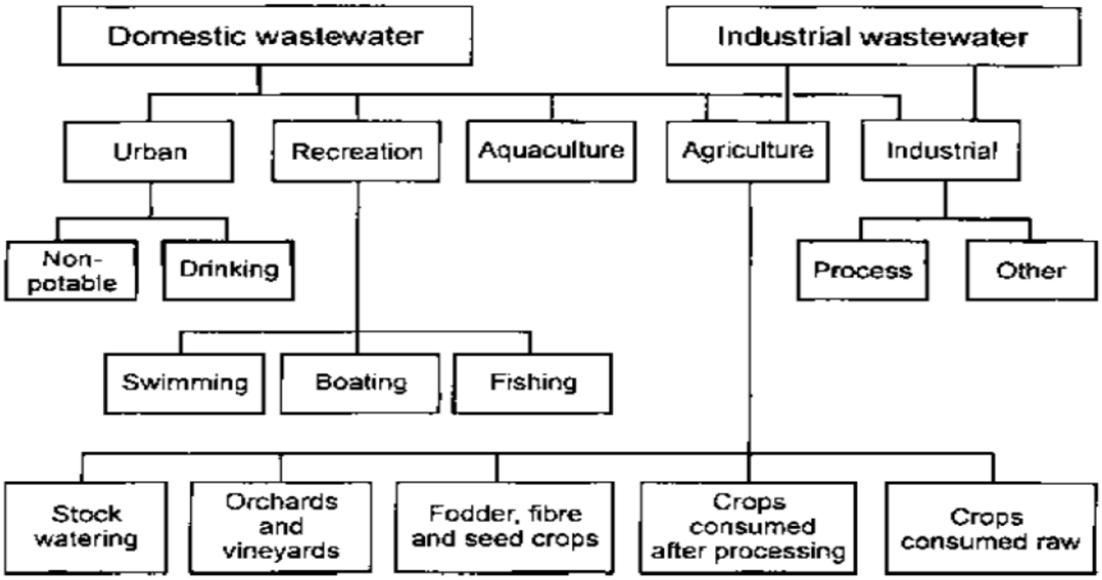


Figure 2: Various purposes of treated wastewater (WHO 1989)

Utilizing treated wastewater for industrial purposes that do not necessarily require high grade water, is widely applied in industrialized countries and has shown to be cost-effective, especially if the manufacturing facility is situated close to urban centers in which secondary treated wastewater is available (WHO/UNEP 1997). The common uses of treated wastewater by industrial facilities are the following (WHO/UNEP 1997):

- Evaporative cooling water, particularly for power stations

- Boiler-feed water
- Process water
- Irrigation of landscaping surrounding industrial plants

Industrial wastewater that does not comply with the permissible law limits are a main source of pollution, as they consist of organic and inorganic pollutants, as well as heavy metals, varying according to the industry.

1.2.1 Classification of Compounds and Pollutants in Wastewater

i *Chemical classification*

The chemical classification of the constituents of wastewater is either organic or inorganic. Organic constituents are mainly made of proteins, fats and carbohydrates, and they are either degradable or non-degradable. Organic matter in wastewater is quantified by the bio-chemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) tests (Munter 2000).

Inorganic pollutants of wastewater are free ammonia, organic nitrogen, nitrites, nitrates, organic phosphorus and inorganic phosphorus, and trace elements, such as heavy metals. Heavy metals, such as lead, cadmium and mercury are very toxic inorganic matters in wastewater (Munter 2000).

ii *Physical classification*

As for the physical classification, wastewater pollutants are classified into either insoluble solids (suspended solids), or soluble solids. Insoluble solids are measured by filtering and drying the sample, and then weighing the filtrate, which when ignited volatile solids, mainly organic, are burnt and released. Around 40-65% of the solids in wastewater are insoluble, and around 60% of those insoluble solids, in municipal wastewater, are settleable which can be removed by sedimentation. The second classification is the soluble (dissolved) solids (Munter 2000).

1.2.2 Heavy Metals in Industrial Wastewater

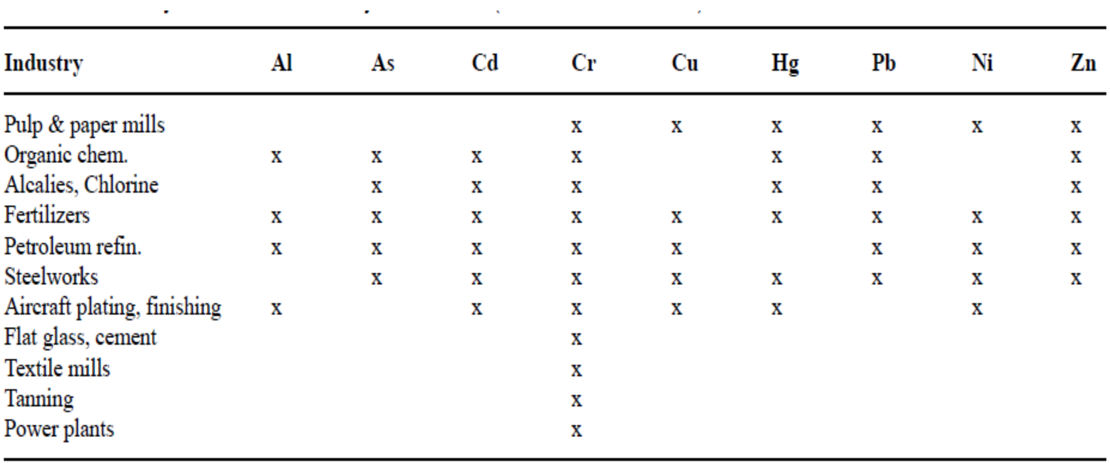
Water contamination by heavy metals is a major environmental problem. Rapid industrial development has increased the release of heavy metals in water bodies. Heavy metals endanger human health and accumulate in food chains (Sarma, Kumar and Pakshirajan 2015). Chromium is the most abundant heavy metal in wastewater, it comes from various sources; however, it is not the most toxic to human beings and living organisms. Lead, cadmium and mercury are more toxic and have adverse effects on human health (Munter 2000).

Lead is one of the most toxic heavy metals. Several industrial applications utilize lead in their process, such as battery manufacturing, electroplating, petrochemical processes (Sarma, Kumar and Pakshirajan 2015), printing pigments, fuels, photographic materials and explosive manufacturing (Jeyakumar and Chandrasekaran 2014). Lead was classified by the US Environmental Protection Agency (EPA) as “a probable human carcinogen” and the International Agency for Research in Cancer considered it “Possibly Carcinogenic to humans” (UNEP 2013). Moreover, lead has adverse impacts on the nervous system, reproductive system, and immune system. Children are the most affected by the toxicity of lead. Whether its source is air, or water, Lead gets into their blood stream and accumulates in their bones. Accumulated lead in the body of a pregnant woman can harm her offspring as well (UNEP 2013). Lead was found to have the highest concentration of heavy metals in industrial wastewater of the crystal glass industry in Egypt (EL Zayat 2014).

As for cadmium, it also has extremely negative impacts on human health, such as: high blood pressure, kidney damage, destruction of testicular tissue, and destruction of red blood cells.

Some of the most toxic effects of mercury on human beings are damage of the nervous system, irritability, paralysis, blindness, insanity, chromosome breakage and birth defects (Munter 2000). Table 1 demonstrates the heavy metals produced from the different industries.

Table 1: Heavy Metals Produced from Various Industries (Munter 2000)



Industry	Al	As	Cd	Cr	Cu	Hg	Pb	Ni	Zn
Pulp & paper mills				x	x	x	x	x	x
Organic chem.	x	x	x	x		x	x		x
Alcalies, Chlorine		x	x	x		x	x		x
Fertilizers	x	x	x	x	x	x	x	x	x
Petroleum refin.	x	x	x	x	x		x	x	x
Steelworks		x	x	x	x	x	x	x	x
Aircraft plating, finishing	x		x	x	x	x		x	
Flat glass, cement				x					
Textile mills				x					
Tanning				x					
Power plants				x					

1.3 Heavy Metals Treatment Methods

Generally speaking, wastewater treatment is essential for the following reasons (Munter 2000):

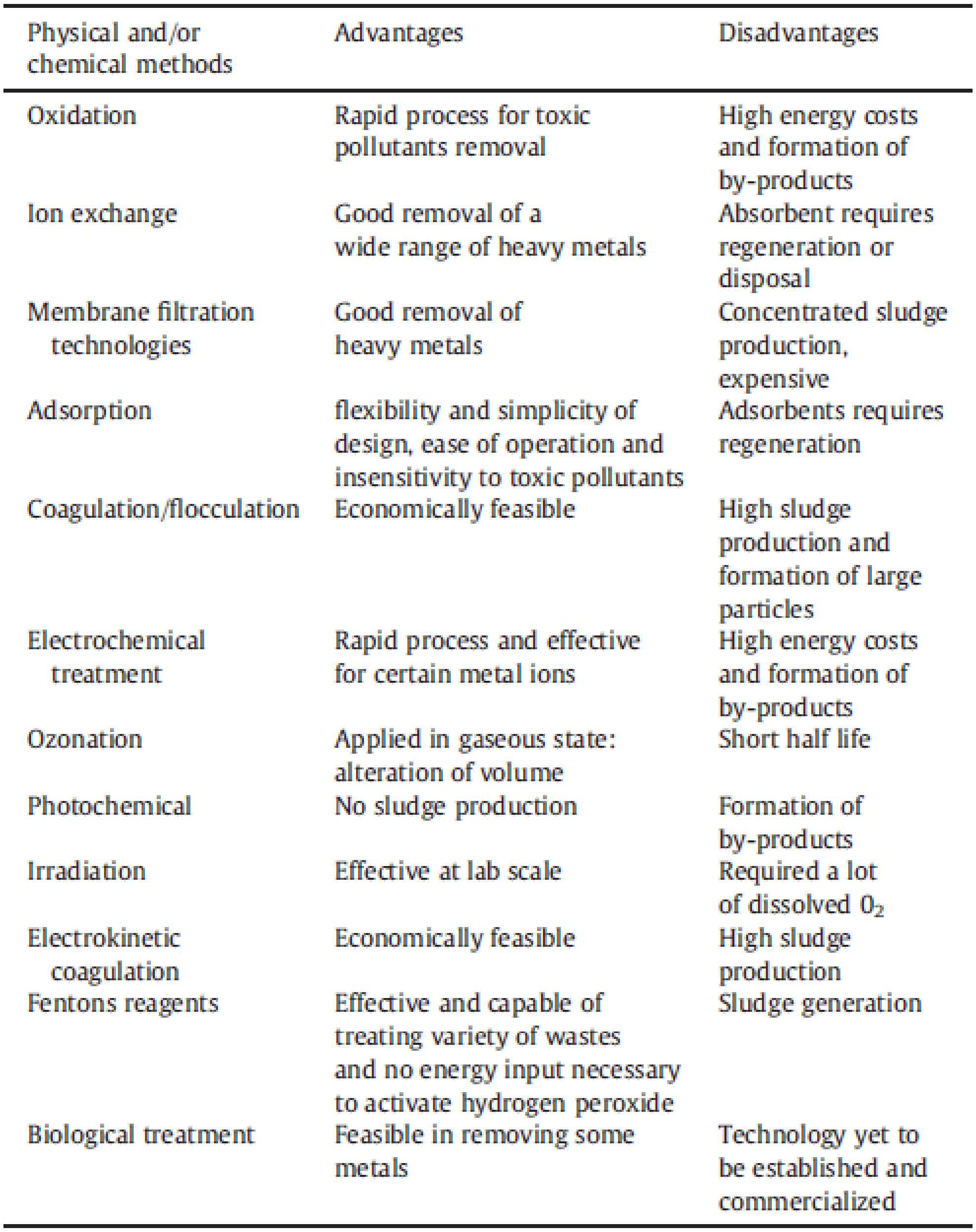
1. Protecting water quality of surface water bodies; rivers and lakes.
2. Consequently protecting the aquatic life; fish.
3. Protecting human health from deterioration due to direct or indirect exposure to water pollutants.
4. Ability to re-use treated wastewater in applications that do not require high water quality, leading to having more control over the water resources; hence, conserving the water resources.

There are multiple methods and technologies of wastewater treatment, and vast research efforts have been exerted in that field in an attempt to reach the most effective treatment method relevant to the degree and type of pollution of wastewater. However, not all treatment processes and technologies are sustainable environmentally, economically, and socially. For a treatment technology to be environmentally sustainable, it has to be environmentally safe; in other words, does not create any source of pollution to the environment and could even have a positive impact on the environment. As for the economic sustainability, some treatment processes are less costly than others, so certainly the most economically sustainable treatment method is the one that can reach the required treatment objective and comply to the permissible limits of the relevant laws and standards, with the least cost. Yet, it has to be socially accepted as well in order to achieve the three elements of sustainability.

1.3.1 Current Treatment Methods

Some of the current treatment methods that can be utilized for the removal of heavy metals from wastewater are chemical precipitation, chemical oxidation, electrochemical treatment, reverse osmosis, ion exchange, membrane technologies, filtration (Sarma, Kumar and Pakshirajan 2015), and coagulation (Soetaredjo, et al. 2013, Won, et al. 2014). Some of those current methods have some drawbacks, including inefficient metal removal, especially in treatment of wastewater contaminated with trace concentrations of heavy metals in the range of 1-100mg/l (Sarma, Kumar and Pakshirajan 2015, Soetaredjo, et al. 2013), high cost (Won, et al. 2014, Ali, Asim and Khan 2012), high energy consumption and production of a secondary waste product; toxic sludge that would require further special handling (Soetaredjo, et al. 2013, Ding, et al. 2012), requiring large quantities of chemical reagents (Ding, et al. 2012), and complicated operation and maintenance. As for adsorption using activated carbon, it is very expensive in large scale applications (Wang and Chen 2009).Therefore, most of those treatment methods cannot be considered as sustainable treatment technologies. Table 2 presents the advantages and disadvantages of an array of treatment methods and technologies of heavy metals in wastewater.

Table 2: Advantages and disadvantages of heavy metals treatment methods (Ahmaruzzaman 2011)



Physical and/or chemical methods	Advantages	Disadvantages
Oxidation	Rapid process for toxic pollutants removal	High energy costs and formation of by-products
Ion exchange	Good removal of a wide range of heavy metals	Absorbent requires regeneration or disposal
Membrane filtration technologies	Good removal of heavy metals	Concentrated sludge production, expensive
Adsorption	flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants	Adsorbents requires regeneration
Coagulation/flocculation	Economically feasible	High sludge production and formation of large particles
Electrochemical treatment	Rapid process and effective for certain metal ions	High energy costs and formation of by-products
Ozonation	Applied in gaseous state: alteration of volume	Short half life
Photochemical	No sludge production	Formation of by-products
Irradiation	Effective at lab scale	Required a lot of dissolved 0_2
Electrokinetic coagulation	Economically feasible	High sludge production
Fentons reagents	Effective and capable of treating variety of wastes and no energy input necessary to activate hydrogen peroxide	Sludge generation
Biological treatment	Feasible in removing some metals	Technology yet to be established and commercialized

1.3.2 Adsorption

Adsorption is an advanced wastewater treatment method implemented for the removal of heavy metals in industrial wastewater. In the following sub-sections, the definition and the mechanism of adsorption and the various conventional and unconventional adsorbents that could be utilized in wastewater treatment will be briefly discussed.

i *Definition and background*

Adsorption is one of the most efficient wastewater treatment technologies because of its low cost, compared to the other technologies highlighted in Section 1.3.1, its simple operation and it does not produce a large amount of sludge (Won, et al. 2014, Grassi, et al. 2012, Ali, Asim and Khan 2012). Adsorption is defined as "a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid–solid interface. The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent" (Grassi, et al. 2012). The materials used as adsorbents must have high content of carbon or oxygen for efficient adsorption (Ali, Asim and Khan 2012).

The main factors that impact the efficiency of adsorption are the following (Grassi, et al. 2012, EL Zayat 2014):

1. Surface area of the adsorbent material
2. Nature and concentration of adsorbate
3. pH of the solution
4. Temperature
5. Properties and dose of the sorbent
6. Contact time

Adsorbents can be classified into two main groups, which are conventional adsorbents/ sorbents, and these are commercial adsorbents and some of them are commonly used, and unconventional adsorbents/ sorbents, which are mainly composed of cheap agricultural, and industrial wastes, naturally existing materials and other organic materials.

ii Conventional Adsorbents

ACTIVATED CARBON

Activated carbon (AC) is the most common adsorbent used in wastewater treatment. It can be made of different materials, such as coal, coconut shells, lignite, wood, and others. Activated carbon is produced through pyrolysis of raw material and subsequent activation via oxidizing gases. AC is characterized by its high porosity and large surface area; 600 to 2,000 m2/g (Grassi, et al. 2012). AC is either in a powder form (PAC), or a granular form (GAC). GAC has a larger particle size and a smaller surface area.

CLAY

Clay minerals are natural low cost adsorbents, have high porosity and naturally available. There are various kinds of clay, namely: smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite, sepiolite, bentonite, kaolinite, diatomite, and Fuller's earth (attapulgite and montmorillonite varieties) (Gupta, et al. 2009). The clay's adsorption property is due to its negatively charged surface that allows clay to adsorb positively charged ions (Grassi, et al. 2012).

MINERALS

Examples of natural minerals are zeolite and goethite. Natural zeolite "results from crystalline silicates and alumino-silicates linked through oxygen atoms, producing a three dimensional network containing channels and cavities of molecular dimensions" (Nwafulugo, et al. 2014); however, zeolite can be synthesized using other materials that can replace the silicon and aluminum for the production of zeolite. Zeolites have very distinctive properties, such as the high porosity, large surface area and pores volume per unit of mass, negatively charged surface, and chemical inertness, that qualify it to be a very efficient adsorbent of heavy metals; however, its only drawback is its high cost (Nwafulugo, et al. 2014).

iii *Unconventional- Low Cost Adsorbents*

This category of adsorbents is much lower in cost than the activated carbon and zeolite because it is composed of agricultural wastes, bacteria, algae, fungi, industrial wastes, or other naturally occurring materials. In addition to the low cost and the availability of agricultural and industrial wastes, two main advantages of using waste products as adsorbents are the re-use of a dumped waste in a useful purpose and the contribution to solving the problem of the solid waste sector by reducing the amount of waste that needs to be landfilled. For all these reasons adsorption using low cost or zero cost waste products can be considered a sustainable method of treatment of industrial wastewater.

Some of those low- cost adsorbents are organic because they are composed of a biological matter; hence, named bio-sorbents, such as agricultural wastes, bacteria, algae, yeasts and fungi. Other low-cost in- organic adsorbents, such as some industrial wastes, are cement kiln dust and marble powder, and naturally available materials, such as lime. Figure 3 shows that low cost adsorbents can be classified either by their nature; organic/ inorganic, or by their availability; natural materials, agricultural/ industrial/ domestic wastes, or synthesized products.

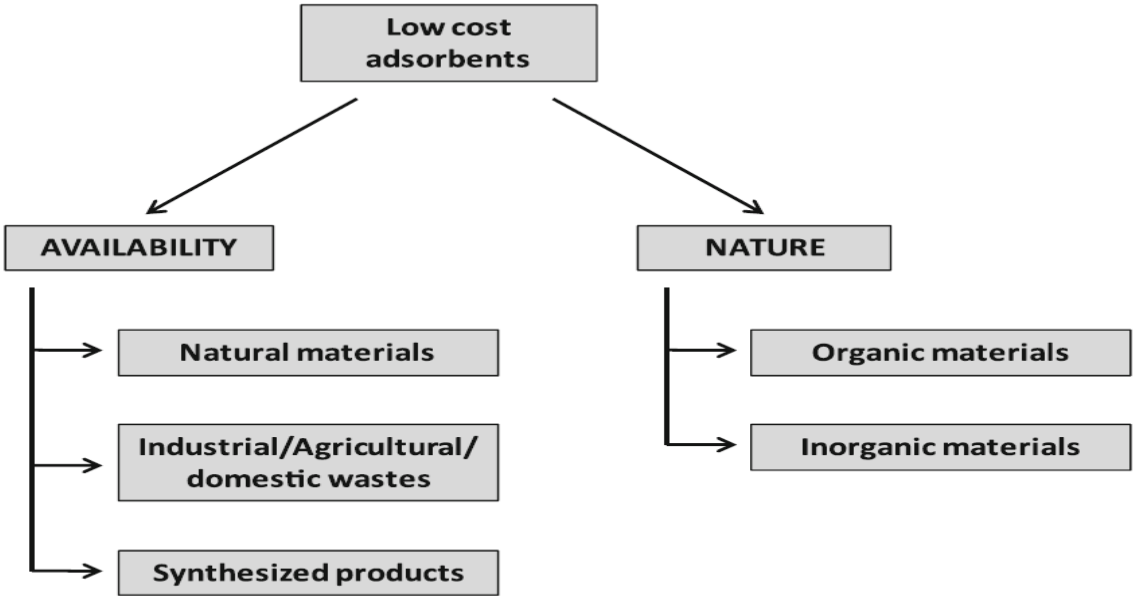


Figure 3: Classification of Low Cost Adsorbents (Grassi, et al. 2012)

AGRICULTURAL WASTES

Agricultural wastes are rich in hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch. They also have multiple functional groups (Grassi, et al. 2012). Examples of agricultural wastes that have been investigated by researchers as bio-sorbents of heavy metals in wastewater are: rice straw (Ding, et al. 2012), rice husk (Sarma, Kumar and Pakshirajan 2015, Wong, et al. 2003a), sugarcane bagasse (Homagai, Ghimire and Inoue 2010, Gurgel, Freitas and Gil 2008), corn stalk (Chen, et al. 2012), orange peels (Chatterjee and Schiewer 2014), and soybean straw (Zhu, Fan and Zhang 2008). Agricultural wastes could be used on its natural state, but sometimes it would be essential to be pre-treated to enhance its sorption capacity (Grassi, et al. 2012).

BACTERIA, ALGAE, YEAST AND FUNGI

This kind of bio- sorbents has been appealing for researches to investigate its sorption capacity and mechanism for the removal of heavy metals because of its efficiency, low cost, and availability. Microorganisms based biosorbents have some disadvantages, which are low density, poor mechanical strength, occasionally swelling, large particle size, and the very fine particles can block the column system in practical applications (Won, et al. 2014).

Examples of that kind of bio-sorbents, according to Wang and Chen (2009), which have been studied by researchers are:

- Bacteria: Bacillus subtillis
- Fungi: Rhizopus arrhizus
- Yeast: Saccharomyces cerevisiae
- Algae: seaweeds
- Industrial waste that is composed of large biomasses: fermentation and food industry

Pre-treatment and modifications are required for the process improvement.

INDUSTRIAL WASTE

According to Ahmaruzzaman (2011), researches have been carried out to test the capability of some industrial wastes to adsorb heavy metals from wastewater, some of those industrial wastes are fly ash, blast furnace slag and sludge, black liquor lignin, red mud, and waste slurry. However, most of them showed higher sorption capacity after undergoing some modifications. Fly ash, a residue of the coal combustion process, could be a good substitute to the high cost activated coal and zeolite in sorption of heavy metals. Sorption capacity of fly ash is influenced by the fly ash origin and chemical treatment. Blast furnace slag is a by-product of steel manufacturing. Sludge is a waste of the electroplating industry, where metal ions in wastewater precipitates with calcium hydroxide forming the sludge. The sludge consists of insoluble metal hydroxides and other salts. Black liquor is a waste produced from paper industry, it contains lignin, which is a substance that has a potential to adsorb heavy metals in wastewater (Ahmaruzzaman 2011).

Cement kiln dust (CKD) is another potential low cost adsorbent of heavy metals. CKD results from the combustion process of the raw material in cement production, and it is carried by the exhausted gases of the cement kiln to be captured by the air pollution control device of the kiln (EL Zayat 2014). The cement industry in Egypt produces around 1.0 million tons of cement dust per year. Due to the elevated concentration of alkalis in the CKD it cannot be re-used in the cement production process (Mostafa, Rashed and Mostafa 2005). There are 22 cement plants in Egypt, producing around 46 million metric ton/ year of cement (EL Zayat 2014). CKD is a major source of air pollution; consequently, imposes health threats, especially diseases related to the respiratory system because it is a very fine dust. Handling CKD and dumping it in landfills is not always done in the proper way that prevents environmental pollution.

LIME

"Limestone is a naturally occurring and abundant sedimentary rock consisting of high levels of calcium and/or magnesium carbonate and/or dolomite (calcium and magnesium carbonate), along with minerals" (National Lime Association).

The calcination process of limestone turns it into quicklime and CO_2. Limestone quarries are abundant in the Eastern desert, Western desert of Egypt and Sinai (EL Zayat 2014). Lime is used for the neutralization of acid wastes and for precipitation of heavy metals in industrial wastewater. According to the National Lime Association, lime has many applications in industrial wastewater treatment, such as the following:

- Steel plants: lime is used for neutralization of sulfuric acid-based waste pickle liquors, allowing iron salts to precipitate. Additionally, Lime is utilized for neutralizing and precipitating chrome, copper, and heavy metals in wastewater of the plating process.
- Rayon plants: lime is utilized for neutralizing sulfuric acid wastes.
- Cotton textile finishing plants (dye works): lime neutralizes and precipitate dissolved solids from wastewater.

- In vegetable and fruit canning and citrus canning process: lime is used for clarifying wastewater instead of keeping the wastewater in lagoons.

1.4 Problem Statement

Due to their acute toxicity, heavy metals impose a major threat to human health and the environment. Yet, until 2011 there were 69 industrial facilities in Egypt that were discharging their wastewater, which did not comply with the Egyptian regulations, directly into the river Nile (EEAA 2012). The amount of untreated industrial wastewater is around 1.3 BCM/yr (EL Zayat 2014). Industrial wastewater re- use in Egypt constitutes only 5% of the total water re-use, compared to agriculture and domestic water re-use, due to the presence of toxic contaminants in industrial wastewater (Fourteenth International Water Technology Conference 2010). Current treatment available technologies have major drawbacks, including high capital and operational costs, generation of toxic sludge, complicated operation and maintenance, and high energy consumption. Therefore, it is very essential to find an economically feasible, simple to operate, efficient and sustainable treatment method in order to protect our surface water bodies, eventually our health from heavy metals contamination.

The quantity of agricultural wastes produced in Egypt in 2012 was 30 M tons (NILE, et al. 2013). Agricultural wastes in Egypt cause serious disposal problems and air pollution resulting from open field burning. Also, several industrial wastes cause environmental and health problems, knowing that the amount of industrial waste generated in Egypt in 2012 was 6 M tons (NILE, et al. 2013). Those low cost waste products are unused resources that can be utilized in solving the heavy metals water contamination problem.

1.5 Research Objectives

The main objective of the current research is to investigate the utilization of low cost waste materials as a sustainable solution for lead removal from industrial wastewater. The waste materials to be studied include various agriculture and industrial solid waste materials. The current research also aims at studying the optimum operating conditions and the possible methods of application for the most successful material in the removal of lead from industrial wastewater.

1.6 Scope of Work

In the current research the scope of work is the following:

1. Conducting a preliminary comparative study using batch equilibrium tests for a group of biosorbents and a group of adsorbents.
2. Running batch equilibrium tests for the most promising sorbent in order to define the optimum conditions of the system.
3. Examining the impact of the system conditions; namely, pH, contact time, Pb^{2+} initial concentration, sorbent dose and particle size on the removal efficiency and the adsorption capacity of the selected sorbent.
4. Conducting batch tests for chemically treated sorbent.
5. Applying isotherm models in order to define the theoretical maximum adsorption capacity of the sorbent and compare it to the maximum adsorption capacity of other sorbents of quite similar nature.
6. Running fixed- bed column experiments in an attempt to investigate the feasibility of the selected sorbent for the uptake of Pb^{2+} in that particular mode of applications.
7. Sorbent characterization using BET surface area measurement, FTIR analysis, and SEM & EDX analysis.

CHAPTER 2 : LITERATURE REVIEW

2.1 Adsorption

2.1.1 Mechanism

As explained in Chapter 1, adsorption is a “mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid–solid interface. The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent” (Grassi, et al. 2012). In the case of wastewater treatment, the interface is between the adsorbent solid surface and the liquid phase of the wastewater. If the bonding between the molecules of the adsorbed substance and the adsorbent solid surface is physical, the adsorption is physisorption, which is controlled by the Van der Waals forces. In that case the adsorption is weak and the reaction is reversible. However, if the bonding is due to chemical attraction, this is called chemisorption and it creates very strong forces of attraction between the adsorbent and the adsorbate. Both forms of adsorption can take place either simultaneously or successively if certain conditions were attained (Grassi, et al. 2012). Because determining whether the adsorption is due to chemical or physical forces is a difficult task, the term Sorption is sometimes used to describe the process (Metcalf & Eddy 2003).

The nature of the adsorption process, such as the kinetics and the equilibrium metal uptake capacity, is related to the physical and chemical characteristics of the adsorbent as well as the conditions of the system, such as the pH and the temperature. Adsorption is a complex mechanism that may occur due to several mechanisms which could differ from one adsorbent to the other based on the type of the adsorbent, its origin, and processing (Rao, et al. 2013). Those complex mechanisms could be ion exchange (Alluri, et al. 2007, Rao, et al. 2013), chelation (Rao, et al. 2013), adsorption due to physical forces (Van der Waals) (Rao, et al. 2013, Alluri, et al. 2007), ion entrapment in the capillaries and spaces of the cell wall of the adsorbent (Rao, et al. 2013), formation of complexes between the hydroxides functional groups (EL Zayat 2014) and the carboxylic functional groups (Wong, et al. 2003a) of the adsorbent and the positively charged metal ions, and co-precipitation of the insoluble metal ions hydroxides on the surface of the adsorbent (Mahmood, Malik and Hussain 2010, Alluri, et al. 2007, Zhigang, et al. 2009). For instance, it was reported that the main mechanism that is responsible for the metal uptake by seaweeds is ion exchange (Rao, et al. 2013). While other researchers believe that acidic functional groups, such as the carboxylic and the phosphate groups are the responsible for the water hyacinth metal uptake affinity (Romero-Guzmán, et al. 2013).

Adsorption can take place on the outer surface or in the macropores (>25nm), mesopores (1nm- 25nm), or the micropores (<1nm); however, the amount of metal ions adsorbed in the macropores and mesopores are usually insignificant compared to the micropores due to their small surface area (Metcalf & Eddy 2003).

2.1.2 Advantages

Adsorption is one of the most efficient wastewater treatment technologies and has several advantages, which are:

- Inexpensive (Ali, Asim and Khan 2012, Grassi, et al. 2012), if low cost waste products are used.
- High efficiency (Ahmaruzzaman 2011)
- Ease of operation (Ali, Asim and Khan 2012)
- Simplicity of design and not generating secondary pollution (toxic sludge) (Grassi, et al. 2012)
- Insensitive to toxic contaminants (Ahmaruzzaman 2011)

2.1.3 Biosorption

Adsorption using biological matter such as plant wastes or microbes is termed biosorption (Sarma, Kumar and Pakshirajan 2015). Researchers defined bio-sorption as “the removal of metal or metalloid species, compounds and particulates from solution by biological material” (Wang and Chen 2009). Sorbents of biological origin (biomasses) have the property of impounding heavy metals; thus, it can hugely reduce the concentration of heavy metals in an aqueous solution (Wang and Chen 2009). Advantages of biosorption are the following:

- Low cost (Won, et al. 2014, Ding, et al. 2012)
- High efficiency (Won, et al. 2014, Ding, et al. 2012)
- Wide selectivity in heavy metals uptake (Ding, et al. 2012)
- Wide availability of sorbents (Demirbas 2008)
- Minimal generation of toxic sludge (Won, et al. 2014)
- Feasibility of recovery of heavy metals via desorption and possibility of regenerating biosorbents (Won, et al. 2014)
- Utilization of waste materials for producing inexpensive sorbents aids in reducing and re- using generated waste (Ali, Asim and Khan 2012)

2.1.4 Adsorption Isotherms

Isotherm models predict the maximum adsorption capacity of a sorption system, which helps in the assessment of the feasibility of the treatment process for a specific application, the required dose of bio-sorbent and the selection of the most suitable sorbent for the given case (Kumar and Bandyopadhyay 2006). Isotherm models simulate the relation between the equilibrium concentration of heavy metals (C_e) and the adsorption capacity of a sorbent (q) (Ding, et al. 2012). Langmuir and Freundlich models are the most commonly used isotherm models in the literature. They are used for describing the isotherm of a single solute adsorption system (Ahmaruzzaman 2011).

i Langmuir Isotherm

Langmuir isotherm describes monolayer adsorption and assumes homogenous sorption sites and sorption energies on the surface of adsorbents (Grassi, et al. 2012, Sarma, Kumar and Pakshirajan 2015). Langmuir isotherm has two assumptions, which are the presence of a fixed number of active sites on the surface of a sorbent, all possessing uniform sorption energy, and reversible sorption (Metcalf & Eddy 2003). Langmuir also assumes that there is not any interaction between the biosorbed molecules (Sarma, Kumar and Pakshirajan 2015).

ii Freundlich Isotherm

According to some researchers, the isotherm of adsorption from an aqueous solution is better described by Freundlich isotherm model, which presumes a heterogeneous surface energy of adsorption (Grassi, et al. 2012). In other words, sorbent surfaces carrying sites of varied strength, that is multi-layer adsorption (Sarma, Kumar and Pakshirajan 2015). Unlike Langmuir isotherm, Freundlich isotherm is an empirical model derived in 1912 (Metcalf & Eddy 2003).

2.1.5 Factors Influencing Adsorption Capacity

Factors that impact the efficiency of adsorption are the following:

i Solubility and Initial Concentration of Adsorbate

The adsorption capacity of a metal decreases with the increasing solubility of the metal species (solute) in a solvent (Grassi, et al. 2012, Homagai, Ghimire and Inoue 2010). The initial concentration of heavy metals has an impact on the sorption capacity because it acts as a driving force to overcome the resistance of the metal or the mass transfer from the liquid phase to the solid phase (Ahmaruzzaman 2011). In general, it is claimed by some researchers that the higher the initial concentration of the heavy metals, the more the metal uptake by the adsorbent (Ahmaruzzaman 2011).

ii Contact Time

Contact time affects the adsorption capacity, where the time required for the adsorption process to reach equilibrium differs based on the adsorbent nature and the available adsorption sites (Ahmaruzzaman 2011). Kardam, et al. (2014) reported an increase in the percent uptake of Pb^{2+}, Cd^{2+} and Ni^{2+}, using modified rice straw (nano-cellulose), with the increase in time until equilibrium was reached and no further increase was observed. Gurgel, Freitas and Gil (2008) reported that the adsorption of Cu^{2+}, Cd^{2+}

and Pb^{2+} ions using modified sugarcane bagasse increased with contact time until equilibrium.

iii The pH of the solution

The amount of metal uptake by adsorbents is greatly affected by varying the pH of a solution due to the consequent change in the distribution of the surface charge of the adsorbent (Ahmaruzzaman 2011, Rao, et al. 2013, Grassi, et al. 2012), as well as its degree of ionization and the speciation of functional groups (Rao, et al. 2013). In general, the adsorption capacity of heavy metal ions increases with the increasing pH (Ahmaruzzaman 2011). This is attributed to the fact that at low pH the adsorbent is protonated by H^+ ions and the surface charge of the adsorbent is positive while the charge of the metal species is positive; hence creating forces of repulsion (Soetaredjo, et al. 2013, Ding, et al. 2012), additionally at low pH the concentration of the H^+ ions is high therefore the competition between the H^+ ions and the metal ions over the active sites on the surface of the sorbent reduces the adsorption (Soetaredjo, et al. 2013, Homagai, Ghimire and Inoue 2010); however, a relatively small amount of metal uptake takes place due to proton H^+ exchange with heavy metal ions (Ahmaruzzaman 2011, Rao, et al. 2013, Soetaredjo, et al. 2013). On the other hand, when the pH is increased, the surface functional groups are activated (Rao, et al. 2013) and the surface functional groups are deprotonated (Soetaredjo, et al. 2013); consequently, the surface charge of the adsorbent becomes negative while the predominant metal ions are positive (Ahmaruzzaman 2011); therefore, adsorption increases due to electrostatic forces of attraction (Soetaredjo, et al. 2013), as well as due to a decrease in the H^+ ions; consequently, leading to a decrease in the competition between the metal ions and the H^+ ions on the available active sites on the surface of the adsorbent (Soetaredjo, et al. 2013, Homagai, Ghimire and Inoue 2010). However, when pH further increases, both the pre-dominant metal ions and the adsorbent are negatively charged, leading to a decrease in the adsorption capacity (Ahmaruzzaman 2011). As adsorption takes place, the pH of a solution drops due to the release of the H^+ ions in the adsorption process (Rao, et al. 2013, Ahmaruzzaman 2011, Homagai, Ghimire and Inoue 2010), indicating that ion exchange is a major mechanism of adsorption. Moreover, the pH has an impact on the solubility of heavy metals, as the pH of the solution increases, the solubility of the metal decreases, eventually as explained before, the adsorption increases (Homagai, Ghimire and Inoue 2010).

iv Particle Size

As the particle size decreases, the specific surface area increases, which is the surface area of the adsorbent available for the adsorption of the solute; consequently, increasing the adsorption capacity of the adsorbent (Ahmaruzzaman 2011). Wong, et al. (2003a) reported an increase in the uptake of Pb^{2+} when the particle size of modified rice straw was reduced.

v Properties and dose of the adsorbent

The nature of the adsorption process, such as the rate and the maximum adsorption capacity, is related to the physical and chemical characteristics of the adsorbent, such as porosity (Grassi, et al. 2012), mechanical strength and rigidity of the adsorbent material (Rao, et al. 2013). The dose of the adsorbent has a great effect on the adsorption capacity (Rao, et al. 2013). Zhigang, et al. (2009) reported that increasing the limestone, adsorbent, dose from 0.5g to 2g has in turn led to an increase in the removal efficiency of Cd^{2+} by a factor of 3.5.

vi Temperature

Adsorption is an exothermic process; therefore, in general, the adsorption capacity is enhanced with decreasing temperature (Grassi, et al. 2012). However, Zhigang et al. (2009) reported that the removal efficiency of Cu^{2+} using pure limestone was improved from 49.5% at 20℃ to 79% at 50℃, and the average increase in the metal uptake was 10.4% for Zn, 10.3% for Cd^{2+}, and 5.2% for Ni^{2+}.

vii Existing Pollutants

Other existing pollutants, whether organic or inorganic may interfere with the adsorption process and impact its efficiency. Several researchers reported the decrease in the adsorption capacity due to the presence of natural organic matter (NOM) in the wastewater (Grassi, et al. 2012). Moreover, the presence of a second heavy metal species in bi-metal solutions decreases the adsorption capacity of a specific heavy metal as compared to single metal solutions (Wong, et al. 2003b)

viii Pre-treatment

In many cases, pretreatment of agricultural and plant wastes is essential for several reasons, which are; getting rid of soluble organic compounds, which when released into the aqueous solution can increase the BOD, COD and TOC, preventing coloring of the solutions, and enhancing the metal adsorption capacity. Many research studies adopted various pretreatment methods using a number of modifying agents such as base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate), mineral and organic acid solutions (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, thioglycollic acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen peroxide), dye (Reactive Orange 13), etc. (Ngah and Hanafiah 2008).

2.2 **Agriculture Wastes as Biosorbents**

Agricultural wastes constitutes the largest amount of waste (32%) generated in Egypt (EEAA 2011), as shown in Figure 4. The quantity of agricultural wastes produced in 2012 was 30 M tons (NILE, et al. 2013), as illustrated in Figure 5. Agricultural residues are low- cost sorbents that can replace expensive commercial adsorbents for the removal of heavy metals from wastewater (Dhir and Kumar 2010). Biosorption using agricultural wastes is a very promising technology because of its capability of reducing the concentration of heavy metals in wastewater to minimal values and because it utilizes inexpensive abundant wastes. Through the following sections, several agriculture wastes and their feasibility to be utilized as biosorbents of heavy metals will be illustrated.

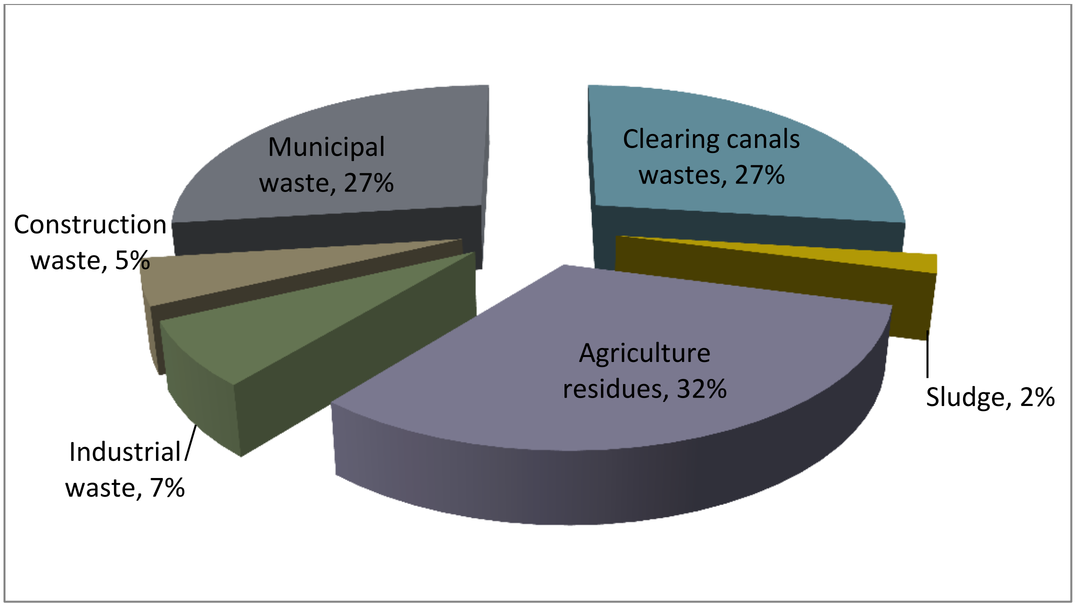


Figure 4: Composition of Solid Wastes in Egypt (EEAA 2011)

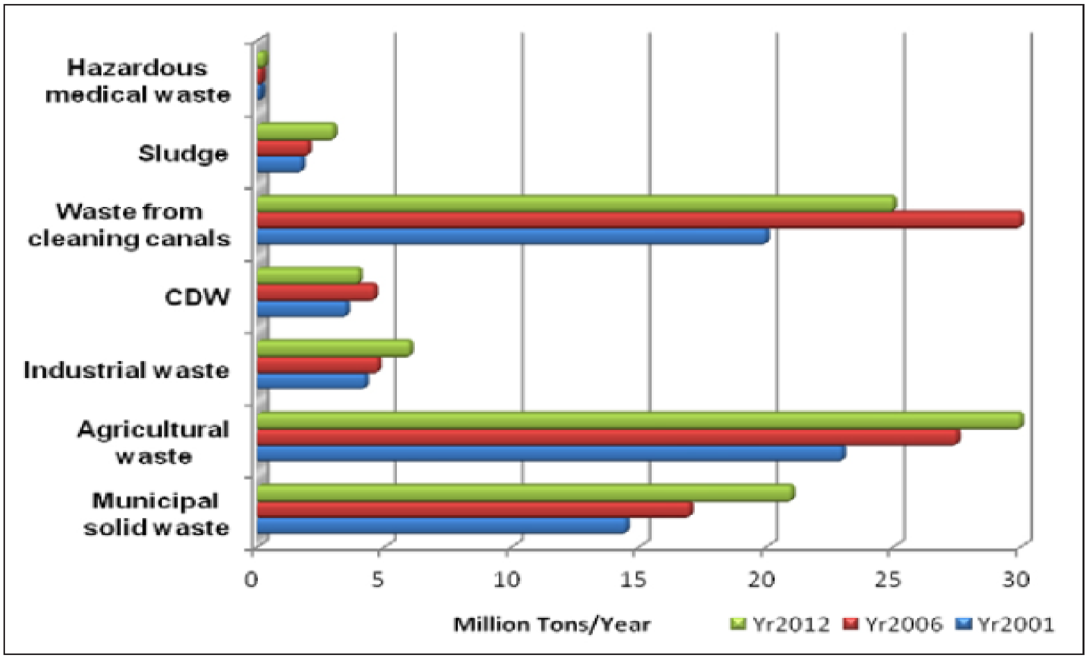


Figure 5: Generated Solid Waste in Egypt (NILE, et al. 2013)

2.2.1 Rice Straw

i Quantities of Rice Straw in Egypt

Egypt produces the largest amount of rice in Africa, it was reported by FAO that Egypt's production of rice in 2013 reached 5.9 million tons, which constituted > 22% of rice production in Africa (Abdelhady, et al. 2014). The amount of rice straw in Egypt, as the crop residue of rice, is about 5 million tons/ year, relatively small amount of it is used as animal fodder and for composting, yet around 3.1 million tons/ year are unutilized and disposed to be burnt in open field (Abdelhady, et al. 2014). This practice causes a severe air pollution problem in Egypt of black cloud. According to Bishay (2010), only 20% of rice straw in Egypt is utilized annually, while the remaining is burnt in open field. The calorific value of Egyptian rice straw is 15.3 MJ/kg, which is considered one of the highest calorific values of agricultural wastes (Bishay 2010).

ii Chemical Composition

Rice straw contains traces of inorganic minerals, namely Na: 0.09%, K: 1.87%, Mg: 0.23% and Ca: 0.52%. As for the composition (weight %) of organic polymers, it was reported to be 17.4% lignin, 38.2%cellulose, and 20.6% hemicellulose (Soetaredjo, et al. 2013). However, an analysis for Egyptian rice straw in specific has shown that the composition of lignin, hemicellulose and cellulose, was around 12%, 28% and 60%, respectively. The composition of rice straw was also classified as 10.2% moisture, 56.8% volatiles, 13.8 % fixed carbon and 16.4% ash. As for the carbon, hydrogen, and oxygen (C–H–O) organic composition in Egyptian rice straw, it was reported to be 47.8%, 6.0 % and 45.3%, respectively, in addition to 0.5% nitrogen and 0.2% sulfur. The chemical composition of rice straw ash is 65.7% SiO_2, 15% K_2O, 3.1% Na_2O, 2.1%MgO and 1.7% CaO (Bishay 2010).

iii Biosorption of heavy metals Using Rice Straw

Rice straw contains lignin, cellulose, organic acids and tannins that help in the metal chelation process (Ding, et al. 2012). In addition to the organic polymers; lignin, cellulose, and hemicellulose, agricultural wastes in general contain extractives; simple sugars, lipids, proteins, starches, hydrocarbons, and ash that comprises several functional groups that facilitates heavy metals absorption (Sud, Mahajan and Kaur 2008). Lignin, cellulose and hemicellulose, which are the basic components of rice straw contains hydroxyl, carboxyl and phenol functional groups that are the main providers of the adsorption sites for heavy metal ions (Soetaredjo, et al. 2013).

Raw Rice straw has the capacity to remove Cd^{2+} from wastewater thanks to its high adsorption capacity and short equilibrium time (Ding, et al. 2012). Rice straw had the maximum adsorption capacity compared to other agricultural residues, such as wheat straw, that were used for the removal of Cr, Ni and Cd from wastewater (Dhir and Kumar 2010). Ding, et al. (2012) carried out a research on the feasibility of utilizing un-modified rice straw of particle size < 0.5 mm for the removal of Cd^{2+} from synthetic wastewater, where he reported that the kinetics of the system was very rapid, as equilibrium was reached in 5 min and the maximum adsorption capacity was 13.9 mg/g at pH 5, the analysis was carried over sorbent doses ranging from 0.25 to 2.5 g/100ml. Soetaredjo, et al. (2013) investigated the adsorption capacity of raw rice straw for the uptake of Pb^{2+} and Cu^{2+} in single metal solutions and for binary metal solutions as well, it was reported that for a 100 mg/l Pb^{2+} solution, rice straw particle size 150-180 µm, and optimum pH 6, the maximum adsorption capacity (q_{max}) of Pb^{2+} was 23.35 mg/g and of Cu^{2+} was 5.66 mg/g in single metal solutions. The adsorption capacity was analyzed over a pH range 2-6 and sorbent dose 10 g/l -200 g/l and contact time 3-4 h. Bishay (2010) utilized rice straw ash for biosorption of heavy metals and uranium. Nano-cellulose fibers prepared from rice straw of average particle size 6nm, were used for heavy metals sorption, where the q_{max} was 9.7 mg/g, 9.42 mg/g, and 8.55 mg/g, and the percentage of removal was 90.7 %, 94.2 %, and 85.5 % for Cd^{2+}, Pb^{2+}, and Ni^{2+}, respectively, at pH 6, initial heavy metals concentration 25 mg/l, and sorbent dose 0.5 g/200 ml (Kardam, et al. 2014). The main mechanism responsible for the metal uptake by rice straw, is ion exchange between the heavy metals ions and K^{+}, Na^{+}, Mg^{2+} and Ca^{2+}, and to a lesser extent the formation of surface complexes with functional groups, such as C=C, C-O, O-H and carboxylic acids (Ding, et al. 2012). On the other hand, Soetaredjo, et al. (2013) has concluded that surface complexation (chelation) was the main mechanism responsible for the uptake of Pb^{2+} and $Cu^{2+,}$ followed by ion- exchange. In addition to ion exchange, chelation is an important mechanism for the removal of metal ions from aqueous solution (Ke, et al. 2009).

iv Regeneration

The purpose of the regeneration process is to allow the same biosorbent to be re-used for adsorption of heavy metals, which in turn should reduce the cost of the treatment process. For the regeneration to be efficient the adsorption capacity of the regenerated biosorbent should be close to the original adsorption capacity and the biosorbent should not be physically deteriorated in any form (Mahmood, Malik and Hussain 2010). Regeneration analysis was applied on Nano cellulose fibers of rice straw using different reagent media; basic, acidic (HCl/HNO_3) and neutral (distilled water). It was reported that the maximum recovery of heavy metals was achieved using 0.5 M HNO_3, as shown in Table 3 and it can be regenerated and re-used as a bio-sorbent up to three cycles (Kardam, et al. 2014). However, Chuah, et al. (2005) believed that due to the availability of agricultural residues it is less costly to replace the spent materials instead of carrying out expensive regeneration processes.

Table 3: Desorption of Cd^{2+}, Pb^{2+}, and Ni^{2+} via 0.5 M HNO_3 (Kardam, et al. 2014)

No. of cycles	**Desorption (%)**		
	Cd (II)	Pb (II)	Ni (II)
1	98.23	96.12	90.31
2	98.72	96.43	90.76
3	99.19	96.61	90.23
4	99.22	96.82	90.57

2.2.2 Rice Husk

i Quantities of Rice Husk

Rice husk (RH) is a byproduct of the rice mill. The world produces about 600 million tons of rice per year, yielding 20%, equivalent to 120million tons, rice husk per year. According to the FAO statistical data, Egypt produces around 5,700,000 tons of rice per year, which yields around 1,000,000 tons of rice husk that upon combustion yields 200,000 tons of rice husk ash. Most countries that produces rice handles rice husk either by burning or dumping it as a solid waste (Abo-El-Enein, et al. 2011).

Rice husk ash (RHA) is the solid residue that results from the burning process of rice husk. Rice husk is used as fuel in the furnaces of boilers of some industries for steam production, where the ash is collected from the stacks filters (Naiya, et al. 2009). RHA constitutes around one- fifth the annual rice production of the world (Naiya, et al. 2009).

ii Chemical Composition and characteristics

RH is composed of 32.24% cellulose, 21.34% hemicellulose, 21.44% lignin, and 15.05% mineral ash (Ngah and Hanafiah 2008), and 1.82% extractives and 8.11% water (Chuah, et al. 2005).Rice husk contains around 20% silica (Chuah, et al. 2005).The physical and chemical characteristics that qualify rice husk to be a bio-sorbent of heavy metals in wastewater are its insolubility in aqueous solutions, chemical stability, granular structure, and mechanical strength (Ngah and Hanafiah 2008). Table 4 presents the physicochemical characteristics of rice husk, and Table 5 shows the chemical composition of rice husk ash.

Table 4: Physical and chemical characteristics of rice husk (Chuah, et al. 2005)

Characteristics	Values
Bulk density (g/ml)	0.73
Solid density (g/ml)	1.5
Moisture content (%)	6.62

Ash content (%)	45.97
Particle size (mesh)	200-16
Surface area (m^2/g)	272.5
Surface acidity (meq/g)	0.1
Surface basicity (meq/g)	0.45

Table 5: Chemical Composition of Rice Husk Ash (Naiya, et al. 2009)

Constituent	Percent by Weight (%)
Loss on ignition	12.2
Fe_2O_3	0.6
Al_2O_3	0.3
CaO	1.4
MgO	0.5
SiO_2	84.3
Na_2O	0.4
K_2O	0.2

iii Biosorption of heavy metals Using Rice Husk

Rice husk can be utilized either in pretreated or in untreated forms; however, various researches have shown that pre-treatment clearly enhances the adsorption capacity of rice husk as it removes lignin and hemicellulose, and decreases the crystallinity of cellulose and increases the surface area and/or the pore volume (Ngah and Hanafiah 2008). Researchers have carried out a study to compare the maximum adsorption capacity of Cd via untreated rice husk versus treated rice husk using NaOH, $NaCO_3$ and epichlorohydrin, the results were: 8.58 mg/g, 20.24 mg/g, 16.18 mg/g and 11.12, respectively. Sodium hydroxide treatment yielded the highest Cd uptake, as it removed alkaline soluble materials off the surface of the rice husk that were interfering with the adsorption mechanism (Kumar and Bandyopadhyay 2006).

Wong, et al. (2003b) analyzed the adsorption of Cu^{2+} and Pb^{2+} via tartaric acid ($C_4H_6O_6$) modified rice husk (TARH) in synthetic wastewater and in electroplating industrial effluent. It was observed in that research that the maximum adsorption capacity was nearly equal for the synthetic solution and the real wastewater, as shown in Table 6; therefore, it was concluded that other soluble matter in the wastewater did not affect the adsorption capacity of the TARH for Cu^{2+} and Pb^{2+}. However, it was reported that the presence of Cu^{2+} and Pb^{2+} simultaneously in the solution (bi-metal solution) has significantly reduced the adsorption capacity due to their competition on the available active sites on the surface of rice husk. The column studies carried out by the researchers, which is a different application than the batch equilibrium experiments, indicated that the bed depth and initial metal concentration had the highest impact on the service time of the column and the wastewater volume treated before breakthrough and exhaustion of the rice husk column occurs; however, the parameter of the flow rate of the influent to the fixed- bed rice husk column had less significance (Wong, et al. 2003b).

Table 6: Rice husk maximum adsorption capacity (q_{max}) of Cu^{2+} and Pb^{2+} (Wong, et al. 2003b)

Metal ion	**N* (mg/g)**	
	Synthetic solution	Wastewater
Cu^{2+} in single metal solution	31.85	_
Pb^{2+} in single metal solution	120.48	_

Cu^{2+} in bi- metal solution	15.58	15.95
Pb^{2+} in bi- metal solution	48.31	48.08

Pre- treatment of rice husk using tartaric acid was believed to be responsible for increasing the carboxylic active groups on the surface of rice husk; consequently, enhancing the uptake efficiency of Cu^{2+} and Pb^{2+}. The percent removal of Cu^{2+} by tartaric acid modified rice husk was 75%, compared to the percent removal of unmodified rice husk; 13% at Cu^{2+} initial concentration 50mg/l. the maximum adsorption capacity calculated using Langmuir isotherm model was 108mg/g at room temperature and Pb^{2+} concentrations ranging from 400 mg/l up to 1200 mg/l (Wong, et al. 2003a).

Sarma, Kumar and Pakshirajan (2015) investigated the sorption capacity of rice husk, betel nut peels, sugarcane molases, tea waste, mustard oil cake and saw dust for the removal of Pb^{2+}, and they reported that rice husk had the maximum Langmuir adsorption capacity of 9.29 mg/g.

The study conducted by Naiya et al. (2009) for the adsorption of Pb^{2+} using rice husk ash at optimum pH 5, adsorbent dose 5 g/L and contact time 1 h, yielded q_{max} of 91.74 mg/g for Pb^{2+}.

Abo-El-Enein et al. (2011) utilized RHA as a source of pure silica (SiO_2), which constitutes around 99% of the weight of RHA, and NaOH to produce sodium silicate (activated silica) which enhances the coagulation process through forming dense settle-able flocs. The researchers also used RHA as a primary source of silica for the preparation of four poly inorganic coagulants, which are poly aluminum chloride silicate (PACSi), poly hydroxy aluminum sulphate silicate (PAHSSi), poly ferric chloride silicate (PFeClSi) and poly ferric aluminum chloride silicate (PAlFeClSi). The PFeClSi had the highest removal efficiency of 97% for Pb^{2+} in industrial wastewater; whereas, the PAlFeClSi showed a maximum removal of 90%, 92%, and 93%, for COD, BOD and TSS in municipal wastewater, respectively (Abo-El-Enein, et al. 2011).

iv Regeneration

As for the regeneration of the tartaric acid modified rice husk (TARH), it was achieved using 0.1 M HCl where 95% of Cu^{2+} and Pb^{2+} were recovered. The TARH was regenerated and re-used up to five cycles while almost preserving its original adsorption capacity (Wong, et al. 2003b).

2.2.3 Sugarcane Bagasse

i Quantities of Sugarcane Bagasse in Egypt

Sugarcane is one of the largest productions of agricultural crops in Egypt. According to the FAOSTAT[1] (2015), Egypt's production of sugarcane in 2013 was 16,100,000 tons. It was reported in the literature that 1 ton of sugarcane produces around 280 kg of sugarcane bagasse, of moisture content 50% (Gurgel, Freitas and Gil 2008). According to that ratio, it can be concluded that Egypt's production of sugarcane bagasse in 2013, was 4,508,000 tons. It was also reported in the literature that the amount of sugarcane residues are 4.8 M tons/year; however, most of it are used as a source of fuel in sugar factories, where only 0.69 M tons/year are un-utilized (Abdelhady, et al. 2014).

ii Chemical Composition

Sugarcane bagasse (SCB) is composed of cellulose (40–50%), polyoses (25–30%), and lignin (20–25%) (Gurgel, Freitas and Gil 2008). Those three organic polymers that constitute sugarcane bagasse are a huge source of hydroxyl and phenolic groups whose sorption properties can be enhanced by chemical modification (Ngah and Hanafiah 2008).

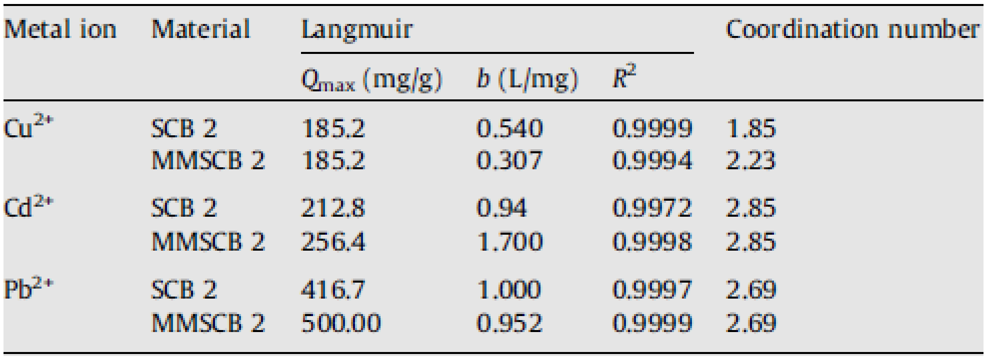
iii Biosorption of heavy metals using SCB

Homagai, Ghimire and Inoue (2010) have investigated the adsorption capacity of charred xanthated sugarcane bagasse (CXSB) for the removal of specific heavy metals. In that research, the sugarcane bagasse (SCB) was washed with de-ionized water for the removal of any acids until neutralization is attained, that is why it is called charred. Then it was xanthated by adding carbon disulfide (CS_2) in the presence of an alkali. The maximum adsorption capacities reached (mol/kg), were 1.95 for Cd (II), 1.58 for Pb (II), 2.52 for Ni (II), 2.40 for Zn (II) and 2.91 for Cu (II), respectively. Those adsorption capacities were considered higher than several other bio-sorbents stated in the literature. The batch equilibrium experiments showed that the optimum pH for Cd (II), Pb (II), Ni (II), Zn (II), and Cu (II) biosorption using CXSB was 5, 4, 4, 6 and 5, respectively. The order of the heavy metals in terms of adsorption capacity of CXSB was $Pb^{2+} > Cu^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+}$ at pH 4 (Homagai, Ghimire and Inoue 2010).

Sugarcane bagasse was modified using the organic compound succinic anhydride ($C_4H_4O_3$) for the uptake of Cu (II), Cd (II) and Pb (II) from a solution. The maximum adsorption capacity in mg/g of adsorbent was determined using Langmuir model to be 114 mg/g for Cu^{2+}, 196 mg/g for Cd^{2+} and 189 mg/g for Pb^{2+} (Junior, et al. 2007).

Gurgel, Freitas and Gil (2008) investigated the impact of the pre- treatment of SCB using each of succinic anhydride acid and mercerization, treatment using NaOH, on the sorption properties of sugarcane bagasse. They compared the adsorption capacity of modified, using succinic anhydride acid, non-mercerized sugarcane bagasse (SCB 1) to modified twice mercerized sugarcane bagasse (MMSCB 1). The results indicated an increase in mass percent gain by 49.2%, which is attributed to the increase in the carboxylic groups and an increase in the concentration of carboxylic acid groups by 0.9 mmol/g. Further treatment was applied on the SCB1 and the MMSCB1 using saturated sodium bicarbonate solution to produce SCB2 and MMSCB2. The results showed an increase in the adsorption capacity (Q_{max}) of the MMSCB2, relative to the SCB2, by 43.6 mg/g for Cd^{2+} and 83.3 mg/g for Pb^{2+}; however, no change was observed for the Cu^{2+}, as shown Table 7 below. Mercerization facilitated the removal of lignin and polyoses which normally pack the cellulose fibers; therefore, their removal allowed easier reaction between the hydroxyl group of the cellulose and the succinic anhydride; hence, facilitated the conversion of cellulose I to cellulose II (Gurgel, Freitas and Gil 2008). The succinic anhydride helps the conversion of the hydroxyl groups in sugarcane bagasse into carboxylic groups (Ngah and Hanafiah 2008). Sorption of heavy metal ions is enhanced with the increase of carboxylic acid group (Gurgel, Freitas and Gil 2008). However, the pre-treatment process adopted in that research is considered very complicated and probably costly because it involved several chemicals; hence, not sustainable.

Table 7: Langmuir constants for the adsorbtion of Cu^{2+}, Cd^{2+}, Pb^{2+} using SCB2 and MMSCB2 (Gurgel, Freitas and Gil 2008)



Metal ion	Material	Langmuir			Coordination number
		Q_{max} (mg/g)	*b* (L/mg)	R^2	
Cu^{2+}	SCB 2	185.2	0.540	0.9999	1.85
	MMSCB 2	185.2	0.307	0.9994	2.23
Cd^{2+}	SCB 2	212.8	0.94	0.9972	2.85
	MMSCB 2	256.4	1.700	0.9998	2.85
Pb^{2+}	SCB 2	416.7	1.000	0.9997	2.69
	MMSCB 2	500.00	0.952	0.9999	2.69

Another research was conducted on the treatment of sugarcane bagasse using succinic anhydride, followed by modification of the adsorption properties by allowing the carboxylic group to react with the following chemicals; $NaHCO_3$, ethylenediamine and triethylenetetramine, each in a separate experiment. The results showed that the sugarcane bagasse treated by triethylenetetramine had the highest adsorption capacity of Pd and Cd, where it reached twice the capacity compared to the unmodified SCB. The reported q_{max} was 133 mg/g for Cu (II), 313 mg/g for Pb (II), and 313 mg/g for Cd (II). However, for the SCB treated by ethylenediamine and triethylenetetramine, the time to reach equilibrium was slower than the SCB treated by $NaHCO_3$ (Ngah and Hanafiah 2008). Moreover, researchers used methanol for modifying SCB; however, the results were not promising, as the maximum metal uptake of Cd was 6.79 mg/g (Ibrahim, Hanafiah and Yahya 2006).

2.3 Industrial Wastes and Natural Materials as Adsorbents

Industrial solid wastes in Egypt constitute 7% of the total solid waste generated in Egypt (EEAA 2011). The amount of industrial waste generated in Egypt in 2012 was 6 M tons (NILE, et al. 2013). The potential of Lime as a naturally occurring material and cement kiln dust and marble powder waste as industrial wastes is elaborated in the following sections.

2.3.1 Lime

Zhigang, et al. (2009) experimented three different forms of limestone, which are carbonaceous limestone (CaO: 45%−54%), brecciated limestone (CaO: 50%−72%) and pure limestone (CaO: 67%−90%) for the adsorption of Cd, Cu, Ni and Zn. Results revealed that pure limestone ground to a particle size of 0.55−0.25 mm, with the addition of Na_2CO_3 (soda solution) had the best removal efficiency of 58.6% for Cd, 100% for Cu, 47.8% for Ni, and 36.8% for Zn at 20℃, and optimum pH in the range of 8.9 to 9.1. The researchers concluded that the main mechanism responsible for the removal of the heavy metals could be the co-precipitation of the metal hydroxides on the surface of the limestone grains at the optimum pH (Zhigang, et al. 2009).

A research was carried out where coarse limestone was pulverized to a particle size less than 100 μm for the adsorption of Pd^{2+} and Zn^{2+}. The maximum adsorption capacity reached by the soaked powdered lime was over 3000 mg of Pb^{2+}/kg. The metal uptake was reported to be due to both precipitation and adsorption; however, the X-ray diffraction analysis showed that the heavy metal uptake was mainly due to chemical precipitation (NÉMETH, MLINÁRIK and TÖRÖK 2013).

EL Zayat (2014) studied the uptake affinity of hydrated lime for some heavy metals. He reported the percent removal to be greater than 90% for Pb^{2+} and Cu^{2+}, and greater than 80% for Cd^{2+}. The relatively high adsorption capacity was attributed to the possible formation of complexes between the oxides and hydroxides functional groups of the hydrated lime, as a major source of CaO, and the positively charged metal cations.

2.3.2 Cement Kiln Dust (CKD)

By means of energy dispersive X-ray microscopy analyses, it was found that Ca constitutes 55.30% by weight of CKD (El Zayat, Elagroudy and El Haggar 2014). The chemical composition of CKD is presented in Table 8 (Mostafa, Rashed and Mostafa 2005).

Table 8: Chemical composition of CKD (Mostafa, Rashed and Mostafa 2005)

Oxides	Composition (wt%)
SiO_2	14.54
Al_2O_3	3.44
Fe_2O_3	2.35
CaO	57.24
MgO	2.14
Na_2O	2.41
K_2O	2.7
SO_3	3.71
Cl^-	4.75
Loss in ignition	12.6
Free Lime	25.08
Density (Kg/m3)	843
pH	13.4

A research was carried out on the utilization of CKD as an adsorbent of Pb^{2+}, Cd^{2+} and Cu^{2+}. The optimum results were reached at pH range of 5.5-6. The order of heavy metals in terms of highest removal efficiency was $Pb^{2+} > Cu^{2+} > Cd^{2+}$. At pH >6, it was noticed that the removal of lead was due to the precipitation of $Pb(OH)_2$, while for Cu^{2+} and Cd^{2+} precipitation took place at pH 8. Below those pH values the metal removal could be due to electrostatic forces of attraction or surface complexations (El Zayat, Elagroudy and El Haggar 2014).

The efficiency of CKD in the treatment of tanneries wastewater, in terms of percentage of removal was 92.1% TSS, 91.3% COD, 18.7% Pb^{2+}, 69% Cd^{2+}, 70.1% Ni^{2+}, 66.9% Cu^{2+}, and 31% total Cr at optimum dose 2 gm/l and pH 8. It was concluded by the researchers that the high coagulation properties of CKD are mainly because lime constitutes 25% of its weight; therefore, when added to acidic wastewater it produced large flocs that can easily settle down (Mostafa, Rashed and Mostafa 2005).

2.3.3 Marble Powder Waste

Marble powder waste is produced from the marble industry. It constitutes an environmental problem. It was reported by researchers that its chemical analysis is 60% calcite ($CaCO_3$) and 6% dolomite ($MgCO_3$), while the rest of its components are quartz, feldspar, clays, pyrite and siderite. Researchers utilized marble powder for the adsorption of Cd2+ in aqueous solutions because of its availability, low cost, and its high affinity to heavy metals. The particle size used was 25-63 µm and the surface area of the samples was 21.8 m^2/g. A maximum removal efficiency of nearly 100% was attained at a pH range of 8-10 (Ghazy, Gabr and Gad 2008).

2.4 **Summary**

Since the removal of Pb^{2+} from synthetic wastewater is the focal point of this research, Table 9 summarizes the findings of some of the researches discussed in the literature review, in terms of maximum adsorption capacity, and/or percent removal of Pb^{2+} via various sorbents.

Table 9: Summary of the q_{max}, or the % removal of Pb^{2+} using an array of sorbents

Main Characteristics	**Q_{max}(mg/g)/ % Removal**	**pH**	**Reference**
Rice Straw			
• Un- treated • Particle size:150-180 µm	23.35 mg/g	6	(Soetaredjo, et al. 2013)
• Nano-cellulose fibers • Particle size:6nm	9.42 mg/g	6	(Kardam, et al. 2014)
Rice Husk			
tartaric acid ($C_4H_6O_6$) pre-treated: I-Single metal solution II-Bi-metal solution	I-120.4mg/g II-48.3 mg/g	_	(Wong, et al. 2003b)
Tartaric acid modified (TARH)	108 mg/g	5.3	(Wong, et al. 2003a)
Un- treated	9.29 mg/g	6	(Sarma, Kumar and Pakshirajan 2015)

Main Characteristics	**Q_{max}(mg/g)/ % Removal**	**pH**	**Reference**
Sugarcane Bagasse			
Pre- treated (CS_2 + alkali)	327.4 mg/g	4	(Homagai, Ghimire and Inoue 2010)
Pre-treated (organic compound: succinic anhydride)	189 mg/g		(Junior, et al. 2007)
• Mesh200 particle size • Pre-treatment: I. succinic anhydride & saturated sodium bicarbonate II. Succinic anhydride ,NaOH & saturated sodium bicarbonate)	I. 416 mg/g II. 500 mg/g	I. 5.4 II.5.5	(Gurgel, Freitas and Gil 2008)
Pre- treated (Succinic anhydride, followed by	313 mg/g	–	(Ngah and Hanafiah 2008)

Main Characteristics	**Q_{max}(mg/g)/ % Removal**	**pH**	**Reference**
allowing the carboxylic group to react with triethylenetetramine(TETA: $C_6H_{18}N_4$)			
Lime			
• Soaked powdered coarse lime • Particle size< 100 µm	>3000mg/kg	_	(NÉMETH, MLINÁRIK and TÖRÖK 2013)
Hydrated lime	>90%	5.5-6	(EL Zayat 2014)
CKD			
___	99%	5.5-6	(EL Zayat 2014)
___	18.7%	8	(Mostafa, Rashed and Mostafa 2005)

2.5 Permissible Limits and Regulations

Since removal of lead from wastewater is the focus of the research, the various international standards, such as the World Health Organization (WHO), US Environmental Protection Agency (EPA), European standards (EU), (Ahmaruzzaman 2011) and the Food and Agriculture Organization (FAO 1985), as well as the Egyptian regulations for lead permissible concentrations based on the specific purpose of use and the disposal method of wastewater are listed in Table 10.

Table 10: Egyptian and international permissible limits of Pb^{2+}

Industrial effluent discharge (mg/l)				Potable Water(mg/l)			Irrigation (mg/l)	
Egyptian Regulations		WHO	EPA	WHO	EPA	EU	Egyptian Regulation	FAO 1985
Public sewers decree 44/2000	River Nile-Main branch law48/1982	Inland Surface water	Discharge wastewater				decree 44/2000	
1	0.05	0.1	0.5[1]	0.01	0.015	0.01	5	5

[1] Sarma, Kumar and Pakshirajan (2015)

CHAPTER 3 : METHODOLOGY

3.1 Overview

All the experimental work in the current study was carried out in the Environmental Engineering laboratory at the American University in Cairo.

3.2 Experimental Setup

The research was divided into three core phases; Phase I, II and III, as shown in Figure 6. In Phase I, experiments were carried out to compare the performance of sorbent materials prepared from agricultural wastes, and inorganic wastes in the removal of lead from a water solution. The main objective of Phase I is to select the most promising sorbent material in the removal of Pb^{2+}. The application of the selected material in removing lead will be investigated intensively in Phases II and III.

Phase II was carried out to investigate the potential of the most promising sorbent depicted from Phase I for the sorption of Pb^{2+} in batch reactors using batch equilibrium experiments. The main purpose of Phase II is to define; the optimum operating conditions, the effect of various parameters on the sorption system, and the maximum adsorption capacity of the selected sorbent in batch reactor applications. Sorbent characterization was carried out for the selected sorbent through the BET surface area and pore volume, FTIR, and SEM- EDX analysis.

Phase III was the final stage of the research. It was conducted using fixed bed column tests (continuous flow). The main objectives of Phase III was to simulate the performance of the most promising sorbent in that specific mode of wastewater treatment and to define the impact of several parameters, which are the influent Pb^{2+} concentration, bed depth and the flow rate.

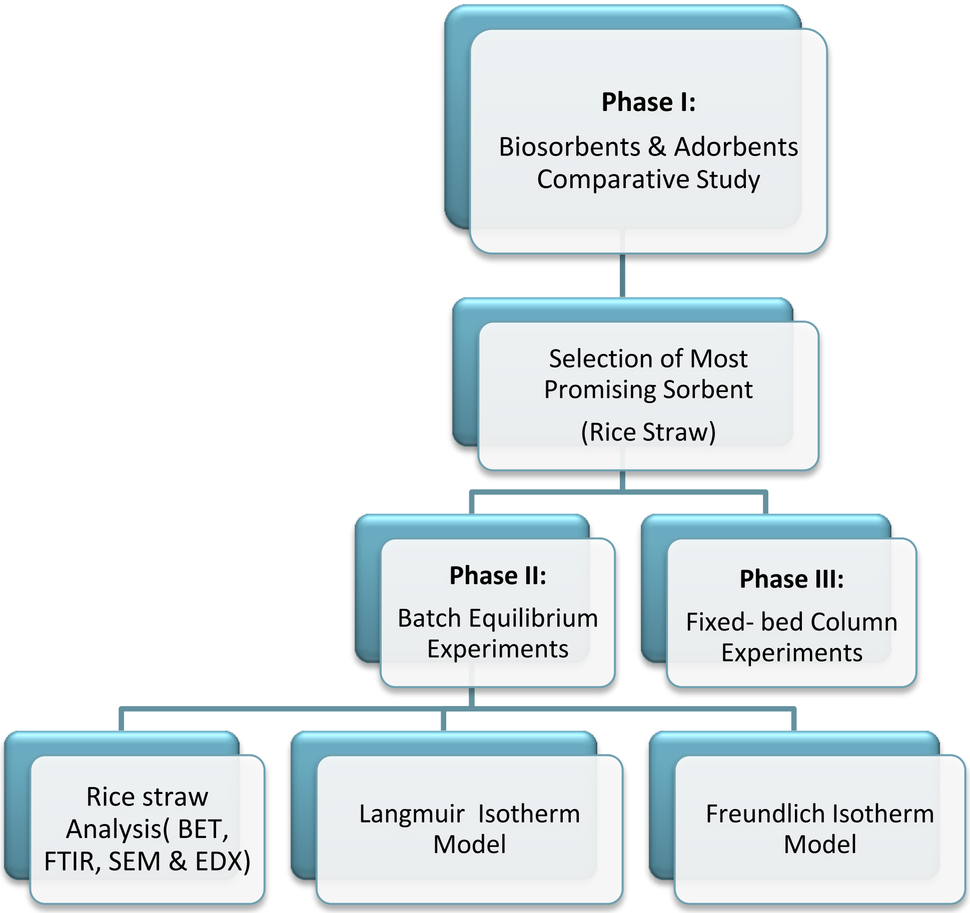


Figure 6: Experimental Plan Flow Chart

3.3 Preparation of Synthetic Lead Solution

Lead synthetic solution was utilized for carrying out the equilibrium batch experiments and the fixed- bed column experiments. The synthetic Pb^{2+} solution used for conducting the batch equilibrium experiments was prepared from a lead stock solution of concentration 1000 mg/l, manufactured by MERCK, diluted in deionized distilled water (DDW) to the required concentration. The standard solutions that were utilized for the calibration of the atomic absorption spectrometer (AAS) were prepared from the same lead stock solution and were diluted in DDW in the same manner.

As for the fixed- bed column experiments, which required larger quantities of the synthetic solution, a 1000 mg/l stock solution was prepared by diluting 1.598 g $Pb(NO_3)_2$, manufactured by Gainland Chemical Company (GCC) in UK of an assay 99% , in 1000 ml of DDW and acidified using 1% HNO3 (10 ml). Afterwards, the 1000 mg/l stock solution was diluted in DDW to the required concentration.

For all prepared synthetic solutions, an ionic background of 0.01 M $NaNO_3$ (0.85 g/l) was added to the synthetic solution in order to simulate the conditions of real wastewater as much as possible (EL Zayat 2014). The ionic background was prepared using $NaNO_3$ salt manufactured by Gain Land Company (GCC) in UK of an assay 99%.

3.4 Phase I- Biosorbents and Adsorbents Comparative Study

Batch experiments were carried out using raw and pre-treated low-cost materials to compare their removal efficiency of Pb^{2+} from synthetic lead solution. These materials are:

1. Agricultural wastes: sugarcane bagasse, rice husk and rice straw,
2. Two industrial wastes: cement kiln dust and marble powder
3. Naturally available material: lime

3.4.1 Biosorbents and Adsorbents utilized in Phase I

The sorbents used in Phase I were divided into two groups; agricultural wastes (bio-sorbents) and industrial wastes and natural materials (adsorbents), as follows:

i Agricultural Wastes (Bio-sorbents)

1. Raw sugarcane bagasse (Raw-SB)
2. Raw rice husk (Raw-RH)
3. Raw rice straw (Raw-RS)
4. Tartaric acid and NaOH modified sugarcane bagasse (TA-N-SB)
5. Tartaric acid and NaOH modified rice husk (TA-N-RH)
6. Tartaric acid modified sugarcane bagasse (TA-SB)
7. NaOH treated sugarcane bagasse (N-SB)

The source of the sugarcane bagasse is the sugar factory in Nagaa Hamadi, while rice straw was brought from the fields in Egypt.

ii Industrial Wastes and Natural Materials (Adsorbents)

1. Cement kiln dust (CKD)
2. Lime
3. Marble Powder waste

Cement kiln dust was collected from a cement factory in Egypt. Marble powder was collected from a marble factory.

3.4.2 Bio-sorbents Preparation and Pre-treatment

Three types of agricultural wastes; sugarcane bagasse, rice straw and rice husk, were initially prepared and then pretreated according to the method reported mainly by Wong, et al. (2003a), and Marshall, et al. (1999), and Zhu, Fan and Zhang (2008), except for some details that were taken from other sources in the literature due to the lack of some data in some of those researches.

i Preparation

1. Sugarcane bagasse (SB) was dried under the sunlight.
2. Then sugarcane bagasse (SB) and rice straw (RS) were cut into small pieces
3. Subsequently, the SB, RS and rice husk (RH) were grinded via a crushing machine and sieved using a mechanical sieving system where the 100-200 sieve fraction was used, so the particle size used in that level of the research was in the range of 75 µm-150 µm (Gurgel, Freitas and Gil 2008), which is smaller than the particle size used by Wong, et al. (2003a) because as the particle size decreases, the surface area increases; consequently, the adsorption capacity increases.
4. The fine particles of the three types of agricultural wastes were rinsed with distilled water 3-4 times over a sieve.
5. Then dried in an oven at 80 ^{o}C for 24 h (Soetaredjo, et al. 2013) and kept in desiccators.

6. Samples were divided so that part of each bio-sorbent was left untreated and the other part was subjected to pre-treatment.

ii Pre- treatment

The pre-treatment process consisted of two main steps, which are NaOH treatment (base extraction) and tartaric acid treatment. Sodium hydroxide was applied on the three bio-sorbents for the removal of lignin which packs the cellulose; therefore, their removal was believed by some researchers to facilitate the reaction between the hydroxyl groups of the cellulose and the chemical treatment (Gurgel, Freitas and Gil 2008), eventually enhances heavy metals uptake. The next step in the pre-treatment was the tartaric acid (TA), a carboxylic acid, in order to increase the carboxyl active groups on the surface of the biosorbent, which is believed to be the main functional group in agricultural residues that forms surface complexation with heavy metals. A sample of raw sugarcane bagasse (Raw-SB) was treated directly with TA, skipping the preceding NaOH treatment step in order to investigate the impact of the TA if applied directly on the agricultural waste.

The pre-treatment process was carried out according to the following procedure:

1. The NaOH pre-treatment step was carried out according to the process stated by Homagai, Ghimire and Inoue (2010), which is mixing each bio-sorbent with 4 M NaOH and placing it on the shaker for 1 hr. In this regard, 25 g of each of the SB and the RH were added to 200 ml of 4 M NaOH (32 g of NaOH dissolved in 200 ml of DDW). Following the same ratio, 15 g of RS were mixed with 120 ml of 4 M NaOH, which was prepared by adding 19.2 g of NaOH into 120 ml of DDW. The three solutions were shaken on the orbital shaker for 1 h, next they were washed with distilled water (each bio-sorbent needed around 15 l of distilled water) until the pH of the suspension reached neutrality.
2. NaOH treated SB, RH and RS were placed in the oven on stainless steel trays to dry at 80 ^{o}C for 24 h.

3. After drying, the materials were weighed; 9.8 g SB, 13.4 g RH, and 7 g RS, and kept in the desiccators. The three agricultural wastes treated by NaOH were named N-SB, N-RH and N-RS.
4. Part of the N-SB was not subjected to the next treatment procedures and was kept as N-SB, in order to assess the impact of NaOH treatment solely on the SB percentage removal of Pb^{2+}.
5. The N-SB, N-RH, N-RS, and Raw-SB were re-grinded to restore their fine particles and allow a larger surface area of the material to get exposed to the next step of treatment since the repeatedly washing process has created small lumps.
6. Tartaric acid (TA), manufactured in UK by Biostain Ready Reagents, of concentration 1.2 M was prepared. 1 M of tartaric acid weighs 150.09 g/l, accordingly 1.2 M is 180.108 g/l, or 45.027 g/250 ml. A total of 250 ml of 1.2 M tartaric acid were prepared by dissolving 45.027 g tartaric acid in 250 ml of de-ionized distilled water (DDW) under constant stirring using a magnetic stirrer. Specific quantities of the 250 ml 1.2 M tartaric acid solution were added to the different weights of the bio-sorbents according to a ratio of 7 ml of acid per 1 g of bio-sorbent (Wong, et al. 2003a, Marshall, et al. 1999).
7. The mix of the TA and the agricultural wastes were placed on the orbital shaker for 30 min at room temperature, then poured on stainless steel plates and heated in the oven at 50 ^{o}C (Zhu, Fan and Zhang 2008) overnight.
8. Subsequently, the thermochemical reaction between the acid and the agricultural wastes was proceeded by raising the oven temperature up to 180 ^{o}C for 10 min (Wong, et al. 2003a).
9. Afterwards, the materials were left to cool down, and then stirred with distilled water via a magnetic stirrer for 10 min. Finally the TA modified materials were placed on Whatman #4 filter paper and washed with 200 ml of distilled water per 1 g of the material, which is reported in the literature to be sufficient to wash off excess unreacted acid (Zhu, Fan and Zhang 2008, Marshall, et al. 1999), in a Buchner funnel under vacuum (Marshall, et al. 1999).
10. The TA modified bio-sorbents; TA-N-SB, TA-N-RH, TA-N-RS, and TA-SB were placed on stainless steel plates and dried at 80 ^{o}C for 24 h.

11. TA-N-SB, TA-N-RH, and TA-SB were re-sieved to retain the 100-200 sieve fractions, and then placed in the oven for 1 h at 80 °C to make sure they were free of moisture, and finally placed in desiccators.

As for the pre- treated rice straw, it was the only material that was burnt in the oven during the TA thermochemical treatment process; therefore, it was not used in the comparative batch experiments.

3.4.3 Conditions of the Batch Experiments- Phase I

- Bio-sorbent dose: 0.1 g/50 ml (2 g/l)
- Contact time: 2 h
- Volume of Pb^{2+} solution: 50 ml
- pH: 5.5 (± 0.05)
- Pb^{2+} concentration: 40 mg/l.
- Temperature: room temperature (22 ± 1 °C).

3.4.4 Experimental Procedure

The first batch of the experiments was carried out for the bio-sorbents, a total of 7 samples and 1 control sample (reagent blank) were prepared. A volume of 50 ml of 40 g/l Pb^{2+} synthetic solution was poured in 125 ml high density polyethylene bottles (HDPE) manufactured in USA by Nalgene Company. The pH was adjusted to 5.5 using 0.1 M NaOH or 0.1 M HNO_3. Few studies which were carried out on the use of different materials for removal of heavy metals from solution, recommended an optimum pH of the solution to be around 5.5 (El Zayat, Elagroudy and El Haggar 2014, Gurgel, Freitas and Gil 2008, Wong, et al. 2003a). Therefore, the pH of the solution used in the experiments of Phase I was selected to be 5.5. Subsequently, 0.1 g of each material was weighed and added to the 50 ml solution in each bottle, except for the control sample where no bio-sorbents were added to it. All samples were placed on the shaker for 2 h, considered enough time for adsorption to take place, and agitated at 175 RPM.

Figure 7 shows the orbital shaker used in the experimental work, manufactured by Cole-Parmer Industrial Company, USA. Afterwards, each sample was filtered on a cellulose acetate filter paper 0.45 µm pore size, as reported in the Standard Methods for the examination of water and wastewater (APHA, AWWA and WEF 1992) by a laboratory built-in vacuum pump in order to separate the sorbents from the treated solution, see Figure 8. The filter paper was initially washed by filtering through it 50 ml of DDW under vacuum and then throwing the water and rinsing the filter cup itself with DDW to make sure that the filter paper and the filter cup are free of any traces of heavy metals or any other residuals. Filter cups were manufactured in U.S.A by Nalgene. Finally the sample was acidified using Nitric acid to a pH <2 (APHA, AWWA and WEF 1992) and the final concentration of Pb^{2+} was analyzed via the Atomic Absorption Spectrometer. The tests were replicated three times for confirmation of the results and average values were used.

The same steps of the batch equilibrium comparative tests were carried out for the second group of adsorbents, which are the CKD, lime and marble powder.

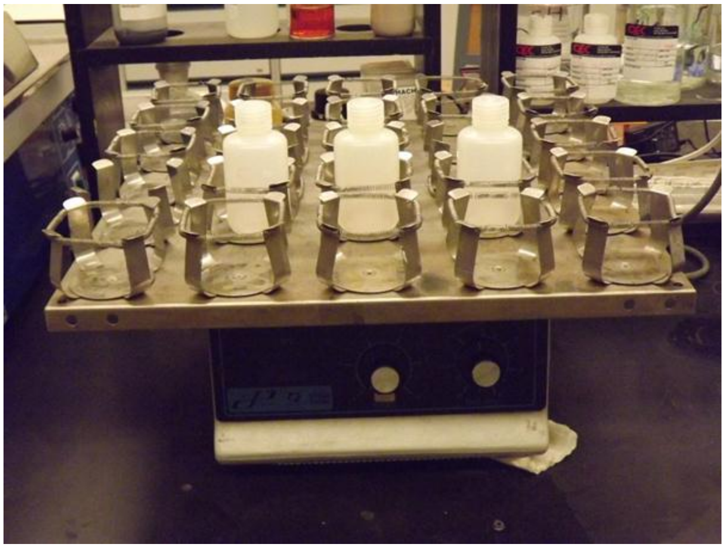


Figure 7: Orbital Shaker

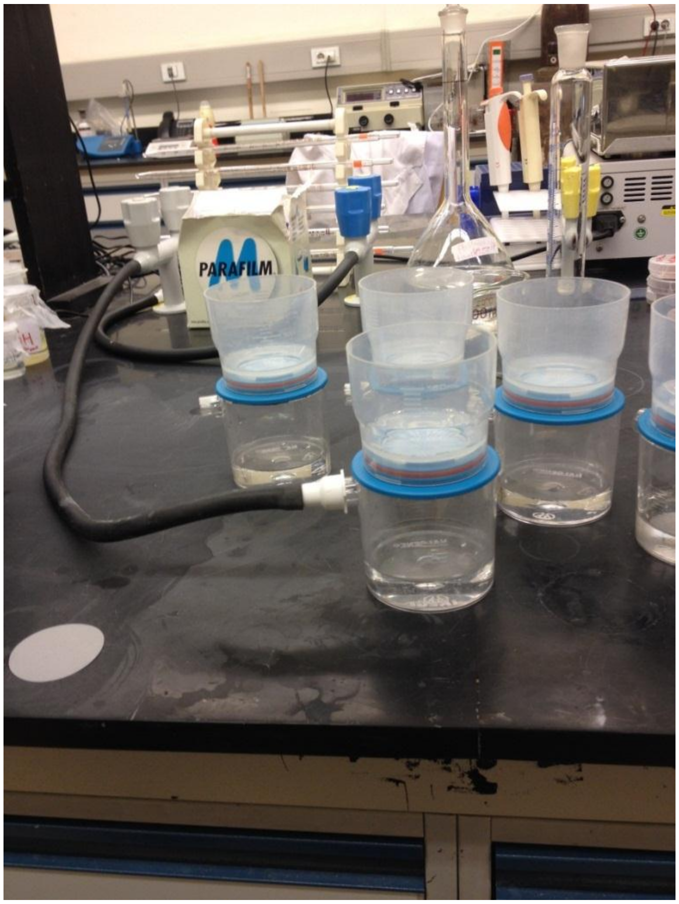


Figure 8: Filtration under vacuum in filter cups

3.5 Phase II- Batch Equilibrium Experiments

3.5.1 Sorbent Used and Objectives of Phase II

Based on the results of the batch comparative study, raw rice straw was the most promising sorbent; hence, it was selected to undergo the deeper analysis of the research. The main objectives of Phase II of the research are the following:

1. Evaluating the impact of various operating parameters on the removal of dissolved Pb^{2+} from synthetic lead solution using rice straw, and on the adsorption capacity of rice straw.
2. Defining the optimum operating conditions of the sorption system.

3. Determining the maximum adsorption capacity of rice straw at the pre-set optimum conditions using isotherm models.

3.5.2 Preparation of Rice Straw

Raw rice straw was prepared to be used as a bio-sorbent of Pb^{2+} as follows:

1. Rice straw was cut into small pieces.
2. Subsequently grinded via a crushing machine.
3. Sieved using a mechanical sieves setup, the fractions retained on the 30/50 sieve (300-600 µm), 100/200 sieve (75-150 µm), and < 200 sieve (<75 µm) were selected.
4. Each of the three sizes was washed on a sieve size smaller than the particles size using distilled water around 3-4 times, except for the < 200 sieve fraction, it was washed on a piece of cloth and squeezed.
5. The rice straw was kept in the oven at 80 ^oC for 24 h to dry (Soetaredjo, et al. 2013).
6. After drying, the three sizes were re-sieved to retain the same particle sizes mentioned above, and then dried in the oven for 1 h at 80 ^oC to make sure they were free of moisture, and finally placed in desiccators, as shown in Figure 9.

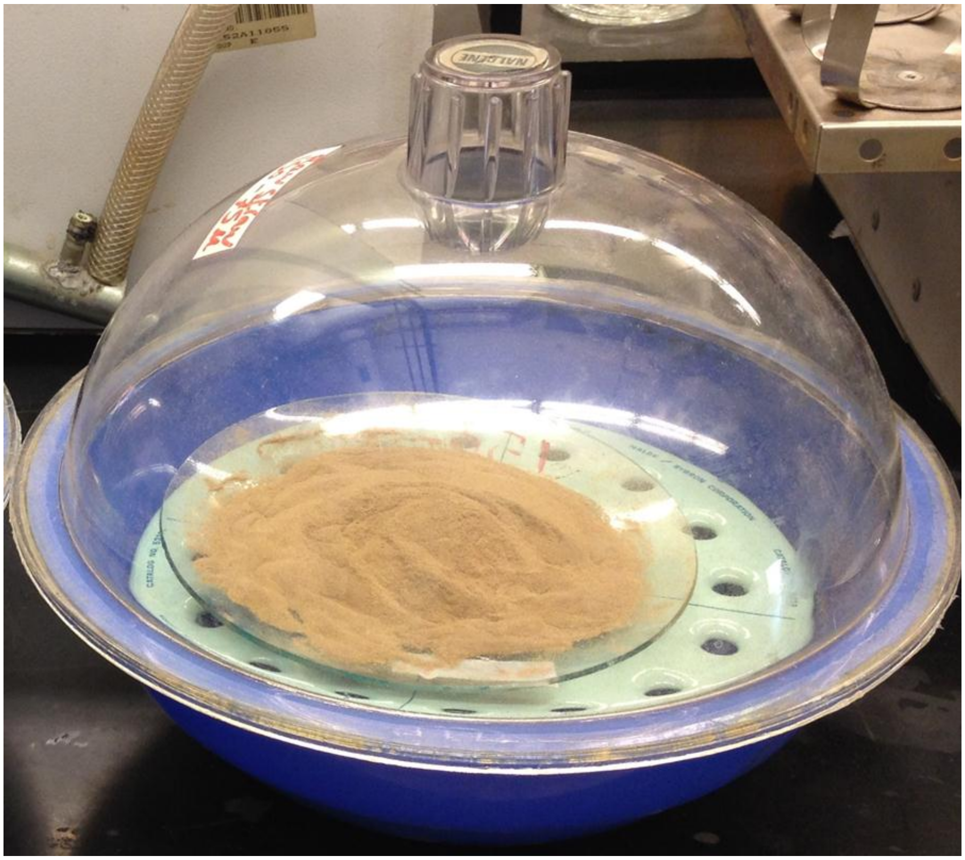


Figure 9: Raw rice straw in a desiccator

3.5.3 Experimental Procedure

Batch equilibrium experiments were carried out according to the following experimental procedure:

1. Lead synthetic solution was prepared by diluting the 1000 ppm of lead stock solution in 1000 ml of DDW to the required concentration, and adding 0.01 M $NaNO_3$ ionic background, as described in Section 3.3.

2. 50 ml of Pb^{2+} synthetic solution was poured in 125 ml high density polyethylene bottles (HDPE, manufactured in USA by Nalgene Company).

3. The pH of the samples was adjusted using 0.1 M NaOH and 0.1 M HNO_3 to the specified pH value.

4. The desired dose of raw rice straw (Raw-RS) was weighed and added to the solution, except for the control samples.
5. The samples were placed on the mechanical shaker up to the desired contact time.
6. Final pH was measured and recorded at the end of each experiment.
7. Each sample was filtered via a vacuum pump on a cellulose acetate filter paper of 0.45 µm pore size, as per the Standard Methods (APHA, AWWA and WEF 1992), in order to separate the rice straw from the treated solution. The filter paper and the filter cups were pre-washed by 50 ml DDW as described in Section 3.4.4. The filter cups are manufactured in U.S.A by Nalgene.
8. Finally the samples were acidified using nitric acid to a pH <2 (APHA, AWWA and WEF 1992) and the equilibrium concentration of Pb^{2+} (C_e) was analyzed via the Atomic Absorption Spectrometer (AAS).
9. The tests were replicated three times for confirmation of the results and average values were used.

3.5.4 Operating Parameters

The main parameters that were studied in the batch equilibrium experiments are:

1. pH of the solution
2. Contact time
3. Particle size
4. Bio-sorbent dose
5. Initial Lead concentration
6. Pre- treatment

3.5.5 Effect of pH on the Removal of Pb^{2+}

The pH of a solution has a crucial influence on heavy metals uptake as it determines the surface charge of the sorbent, the degree of ionization and specification of the heavy metal ions (Singh, Ali and Prakash 2014). The studied pH values were in a range of 2-7, which are: 2.12, 2.96, 4.09, 4.92, 5.48, 6.15, and 7.05. The samples were placed on the shaker for 4 h as per Soetaredjo, et al. (2013) who reported that bio-sorption equilibrium of raw rice straw was attained in 3-4 h, and Wong, et al. (2003a) has run the batch equilibrium experiments of rice husk over 4 h. The pH of each sample was measured after 2 hours to make sure that the deviation from the initial pH was not huge. The conditions of the experiment are the following:

- Bio-sorbent dose: 0.1 g/50 ml (2 g/l)
- Particle size: 75-150 µm
- Contact time: 4 h
- Volume of Pb^{2+} standard solution: 50 ml
- pH of the synthetic solution: 2.12, 2.96, 4.09, 4.92, 5.48, 6.15, and 7.05
- Initial Pb^{2+} concentration: $C_0 \approx 40$ mg/l.
- Temperature: room temperature (22 ± 1 ^oC).

3.5.6 Effect of Contact Time

The time intervals studied for the medium particle size, 75-150 µm, were 1 min, 2 min, 5 min, 7 min, 10 min, 15 min, 20 min, 30 min, 45 min, 60 min, 120 min, 180 min, and 240 min. The optimum contact time was assessed for the largest particle size as well (300-600 µm) because it was anticipated that larger particle sizes would require longer time to reach equilibrium between dissolved Pb^{2+} ions in a solution and rice straw. This is because the surface area has a great impact on the uptake of metal ions (Wong, et al. 2003a). For the 300-600 µm particle size, the studied time intervals were 30 min, 45 min, and 60 min. The pH was selected based on the optimum pH defined from the preceding experiment. The batch experiments were carried out under the following conditions:

- pH of the synthetic solution: 5.5 (± 0.05)
- Bio-sorbent dose: 0.1 g/50 ml
- Sorbent particle size: 75-150 μm; 300-600 μm
- Contact time: 1 min, 2 min, 5 min, 7 min, 10 min, 15 min, 20 min, 30 min, 45 min, 60 min, 120 min, 180 min, and 240 min
- Volume of Pb^{2+} standard solution: 50 ml
- Initial Pb^{2+} concentration: $C_0 \approx 40$ mg/l.
- Temperature: room temperature (22 ± 1 ^oC).

3.5.7 Effect of Rice Straw Dose

The impact of the sorbent dose on Pb^{2+} uptake was analyzed in order to determine the optimum dose of rice straw. The doses studied were; 0.12, 0.21, 0.51, 0.71, 1.02, 2.04, 4.03 and 6 g/l. The contact time is set based on the optimum contact time defined in the preceding experiment. The conditions of the experiment are the following:

- Optimum pH of the Pb^{2+} synthetic solution: 5.5 (± 0.05)
- Optimum Contact Time: 30 min
- Sorbent particle size: 75-150 μm
- Sorbent dose: 0.12, 0.21, 0.51, 0.71, 1.02, 2.04, 4.03 and 6 g/l
- Volume of Pb^{2+} standard solution: 50 ml
- Initial Pb^{2+} concentration: $C_0 \approx 40$ mg/l
- Temperature: room temperature (22 ± 1 ^oC).

3.5.8 Effect of Particle Size

In order to evaluate the combined impact of the particle size and the dose of a specific particle size on Pb^{2+} uptake by rice straw, a batch equilibrium experiment was carried out for three particle sizes, which are 300-600 µm, 75-150 µm, and <75 µm over a range of doses starting from 0.1g/l up to 6 g/l. For the 300-600 µm particle size, the impact of the rice straw dose on Pb^{2+} uptake was tested once at 30 min contact time to be comparable with the other particle sizes, and was additionally tested at 60 min contact time, which is the optimum contact time for that specific particle size. The conditions of the experiments are the following:

- Optimum pH of the Pb^{2+} synthetic solution: 5.5
- Particle size: 300-600 µm, 75-150 µm, and <75 µm
- Contact Time: 30 min, and 60 min (300-600 µm)
- Sorbent Dose:
  - 75-150 µm and <75 µm: 0.1, 0.2, 0.5, 0.7, 1, 2, 4 and 6 g/l
  - 300-600 µm (contact time: 30 min): 0.5, 1, 2, 4 and 6 g/l
  - 300-600 µm (contact time: 60 min): 0.5, 1, 2, 4 and 6 g/l
- Volume of Pb^{2+} standard solution: 50 ml
- Initial Pb^{2+} concentration: $C_0 \approx 40$ mg/l
- Temperature: room temperature (22 ± 1 ^{o}C).

3.5.9 Effect of Initial Pb^{2+} Concentration

The impact of the initial lead concentration on the sorption of lead by rice straw has been studied for the two particle sizes; <75 µm and 75- 150 µm at the optimum dose of each deduced from the previous experiments. The conditions of the experiment are the following:

- pH of the Pb^{2+} synthetic solution: 5.5
- Contact Time: 30 min
- Particle size: <75 µm and 75-150 µm
- Optimum dose:
    - 75 µm-150 µm: 4 g/l
    - <75 µm: 2 g/l
- Volume of Pb^{2+} standard solution: 50 ml
- Initial Pb^{2+} concentration:
    - 75 µm-150 µm: 2,5,10,15,20,40,60,80 and 105 mg/l
    - <75 µm: 5,10,15,20,40, and 60 mg/l
- Temperature: room temperature (22 ± 1 ^{o}C).

3.5.10 Effect of Pre-treatment of Rice Straw

Rice straw was chemically pre-treated in order to investigate whether chemical treatment would enhance the sorption properties of rice straw for Pb^{2+} or not. Tartaric acid treatment was employed because of the promising results it has achieved for sugarcane bagasse in the first stage of the research where multiple sorbents were comparatively analyzed. Chemical treatment using tartaric acid, one of the carboxylic acids, was applied in order to enhance the adsorption capacity by increasing the carboxylic groups on the surface area of the adsorbent (Wong, et al. 2003a). Pre-treatment was carried out according to the same method reported in Section 3.4.2. However, since the temperature of the thermochemical treatment; 180 ^{o}C, was too high for rice straw that it got burnt in the pre-treatment process illustrated in Phase I, the temperature was lowered to 120 ^{o}C, but the time of the reaction was elongated to 90 min, as reported by Zhu, Fan and Zhang (2008). Moreover, treatment using NaOH was excluded because based on the results of the biosorbents preliminary comparative analysis in this research (section 4.1.1) and the results reported by Wong, et al. (2003a), NaOH did not enhance the sorption properties of the sorbent; hence, it was excluded to cut the cost and simplify the treatment process.

i Preparation

Preparation of rice straw was conducted according to the same steps in Section3.5.2; however, only the fraction of 100/200 sieve (particle size: 75-150 µm) was used.

ii Pre-treatment

Pre-treatment of rice straw was carried out according to the following steps:

1. Preparing 1.2 M tartaric acid, manufactured in UK by Biostain Ready Reagents. 1 M of tartaric acid weighs 150.09 g/l, accordingly 1.2 M is 180.108 g/l, or 18.011 g/100 ml. A total of 100 ml of 1.2 M tartaric acid was prepared by dissolving 18.011 g tartaric acid in 100 ml of de-ionized distilled water (DDW) and constantly stirring using a magnetic stirrer to assure full dissolution.
2. Mixing 1.2 M tartaric acid with rice straw in a ratio of 7 ml of acid per 1 g of bio-sorbent (Wong, et al. 2003a, Marshall, et al. 1999); therefore, 70 ml of 1.2 M tartaric acid was added to 10 g of rice straw.
3. The tartaric acid modified rice straw (TA-RS) was placed on the orbital shaker for 30 min at room temperature, then poured on stainless steel trays and heated in the oven at 50 ^{o}C for 24 h (Zhu, Fan and Zhang 2008). Subsequently, the thermochemical reaction between the acid and RS was proceeded by raising the oven temperature up to 120 ^{o}C for 90 min (Zhu, Fan and Zhang 2008).
4. Afterwards, TA- RS was left to cool down, and then stirred with distilled water via a magnetic stirrer for 10 min. Finally the TA modified rice straw was washed with 200 ml of distilled water per gram of the material, which is reported in the literature to be sufficient to wash off excess unreacted acid (Zhu, Fan and Zhang 2008, Marshall, et al. 1999).
5. TA- RS was dried at 80 ^{o}C for 24 h.
6. After drying, TA-RS was re-sieved to retain the same particle size mentioned above.

7. Dried for 1 h at 80 °C to make sure it was free of moisture, and finally placed in a desiccator.

iii Pre- treated Rice Straw (TA-RS) Batch Equilibrium Experiments

Batch equilibrium experiments using TA- RS were conducted according to the same steps illustrated in Section 3.5.3.

EFFECT OF CONTACT TIME ON THE REMOVAL OF LEAD

Optimum contact time for the sorption of Pb^{2+} by TA- RS was assessed over a range of time intervals; 15, 30, 45, and 60 min, at the experimental conditions below:

- pH of the synthetic solution: 5.5 (± 0.05)
- Bio-sorbent dose: 0.1g/50ml (2 g/l)
- Sorbent particle size: 75-150 µm
- Contact time: 15 min, 30 min, 45 min, and 60 min
- Volume of Pb^{2+} standard solution: 50 ml
- Initial Pb^{2+} concentration: $C_0 \approx 40$ mg/l.
- Temperature: room temperature (22 ± 1 °C).

EFFECT OF TA-RS DOSE ON THE REMOVAL OF LEAD

Impact of TA-RS dose on the removal of Pb^{2+} was investigated by varying its amount from 2 g/l, 4 g/l, and 6 g/l in a constant volume of synthetic solution and a constant initial Pb^{2+} concentration, while analyzing the effect on the equilibrium concentration of Pb^{2+} (C_e). The conditions of the experiments are as follows:

- Optimum pH of the Pb^{2+} synthetic solution: 5.5
- Optimum Contact Time: 30 min
- Sorbent particle size: 75 µm-150 µm

- Sorbent dose: 2, 4 and 6 g/l
- Volume of Pb^{2+} standard solution: 50 ml
- Initial Pb^{2+} concentration ≈ 40 mg/l
- Temperature: room temperature (22 ± 1 ^{o}C).

A summary of all the batch equilibrium experiments conducted in the research are summarized in Table 11 below:

Table 11: Summary of batch equilibrium experiments

pH	Contact time (min)	Dose (g/l)	Particle size (μm)	C_o (mg/l)	Treatment
2-7	240	2	75-150	40	Raw
5.5	1 - 240	2	75-150	40	Raw
5.5	30 - 60	2	300-600	40	Raw
5.5	30	0.12-6	75-150	40	Raw
5.5	30	0.12-6	< 75	40	Raw
5.5	30	0.5-6	300-600	40	Raw
5.5	60	0.5-6	300-600	40	Raw
5.5	30	4	75-150	2-105	Raw
5.5	30	2	<75	5-60	Raw
5.5	15-60	2	75-150	40	TA-RS
5.5	30	2-6	75-150	40	TA-RS

3.5.11 Sorption Isotherm Models

Isotherms models predict the maximum metal uptake capacity from an aqueous solution in an equilibrium batch adsorption system. Langmuir and Fruindlich isotherm models are the most popular models in the literature. The batch equilibrium data of raw rice straw of particle size in the range of 75 µm-150 µm, optimum dose 4 g/l, and initial Pb^{2+} concentrations in the range of 10-105 mg/l were fitted and analyzed by Langmuir and Fruindlich isotherms.

3.6 Phase III- Fixed Bed Column Experiments Using Raw Rice Straw

The second mode of application, after the batch equilibrium tests of rice straw, is the fixed bed column tests. Fixed- bed column/ continuous flow system is a different application than batch experiments. Batch equilibrium studies give an insight into the efficiency of an adsorbent for the adsorption of specific heavy metals; however, they do not provide data that can be used for the scaling up necessary for practical industrial applications; on the other hand, column studies provide data that can be used for the scaling up required for industrial applications (Wong, et al. 2003b). The data obtained from the batch equilibrium studies gives useful information on the optimum conditions, such as the optimum pH, and optimum particle size that can be used in column experiments. Fixed bed systems are normally used for ion-exchange resins and adsorption using activated carbon, and are also recommended for the bio-sorption process due to the enhanced mass transfer kinetics and higher treated water quality in comparison to batch systems (Chatterjee and Schiewer 2014).

Fixed- bed column tests were conducted using raw rice straw of the optimum particle size; 75-150 µm and at the optimum pH 5.5 deduced from the batch experiments. Raw rice straw was prepared according to the same procedure stated in Section 3.5.2.

3.6.1 Objectives of Phase III

The main objectives of running fixed- bed column experiments are:

1. Simulate the performance of rice straw in full- scale continuous flow wastewater treatment systems
2. Study the impact of several operating parameters on the process performance. The operating parameters include; the influent Pb^{2+} concentration (C_o), bed depth and the flow rate (Q). The process performance was evaluated based on the number of treated bed volumes and the service time of the column to breakthrough and to exhaustion, and the adsorption capacity of rice straw at breakthrough and exhaustion.
3. Observe the variation in the effluent Pb^{2+} concentration throughout the service time of the column.

3.6.2 Experimental Setup

The laboratory scale fixed-bed column system consists of:

1. Polypropylene 10 L container
2. Positive displacement pump, reciprocating type manufactured in U.S.A by Eldex Laboratories, Inc.
3. Stainless steel columns with diameters of 0.75 cm and 0.7 cm and lengths of 8 cm and 16.5 cm, respectively.
4. Two- way valve at the bottom of the column that either directs the solution up to the column, or downwards to be collected as an influent sample
5. Effluent polypropylene 10 L container

Figure 10 and Figure 11 show the stainless steel column and the experimental setup of the fixed- bed column experiment. Figure 12 is a schematic diagram of the experimental set-up.

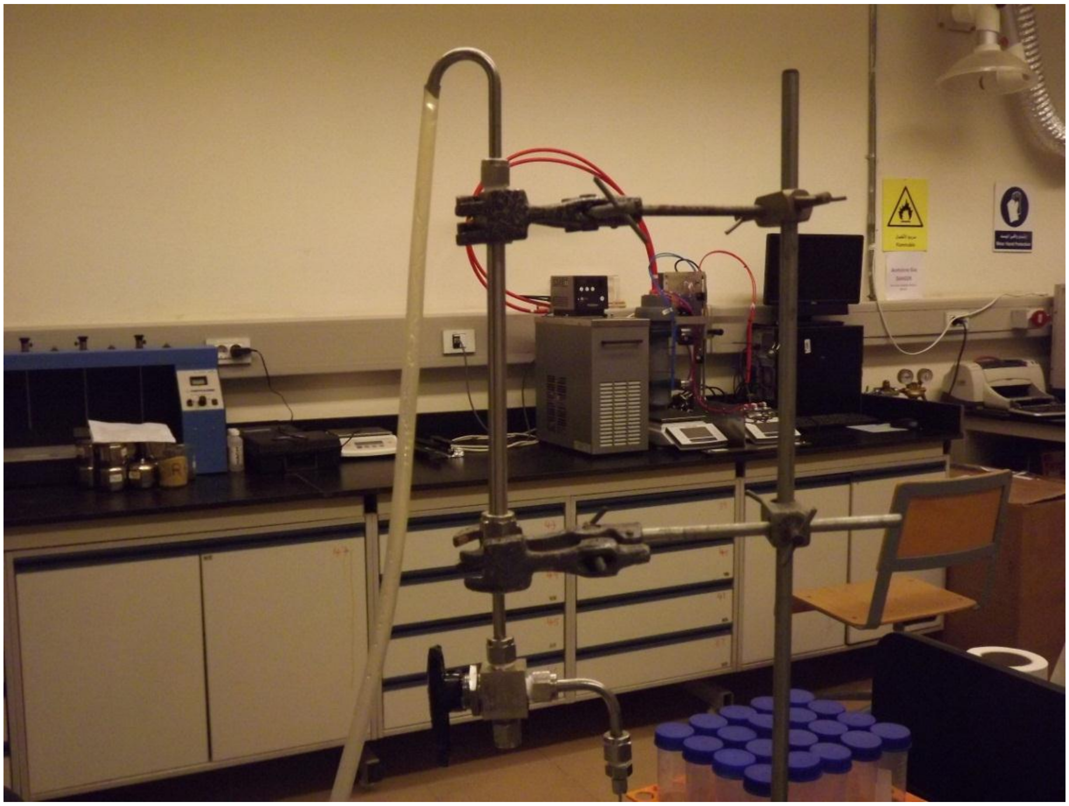


Figure 10: Stainless steel column and a two-way valve fixed at the bottom

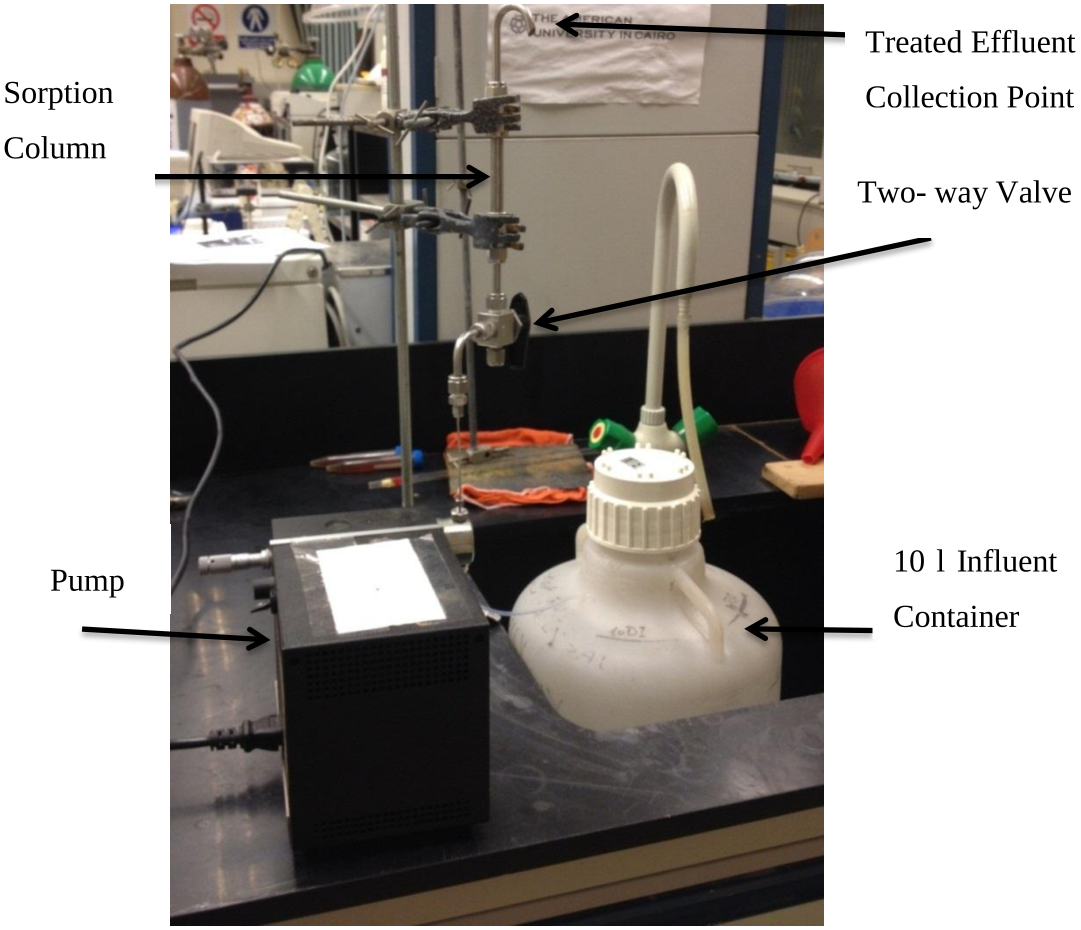


Figure 11: Experimental setup of a fixed- bed column experiment

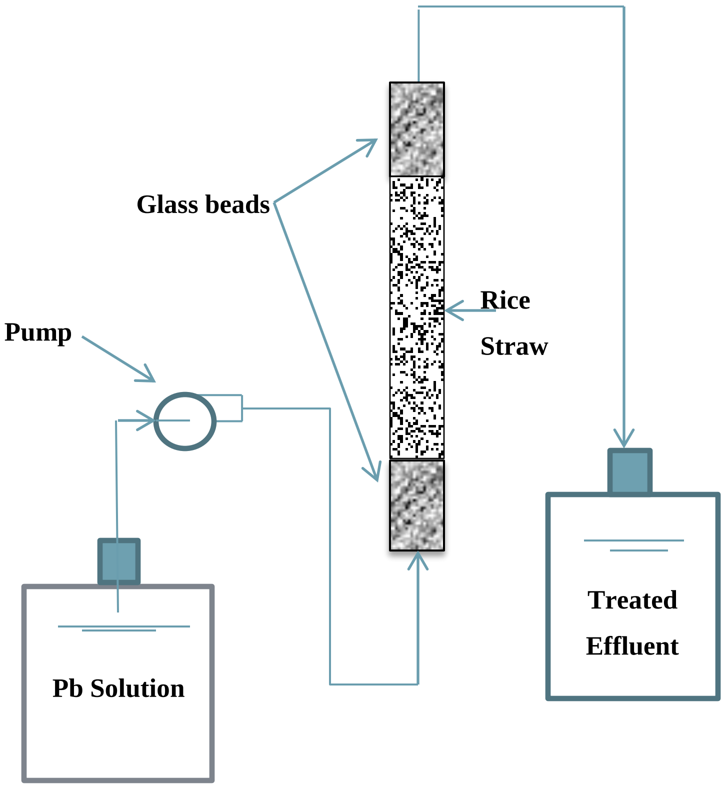


Figure 12: Schematic diagram of the column experimental setup

3.6.3 Operating Parameters

The main parameters which their impacts on the performance of the rice straw column and the breakthrough curves were studied are the following:

1. Initial Pb^{2+} Concentration
2. Bed depth
3. Flow rate

3.6.4 Experimental Procedure

Fixed- bed column studies were carried out according to the following procedure:

1. Preparing 1000 ppm stock solution of Pb^{2+} by diluting $Pb(NO_3)_2$ salt in 1 L of DDW

2. Diluting the 1000 ppm stock solution to the required concentration and adding an ionic background of 0.01M $NaNO_3$, as explained in Section 3.3, in a 10 liter polypropylene container.
3. Adjusting the pH of the solution to 5.5, optimum pH from the batch equilibrium experiments, using NaOH solution and HNO_3.
4. Weighing the rice straw to be packed in the column using the analytical balance.
5. Packing the stainless steel column with a layer of glass beads at the bottom, followed by the raw rice straw to the required depth, while manually compressing each layer of rice straw by a glass rod to assure uniform packing and to allow a larger amount of rice straw in the column. Finally, adding another layer of glass beads until it reaches the tip of the column. Glass beads facilitate uniform flow of the solution through the column.
6. Adjusting the flow rate of the feed solution to the desired flow in ml/min by observing the time taken for the effluent of the column to fill a particular pre-defined volume. Subsequently, tuning the pump until the required flow is reached.
7. A positive displacement pump lifts the solution from the 10 liter polypropylene container to the bottom of the column where upward flow of the solution through the packed material takes place.
8. At specified time intervals, influent and effluent samples are collected in small test tubes, as shown in Figure 13.

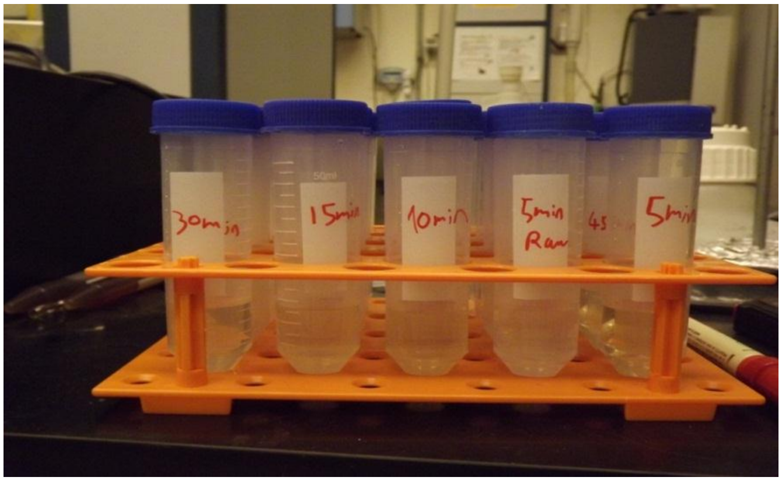


Figure 13: Small test tubes for collecting effluent samples

9. Immediately measuring and recording the pH of the samples, and adjusting the pH of the feed solution if a large deviation from the initial pH was noticed.
10. Finally acidifying the samples using nitric acid to a pH <2 as per the Standard Methods (APHA, AWWA and WEF 1992).
11. Diluting samples of effluent Pb^{2+} concentration (C_e) higher than the measuring limit of the A.A.S prior to the analysis, as illustrated in Section 3.7.2.
12. Analyzing equilibrium concentration of Pb^{2+} (C_e) via the Atomic Absorption Spectrometer (AAS). The AAS analysis was triplicated and average values were reported.

3.6.5 Effect of Initial Pb^{2+} Concentration

Lead concentrations of 15 mg/l, 40 mg/l, and 80 mg/l were used to assess the impact of initial Pb^{2+} concentration on the performance of the column and breakthrough curves, at pH 5.5, flow rate 6 ml/min, and bed depth of 3 cm.

3.6.6 Effect of Bed Depth

Rice straw was packed in the column at bed depths of 3 cm, 6 cm, and 12.5 cm to evaluate the effect of the bed depth, at pH 5.5, flow rate 6 ml/min, and initial Pb^{2+} concentration around 40 mg/l.

3.6.7 Effect of Flow Rate (Q)

The column was run once at a solution flow rate of 6 ml/min and another time at 3 ml/min, at pH 5.5, bed depth 6 cm, and initial Pb^{2+} concentration around 40 mg/l. A summary of the fixed- bed column experiments are illustrated in Table 12.

Table 12: Summary of Fixed- bed column experiments using raw rice straw of partcle size 75 µm- 150 µm at pH 5.5

Pb^{2+} concentration (mg/l)	Column diameter (cm)	Bed depth (cm)	Flow rate (ml/min)	Run time (h)
15	0.75	3	6	25
40	0.75	3	6	24
80	0.75	3	6	23
40	0.75	6	6	25
40	0.7	12.5	6	24
40	0.75	6	3	25

3.7 Sampling and Sample Analysis

Sample analysis was carried out for the Pb^{2+} equilibrium concentration and the pH of the samples, as follows:

3.7.1 pH Analysis

The pH of the samples was adjusted by adding few drops 0.1 M NaOH and/ or 0.1 M HNO_3 using a micro-pipette (0-50 µl). The pH value was analyzed using Thermo Scientific- ORION STAR A211 pH Benchtop Meter, manufactured in the USA. It was calibrated using buffers of pH 4 and pH 7 before the analysis of the samples. The samples are stirred via a meter-controlled Orion Star stirrer probe, while the pH is measured. Figure 14 shows the pH meter used in the analysis.

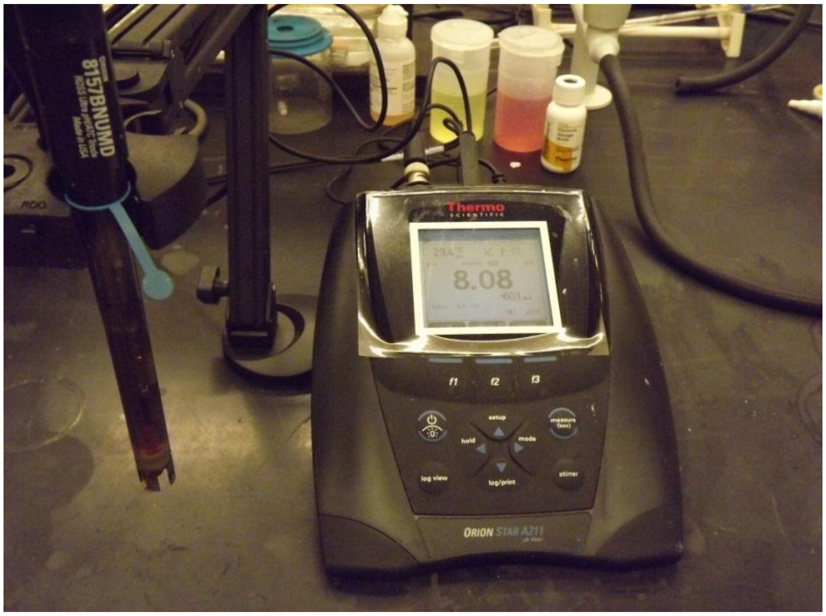


Figure 14: pH meter- ORION STAR A211

3.7.2 Pb^{2+} Analysis

The equilibrium/ final concentration of Pb^{2+} was analyzed via an Atomic Absorption Spectrometer (AAS), flame type, SensaAA dual flame atomization system model, manufactured by GBC Scientific Equipment in USA, see Figure 15. The analysis was conducted according to the Standard Methods for the Examination of Water and Wastewater, method No. 3500-Pb (APHA, AWWA and WEF 1992). At the beginning of each run, the operating conditions of the AAS were adjusted, and the device was calibrated using a calibration blank and four calibration Pb^{2+} standards in the range of 2.5mg/l–15mg/l, prepared using the same lead stock solution used for preparing the synthetic solution. The minimum regression coefficient of the AAS calibration curve was 0.99. Calibration standards were checked after every ten samples to monitor the device response. The calibration blank is a volume of DDW similar to the volume of the samples (50ml) that is acidified with the same type (HNO_3) and concentration of acid as the calibration standards and the samples to be analyzed. The calibration blank defines the zero point of the measuring device.

The A.A.S used for the analysis of Pb^{2+} provides quantitative information of the heavy metals using an analytical technique of analysis. Acetylene gas was used. The sample is subjected to a flame, then thermal and chemical reactions produce free atoms that can absorb specific wavelengths, providing Atomic Absorption Spectroscopy (EL Zayat 2014). Its measuring limit of Pb^{2+} is in the range of 2.5 mg/l- 20 mg/l.

Figure 15: Atomic Absorption Spectrometer (A.A.S)

Samples obtained from the experimental work that exceeded the measuring range of the atomic absorption spectrometer (AAS), were diluted using DDW to a ratio of 1: 10, according to the following steps:

1. Adding DDW in a 50 ml volumetric flask below the mark indicating the volume
2. Adding 5ml of the samples
3. Mixing the solution very well
4. Adding more DDW to reach 50ml

3.8 Rice Straw Sample Characterization

Rice straw samples were analyzed in order to define its surface area, pore volume, dominating chemical bonds and functional groups responsible of the surface complexations, surface characteristics, chemical constituents and most important, the mechanisms responsible for the sorption of Pb^{2+} by rice straw. The following sub-sections illustrate the different analysis carried out.

3.8.1 BET Surface Area and Pore Volume

The BET surface area, pore volume and average pore size of raw rice straw samples of particle size in the range of 75-150 µm was measured via a Micromeritics-ASAP 2020 apparatus, manufactured in the USA. The process consisted of two stages, which are the sample preparation stage (Degassing) for 6 h at 65 ^{o}C, and sample analysis through the continuous application of nitrogen gas on the surface of rice straw. Nitrogen adsorption measurements were determined at 77 K. The time required for each point of the adsorption or desorption isotherm to attain equilibrium was between 15-20 min. The specific surface areas of the samples were calculated by the B.E.T. method.

3.8.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy analysis was performed using a Thermo Scientific- NICOLET 380 FTIR spectrometer, manufactured in the USA. The analysis method adopted by the device is KBr pellet method. The Spectral range is 7800 – 350 cm^{-1} using proprietary KBr beam splitter (Fourier Transform Infrared Spectroscopy (FTIR) Analysis). Fourier transform infrared spectroscopy analysis was carried out for raw rice straw samples pre and post biosorption of Pb^{2+} in order to determine the main functional groups responsible for the biosorption of Pb^{2+}. FTIR was also carried out for TA-RS samples to identify the effect of the pre-treatment on the carboxylic groups on the surface of rice straw. The analysis technique is based on measuring the absorption of different infrared wave lengths by the material and producing an infrared absorption spectrum; consequently, the created chemical bonds in a molecule can be identified, FTIR is an analytical instrument for defining functional groups and providing covalent bonding information (Fourier Transform Infrared Spectroscopy (FTIR) Analysis).

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

Field Emission Scanning Electron Microscope LEO SUPRA 55, manufactured by ZEISS, Germany, see Figure 16, was utilized to analyze the surface characteristics of fresh rice straw samples and metal loaded rice straw samples in order to detect the impact of Pb^{2+} sorption on the surface walls of rice straw. Energy dispersive X-ray (EDX), which is a complementary technology of the SEM was used to analyze the chemical composition of rice straw samples before and after sorption of Pb^{2+}, in an attempt to define whether ion exchange is one of the pre-dominant mechanisms of the uptake of Pb^{2+}. A small amount of dry samples were coated with carbon tape to be scanned and analyzed by the SEM and EDX unit. SEM scans the sample with a focused electron beam; consequently, delivers images with information about the samples' topography and composition. It has a very wide operating voltage range from 0.02 to 30 kV (Zeiss). Samples were scanned at magnifications starting from 150 X up to 5000 X. Surface analysis is conducted down to nanometer scales under vacuum. The output of the EDX was the chemical constituents of the sample in terms of percent of weight, and a spectrum of the chemical composition.

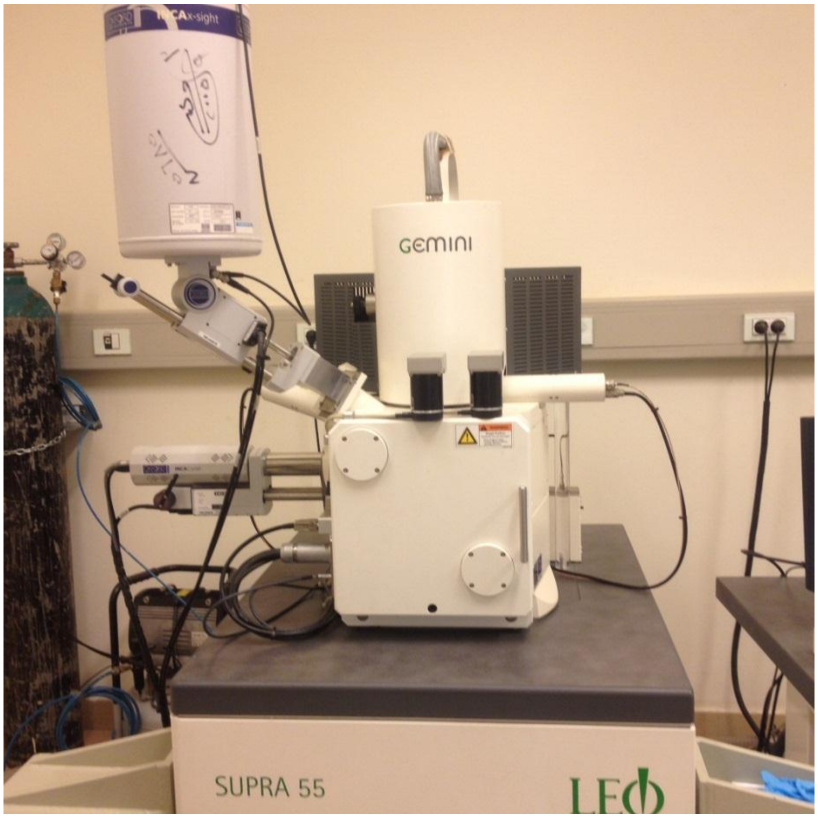


Figure 16: LEO SUPRA 55 SEM and EDX

CHAPTER 4 : RESULTS AND DISCUSSION

4.1 Phase I- Bio-sorbents and Adsorbents Comparative Study

A comparative analysis using preliminary equilibrium batch tests was carried out for three types of bio-sorbents (agricultural wastes); sugarcane bagasse, rice husk and rice straw, both raw and pre-treated using different pre-treatment methods. In addition to three inorganic adsorbents; cement kiln dust (CKD), lime and marble powder waste, in order to assess their percent uptake of Pb^{2+} in an aqueous solution. The conditions of the experiment were:

- Bio-sorbent dose: 0.1 g/50 ml (2 g/l)
- Contact time: 2 h
- Volume of Pb^{2+} standard solution: 50 ml
- pH: 5.5 (±0.05)
- Initial Pb^{2+} concentration ≈ 40 mg/l.
- Temperature: room temperature ($22 \pm 1\ ^{o}C$).

The percent removal was calculated using the following equation:

$$\%\ \boldsymbol{Removal} = \frac{(\boldsymbol{C_0}-\boldsymbol{C_e})*\mathbf{100}}{\boldsymbol{C_0}} \qquad \text{(4-1)}$$

Where,

C_0: Initial Pb^{2+} ions concentration in liquid phase (mg/l)

C_e: Pb^{2+} ions concentration at equilibrium in liquid phase (mg/l)

4.1.1 Agricultural wastes/ Biosorbents Comparative Batch Equilibrium Tests

The tests were triplicated and the average values are presented in Figure 17. The results show that tartaric acid modified sugarcane bagasse (TA-SB) achieved the highest removal efficiency of Pb^{2+}, followed by raw rice straw (Raw-RS).

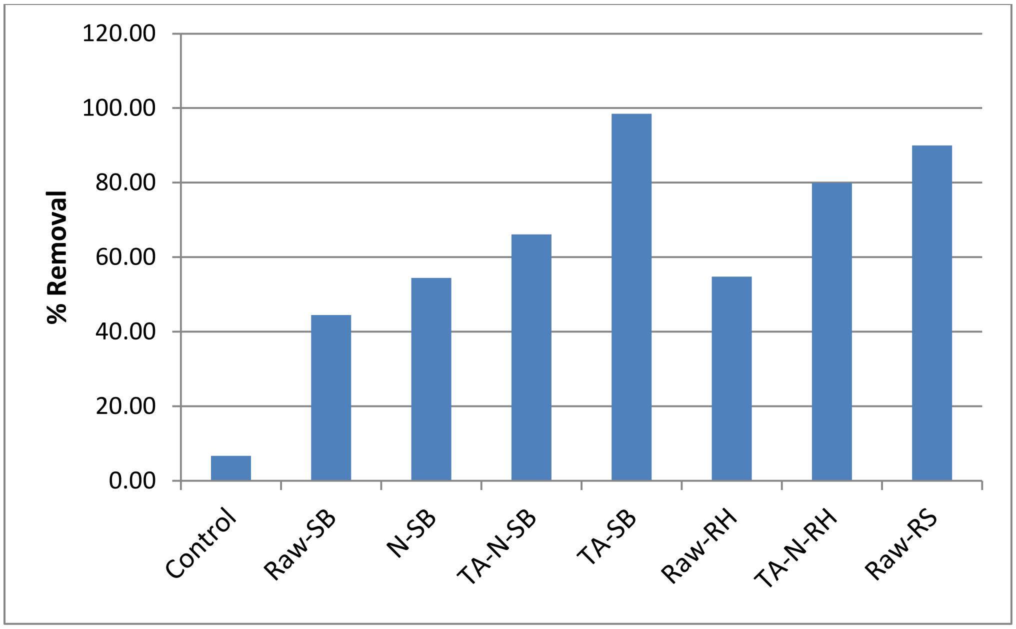


Figure 17: % Removal of Pb^{2+} via various raw and pre-treated agricultural wastes (pH 5.5, dose 2 g/l, contact time: 2h)

Small fraction of lead, which is the in-soluble fraction, has been removed in the process of the filtration. This is manifested in the control sample, which is a 50 ml of the Pb^{2+} synthetic solution that does not include any bio-sorbent and undergoes the same process as the other samples; that is the shaker, filtration, and acidification up to pH< 2 prior to Pb^{2+} equilibrium concentration analysis via the Atomic Absorption Spectrometer. In the control sample the Pb^{2+} has decreased from the initial concentration of 40mg/l to 37.333 mg/l, which is 6.67% removal, at final pH 5.81, as presented in Table A-1 in Appendix A. This minor percent of removal is believed to be due to some precipitation of Pb hydroxide. The degree of solubility of lead is mainly governed by the pH value. The raw sugarcane bagasse (Raw-SB) sample has achieved only 44.51% removal efficiency, which was the lowest uptake efficiency compared to the raw rice husk (Raw-RH); 54.80% and the raw rice straw (Raw-RS); 89.95%. As for the pre-treated agricultural wastes, the tartaric acid modified sugarcane bagasse (TA-SB) reached 98.50% removal of Pb^{2+}. The high removal efficiency of TA-SB is believed to be mainly due to the increase of the carboxyl groups on the surface of the SB (Gurgel, Freitas and Gil 2008) that was achieved by the pre-treatment using Tartaric acid (TA), which is a carboxylic acid (Wong, et al. 2003a). The treatment using NaOH prior to the Tartaric acid treatment did not show any enhancement to the removal efficiency of Pb^{2+}, as TA-N-SB has only yielded 66.14% uptake, the same trend was reported by Wong, et al. (2003a). Solely applying the NaOH treatment, while excluding the tartaric acid did not prove to be an efficient pre-treatment as the achieved removal of Pb^{2+} for N-SB was only 54.4%. As for modified rice straw, the removal efficiency of Pb^{2+} by tartaric acid and NaOH treated rice straw (TA-N-RS) was not examined because TA-N-RS was burnt at the high temperature (180 ^{o}C) of the pre-treatment process.

4.1.2 Inorganic Adsorbents Comparative Batch Equilibrium Tests

In this preliminary equilibrium batch tests, the uptake efficiencies of Pb^{2+} by CKD, lime and marble powder waste were assessed under the same operating conditions explained above. Tests were triplicated and average values are presented in Figure 18.

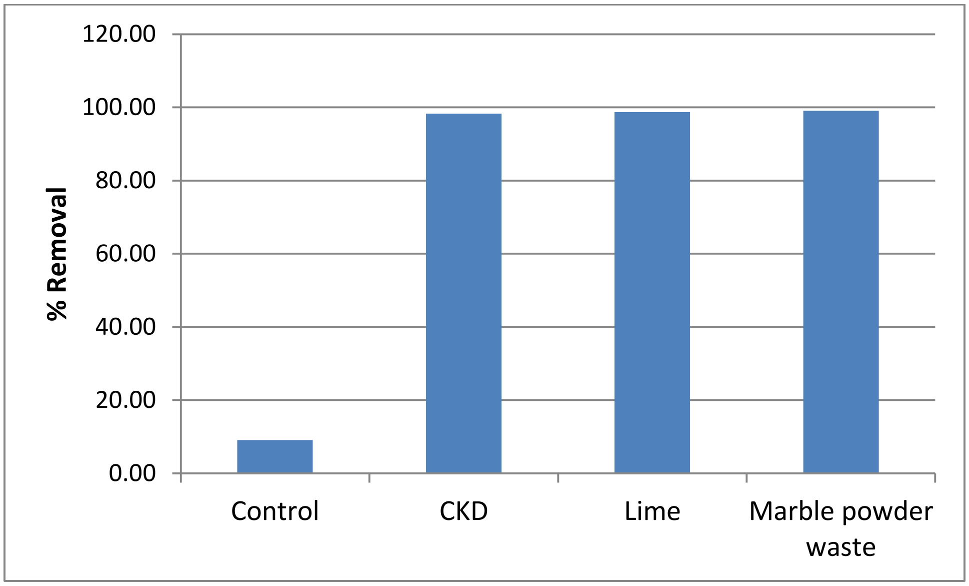


Figure 18: % Removal of Pb^{2+} yielded by CKD, lime & marble powder (pH 5.5, dose:2 g/l, contact time:2 h)

The % removal of Pb^{2+} using the three adsorbents was very close, as shown in Figure 18. The pH was adjusted to 5.5 at the beginning of the batch experiment; however, there was a drastic increase in the pH after the samples were taken off the orbital shaker, see Appendix A. Therefore, it can be concluded that the main reason for the removal of

Pb^{2+} in that case was the precipitation of $Pb(OH)_2$, especially that precipitation of lead hydroxide $Pb(OH)_2$ takes place at pH> 6 (El Zayat, Elagroudy and El Haggar 2014, Soetaredjo, et al. 2013). Marble powder had the least significant alkaline impact on the pH of the solution among the three materials, as it has only raised the pH by around 1 pH value.

4.1.3 Most Promising Sorbent Selection

Based on the results of the conducted preliminary batch tests, raw rice straw and tartaric acid modified sugarcane bagasse have yielded the highest results compared to the rest of the investigated agricultural wastes. Moreover, the three investigated adsorbents, CKD, lime and marble powder, have also achieved very high percent of Pb^{2+} uptake. However, raw rice straw (Raw-RS) is considered the most promising sorbent; hence, selected to undergo a deeper analysis of the optimum operating conditions, such as the pH, equilibrium time, sorbent dose, initial Pb^{2+} concentration and particle size, for the following reasons:

1. Raw rice straw yielded the highest Pb^{2+} removal efficiency compared to the other investigated raw agricultural wastes; sugarcane bagasse and rice husk; therefore, it is worth investigating its optimum operating parameters and maximum adsorption capacity.

2. Rice straw constitutes a large quantity of the agricultural wastes in Egypt; 5 M tons/year, and the quantity of rice straw that is unused in purposes, such as animal fodder and composting is 3.1 M tons/year (Abdelhady, et al. 2014). Open- field burning of rice straw causes the black cloud, which is an environmental catastrophe, and has adverse effects on the human health.

3. Raw rice straw is a low cost raw material ready for use without pre-treatment. Utilizing a raw material in industrial wastewater treatment eliminates the extra cost and effort associated with the pre-treatment process.

4. CKD and lime are not very practical in industrial applications due to their severe alkalinity, which raises the pH value up to extremely high levels; around pH 9 for CKD and pH 11.6 for lime. Hence, requiring large quantities of acid to re-adjust the pH.

4.2 Phase II- Batch Equilibrium Experiments

Batch equilibrium experiments were conducted in order to depict the impact of six essential factors on the percentage removal of Pb^{2+} and adsorption capacity of rice straw. Experiments were triplicated and mean values are reported. The studied factors are the following:

1. pH of the solution
2. Contact time
3. Sorbent dose
4. Particle size
5. Initial Pb^{2+} concentration
6. Pre-treatment

The adsorption capacity or the amount of Pb^{2+} ions adsorbed on the rice straw was calculated as follows:

$$\boldsymbol{q_e = \frac{(C_0 - C_e)V}{m}} \qquad \text{(4-2)}$$

Where,

q_e: Mass of metal ions adsorbed per unit mass of the sorbent; adsorption capacity (mg/g)

C_0: Initial Pb^{2+} ions concentration in liquid phase (mg/l)

C_e: Pb^{2+} ions concentration at equilibrium in liquid phase (mg/l)

V: Volume of the Pb^{2+} solution (0.05 l)

m: mass of the bio-sorbent (g)

4.2.1 Effect of pH on the Removal of Pb^{2+}

Batch equilibrium experiments were carried out in order to assess the optimum pH of the solution. The conditions of the experiment are the following:

- Bio-sorbent dose: 2 g/l
- Particle size: 75-150 µm
- Contact time: 4 h
- Volume of Pb^{2+} standard solution: 50 ml
- pH of the synthetic solution: 2.12, 2.96, 4.09, 4.92, 5.48, 6.15, and 7.05
- Initial Pb^{2+} concentration ≈ 40 mg/l.
- Temperature: room temperature (22 ± 1 ^{o}C).

As explained in Chapter 2 of this research, The amount of metal uptake by adsorbents is highly affected by varying the pH of a solution due to the consequent change in the distribution of the surface charge of the adsorbent (Grassi, et al. 2012, Ahmaruzzaman 2011, Rao, et al. 2013), as well as its degree of ionization and its functional groups (Rao, et al. 2013). Figure 19 illustrates that at low pH , in the range of 2-3.5, adsorption of Pb^{2+} via rice straw was relatively low in a range of 12%-45%. At higher pH in the range of 3.5-6, the % removal of lead ions has remarkably increased to reach around 90%. Whereas, at pH 7.6 the % removal has further increased to reach 97.22%, as presented in Figure 19. This relation between the pH and the amount of lead uptake by rice straw can be attributed to the fact that at low pH values, the surface functional groups, basically carboxylic groups, of the bio-sorbent gets protonated by H^+ ions leading to a net positive charge on the surface of the bio-sorbent, as explained by equation 4-3 (Soetaredjo, et al. 2013). As a consequence, this creates a repulsive force between cationic species of the metal (Pb^{2+}) and the positively charged surface of the sorbent, which hinders the bio-sorption process. Additionally, the increase of the H^+ ions creates a competition between them and the metal ions over the active sorption sites on the surface of the rice straw (Soetaredjo, et al. 2013).

$$\boldsymbol{R-COOH+H^{+}\ \rightarrow R-COOH_{2}^{+}} \qquad (4\text{-}3)$$

However, the small amount of removal achieved at low pH is due to protons H^+ exchange with heavy metal ion (Ahmaruzzaman 2011, Rao, et al. 2013). On the other hand, at higher pH values, the carboxylic acid groups are deprotonated and dissociates into carboxylate anions ($R\text{-}COO^-$), which occurs at pH in the range of 3.5-5.5 (Soetaredjo, et al. 2013). Therefore, leading to an increase in the negative charge on the surface of rice straw and electrostatic forces of attraction, van der Waals forces, are created between the positively charged ions of lead and the negatively charged surface of rice straw, which in turn facilitates the process of biosorption (Soetaredjo, et al. 2013). Upon the increase in the pH, the surface functional groups are activated (Rao, et al. 2013) and the surface charge of the adsorbent becomes negative, while the predominant metal ions are positive; therefore, adsorption increases (Ahmaruzzaman 2011). Moreover, as the pH of the solution increases, the H^+ ions concentration decreases; hence, the competition between the H^+ ions and the Pb^{2+} over the active sites on the surface of rice straw decreases (Soetaredjo, et al. 2013). Also, the pH of a solution has an impact on the solubility of the metal ions. To illustrate, as the pH increases, the solubility of metal ions decreases; hence, facilitating the sorption process (Homagai, Ghimire and Inoue 2010), through co-precipitation on the surface of the adsorbent (Mahmood, Malik and Hussain 2010).

As for the further increase in the % removal at pH>6, it is basically due to precipitation because the insoluble metal species of Pb are formed at pH >6 (Soetaredjo, et al. 2013, EL Zayat 2014). This trend is manifested in Figure 19, where the % removal in the control samples that do not contain rice straw was very low at pH values < 6; however, it has suddenly increased from 9.84% at pH 5.86 up to 90.62% at pH 6.6. The maximum % removal; 97.22%, occurred at pH above 7; however, the optimum pH selected to study the sorption capacity of rice straw in this research is around 5.5 in order to avoid the distortion of the analysis of the sorption capacity of rice straw by the impact of metal hydroxides precipitation. Figure 20 shows that the adsorption capacity increases with the increase in the pH.

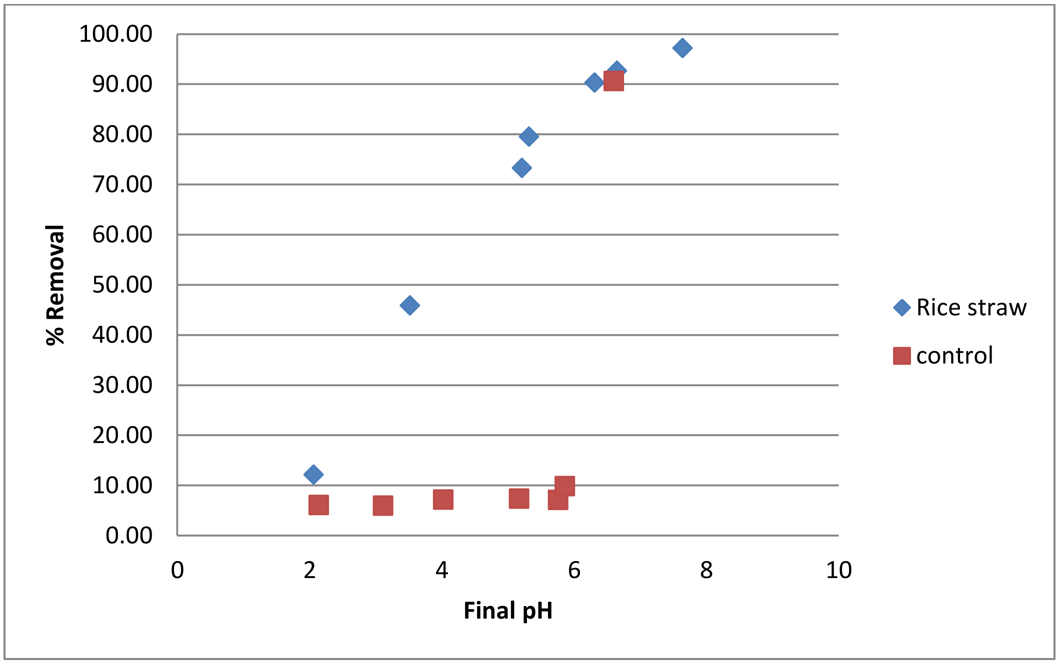


Figure 19: Final pH of the solution vs. the % removal of Pb^{2+} (dose 2g/l, contact time: 4h, 40mg/l Pb^{2+})

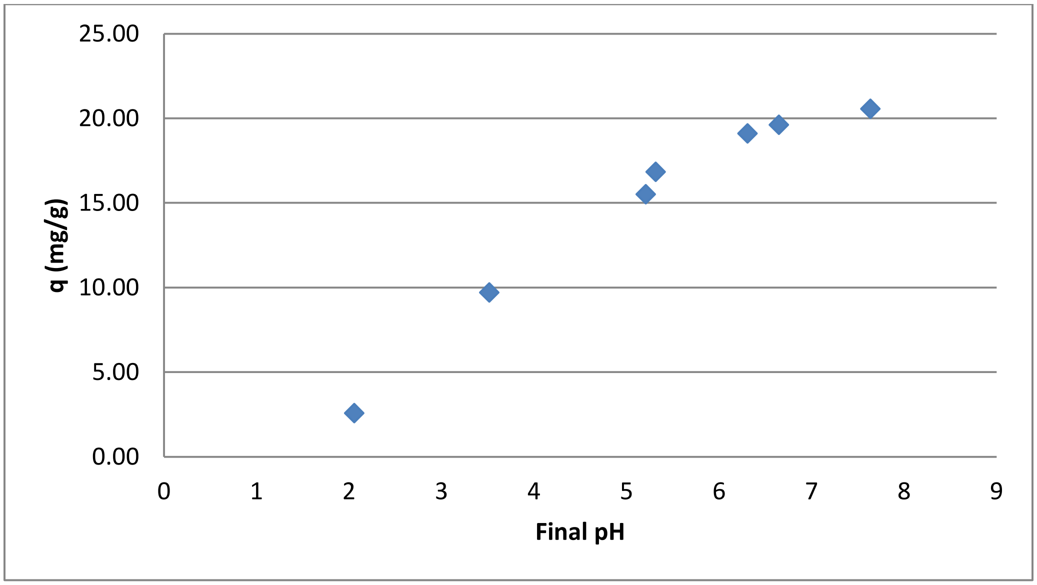


Figure 20: Impact of pH on the adsorption capacity of rice straw for the removal of Pb^{2+} (dose 2g/l, time: 4h, 40mg/l Pb^{2+})

4.2.2 Effect of Contact Time

This experiment was carried out in order to detect the time needed for the bio-sorption process between rice straw and lead to reach equilibrium. Time intervals studied were 1 min, 2 min, 5 min, 7 min, 10 min, 15 min, 20 min, 30 min, 45 min, 60 min, 120 min, 180 min, and 240 min. Rice straw of particle size 75-150 µm was used. The batch experiments were carried out under the following conditions:

- Bio-sorbent dose: 0.1 g
- Sorbent particle size: 75-150 µm
- Volume of Pb^{2+} standard solution: 50 ml
- pH of the synthetic solution: 5.5
- Initial Pb^{2+} concentration $\approx$ 40 mg/l
- Temperature: room temperature (22 ± 1 ^{o}C).

As shown in Figure 21, the sorption kinetics of lead via raw rice straw was rapid. During the first few minutes the rate was very fast; 82% removal was achieved in the first 10 min, afterwards the rate of sorption slowed down until it reached equilibrium. This performance could be due to the fact that rapid mass transfer on the outer surface of the adsorbent has taken place first, afterwards a slower internal diffusion process has started to occur (Wong, et al. 2003a). At the beginning of the sorption process, the active sites on the surface of the sorbent are still unoccupied; however, along with time the active sites starts to get saturated by the heavy metal ions; therefore, the sorption rate gets slower (Ding, et al. 2012). At 30 min the sorption system had almost reached equilibrium yielding 86.15% removal. The % removal has slightly increased up to 89.65% after 3 hours; however, the difference is considered insignificant. Control samples at the various contact times were also analyzed and their results are presented in Figure 21 to demonstrate the impact of rice straw on the uptake of Pb^{2+} from an aqueous solution.

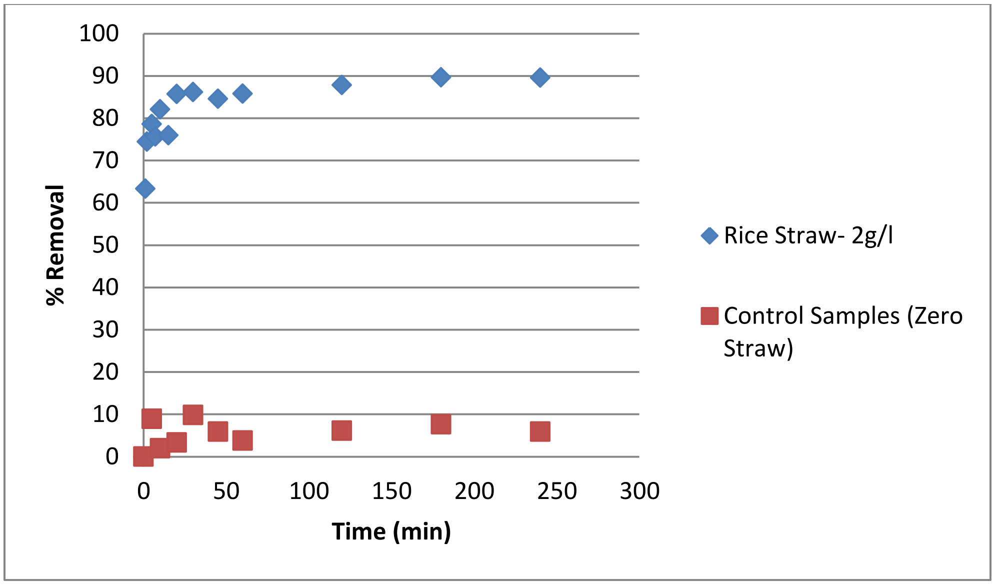


Figure 21: Impact of Contact Time on % Removal of 40mg/l Pb^{2+} by Rice Straw (2 g/l) at pH 5.5

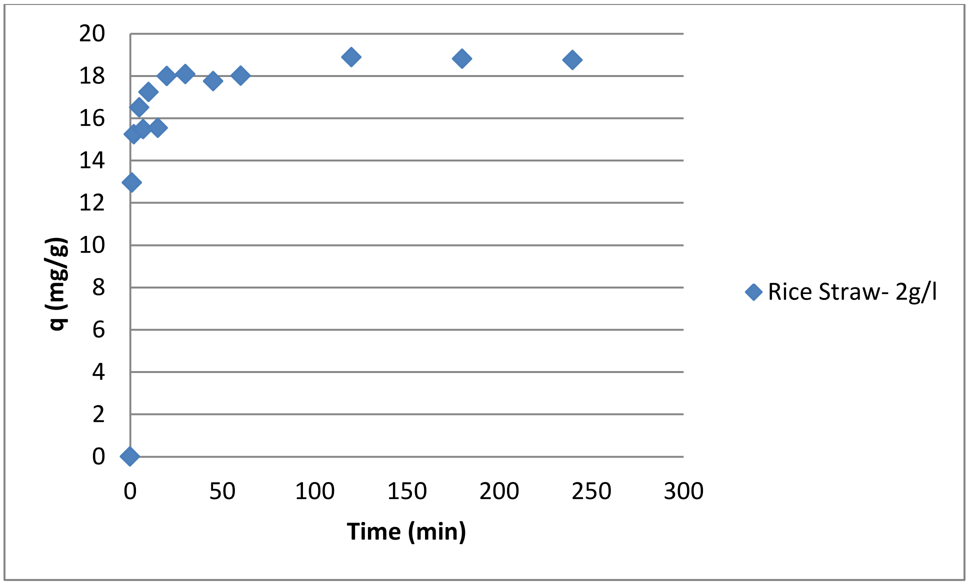


Figure 22: Impact of Contact Time on the Adsorption Capacity of Rice Straw (2g/l) at pH 5.5 and 40mg/l Pb^{2+}

After a contact time of 30 min the change in the adsorption capacity of lead was minor, < 1 mg/g, and the curve tended to be almost flat, as shown in Figure 22. At 30 min, the q was 18.08 mg/g and at 4 h the maximum q was 18.8 mg/g, as presented in Figure 22 and Table B-2 in Appendix B. The optimum time of the rice straw and Pb^{2+} sorption system is considered to be 30 min.

In order to make sure that 30 min were enough to reach equilibrium for a larger particle size of rice straw; 300-600 µm, the impact of contact time was analyzed at 30 min, 45 min and 60 min. The results proved that 30 min were not enough for the larger particle size to attain equilibrium, as shown in Figure 23. Therefore, for the 300-600 µm particle size, 60 min were selected as the optimum contact time, other researchers who reported the equilibrium contact time using rice straw to be not more than 60 min was Kardam, et al. (2014) who reported the equilibrium contact time for modified rice straw to be 40 min.

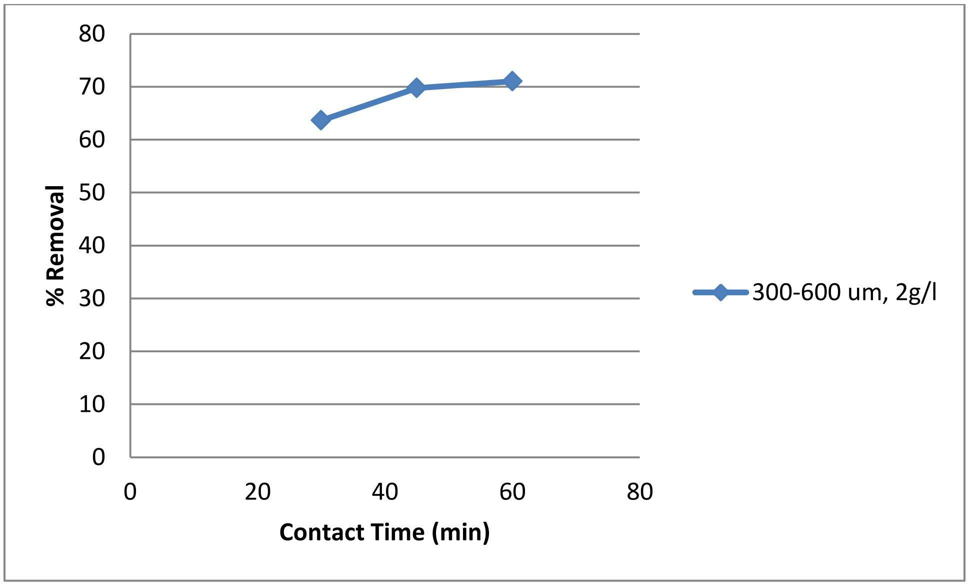


Figure 23: Impact of Contact Time on Pb^{2+} Removal by Rice Straw of Particle Size: 300-600 µm (dose 2g/l, pH 5.5, 40mg/l Pb^{2+})

4.2.3 Effect of Sorbent Dose

A batch study was conducted for a range of doses of rice straw of particle size 75-150 µm, in order to assess the impact of the sorbent dose on the lead uptake. The doses studied were; 0.116, 0.206, 0.51, 0.71, 1.02, 2.04, 4.03 and 6 g/l, and the equilibrium data are presented in Table B-3 in Appendix B. The conditions of the experiment are the following:

- Optimum pH of the Pb^{2+} synthetic solution: 5.5

- Optimum Contact Time: 30 min
- Sorbent particle size: 75-150 µm
- Volume of lead standard solution: 50 ml
- Initial Pb^{2+} concentration ≈ 40 mg/l
- Temperature: room temperature (22 ± 1 ^{o}C).

Doses of rice straw in the range of 0.1 g/l- 1 g/l resulted in a very low efficiency of removal. The percent of Pb^{2+} removed was increasing with the increase in the rice straw dose until it reached around 94% at the optimum dose; 4 g/l, then tended to keep constant as the rice straw dose was increased up to 6 g/l, as presented in Figure 24. The percent removal of Pb^{2+} is directly proportional to the dose of rice straw (Ding, et al. 2012). For a 4 g/l and 6 g/l there was not a significant change in the % removals, 94.12% and 95.49% respectively, this could be due to a state of equilibrium between the bio-sorbent and the heavy metal preventing the bio-sorbent from further bio-sorption (Kardam, et al. 2014) ,as shown in Figure 24. The optimum dose of rice straw is 4 g/l. Since the difference in the percent removal compared to the 6 g/l is insignificant, it is preferred to achieve the best results using the least quantity of bio-sorbent in order to reduce the sludge resulting from the treatment process and to reduce the quantity of rice straw needed; consequently, reduce the cost of transportation and preparation of the material. Additionally, upon utilizing 6 g/l, a light yellow color caused by the natural pigments of rice straw was observed in the treated water; therefore, it is preferred not to exceed 4 g/l. As for the adsorption capacity, it is noticed from the results in Figure 26 that it decreases with increasing the dose of rice straw, at 4 g/l the q is 10.19 mg/g of rice straw.

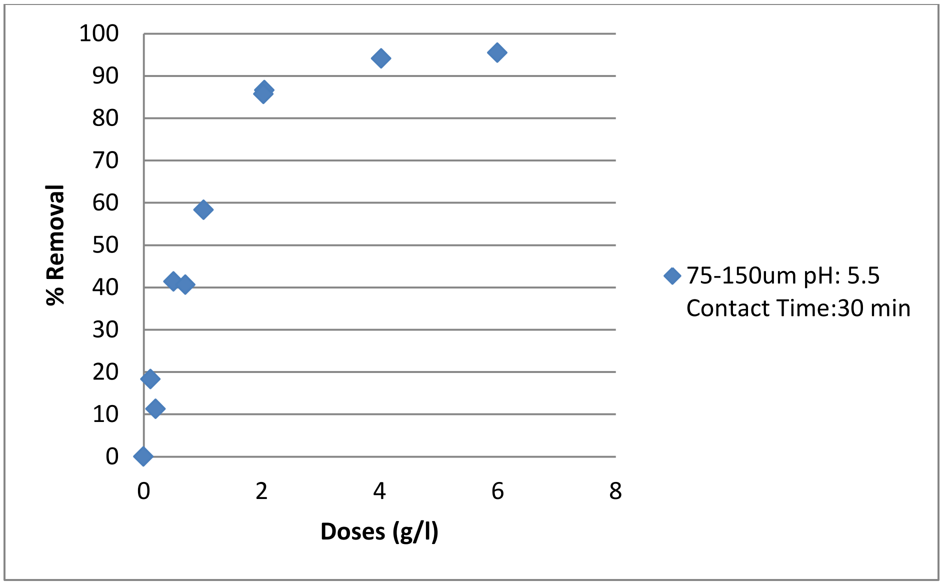


Figure 24: Impact of Rice Straw Dose on the Uptake of Pb^{2+}

4.2.4 Effect of Particle Size

The particle size, consequently the surface area of a sorbent plays an important role in the adsorption process (Wong, et al. 2003a). As illustrated in Chapter 2, the adsorption capacity and the metal uptake efficiency are enhanced with the increase in the surface area because the functional groups responsible for the chelation of heavy metals, such as the carboxylic groups, increase as well. In an attempt to practically assess the impact of the particle size and the surface area, a batch experiment was carried out for three different particle sizes; 300-600 µm, 75-150 µm, and <75 µm over a range of doses starting from 0.1 g/l up to 6 g/l. The conditions of the experiments are the following:

- pH of the Pb^{2+} synthetic solution: 5.5
- Contact Time: 30 min
- Volume of lead synthetic solution: 50 ml
- Initial Pb^{2+} concentration ≈ 40 mg/l
- Temperature: room temperature (22 ± 1 °C).

i Particle size: <75µm

This is the finest particle size of rice straw studied in this research, the results of the batch equilibrium tests are demonstrated in Table B-4 in Appendix B. Figure 25 shows that for particle size <75 µm, the percentage of removal has increased steeply by increasing the dose until it reached 2 g/l. Afterwards, further increase in the metal uptake was very low till the maximum dose; 6 g/l. The <75 µm particle size had the highest % removal, as shown in Figure 25. As the particle size decreases, the specific surface area would increase, which is the surface area of the adsorbent available for the adsorption of the solute; consequently, increasing the adsorption capacity of the adsorbent (Ahmaruzzaman 2011).

The maximum percentage removals were 92.55%, 96.78% and 97.21% for 2 g/l, 4 g/l and 6 g/l doses, respectively; however, the difference is insignificant; hence, a dose of 2 g/l is considered the optimum dose for the <75 µm particle size in order to reduce the quantity of rice straw used in the treatment; hence, reduce the amount of produced sludge and the cost of preparation, for instance the cost of the grinding process. The adsorption capacity for the optimum dose is 20.05 mg of Pb^{2+}/g of rice straw, as shown in Figure 26.

ii Particle Size: 75-150 µm

As illustrated in section 4.2.3, the optimum dose is 4 g/l, achieving 94.12% removal of Pb^{2+} and 10.19 mg/g adsorption capacity, as presented in Figure 24 and Figure 25, respectively.

iii Particle Size: 300-600 µm

The 300-600 µm particle size is the largest studied particle size .The batch equilibrium results are presented in Table B-5 in Appendix B. The curves presenting the batch equilibrium analysis of that size demonstrate that it achieved the least percentage removal and least adsorption capacity of Pb^{2+} compared to the other two sizes, as shown in Figure 25 and Figure 26, respectively. That poor performance is attributed to the small specific surface area available for the adsorption process. Upon extending the contact time to 1 h instead of 30 min, the performance of the 300-600 µm particle size rice straw has slightly improved, as shown in Figure 25 and Figure 26, which confirms the results explained in Section 4.2.2 regarding the impact of contact time on the percentage of metal uptake. Figure 25 shows that upon reducing the particle size from 300-600 µm to <75 µm at contact time 30 min, the % removal increased by about 29% at a dose of 2 g/l, and about 13% at the dose of 4 g/l. This explains the impact of the particle size on the percent of metal uptake, a similar effect of the particle size was described by Wong, et al. (2003a) in using rice husk for the uptake of Pb^{2+} and Cu^{2+}. In order to achieve a relatively high efficiency of adsorption using the 300-600 µm particle size, a dose of 4 g/l for a contact time 60 min, or a dose of 6 g/l for a contact time of 30 min is the optimum, which is relatively a large quantity of straw. Therefore, it is recommended to use either 2 g/l of <75 µm particle size, or 4 g/l of the 75-150 µm particle size for their higher efficiency of adsorption and shorter contact time required to reach equilibrium. However, very fine particle sizes would be more difficult to remove by settling after treatment. For all the curves in Figure 25, except the 300-600 µm at 30 min, the % removal became almost constant starting the 4 g/l dose.

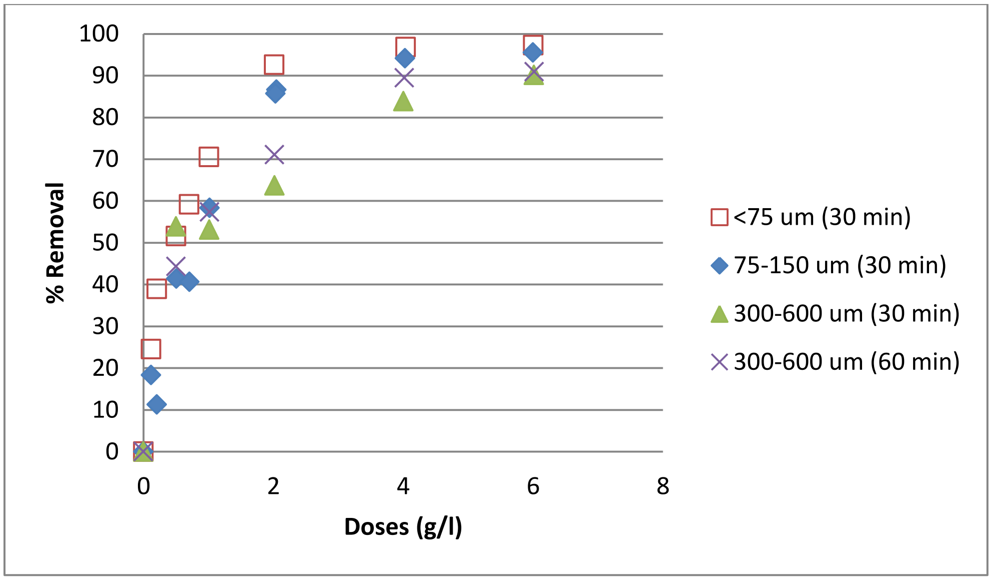


Figure 25: The Impact of Rice Straw particle size and Dose on the Percentage Removal of Lead (Contact Time 30 min, pH 5.5, 40mg/l Pb^{2+})

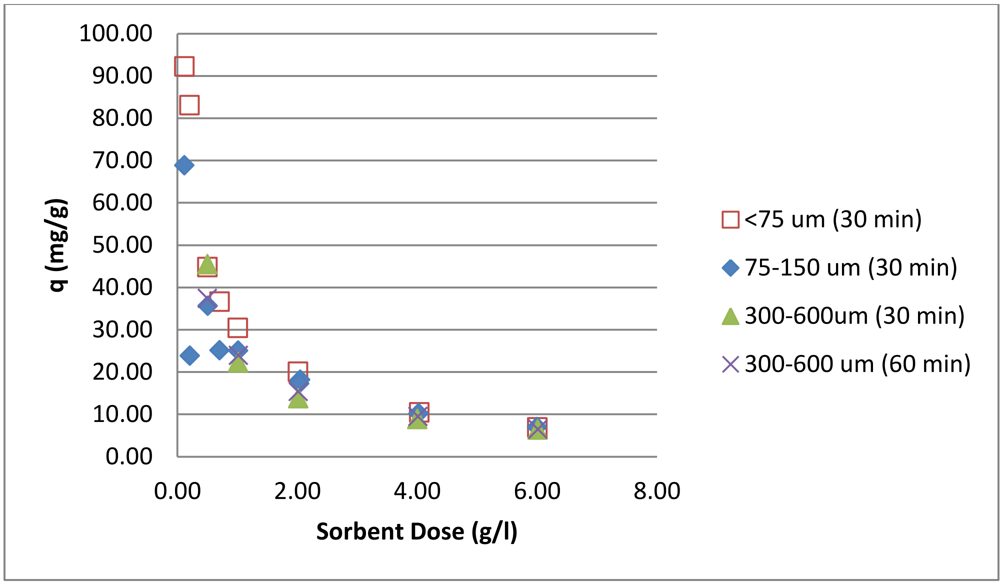


Figure 26: The Impact of Rice Straw particle size and Dose on the sorption of Pb^{2+} (Contact Time 30 min, pH 5.5, 40mg/l Pb^{2+})

4.2.5 Effect of Initial Pb^{2+} Concentration

The impact of the initial lead concentration on the sorption of lead by rice straw has been studied for two particle sizes; <75 µm and 75- 150 µm. The conditions of the experiment are the following:

- pH of the Pb^{2+} synthetic solution: 5.5
- Contact Time: 30 min
- Volume of lead synthetic solution: 50 ml
- Temperature: room temperature (22 ± 1 °C).

i Particle Size: <75 µm

The optimum dose for that fine size; 2 g/l, was used to investigate the impact of the initial lead concentration. The concentrations used were 5, 10, 15, 20, 40 and 60 mg/l, the results are reported in Table B-6 in Appendix B. It is obvious from Figure 27 that the % removal relatively decreased with the continuously increasing Pb^{2+} concentration. To illustrate, at a high concentration of Pb^{2+}, such as 60 mg/l the metal uptake was low compared to lower concentrations of Pb^{2+}. This is attributed to the competition between the increasing metal ions on the available active sites on the surface area of the adsorbent. Upon the increase of metal ions, while the dose of adsorbent is kept constant, the available active sites get rapidly saturated (Kardam, et al. 2014).

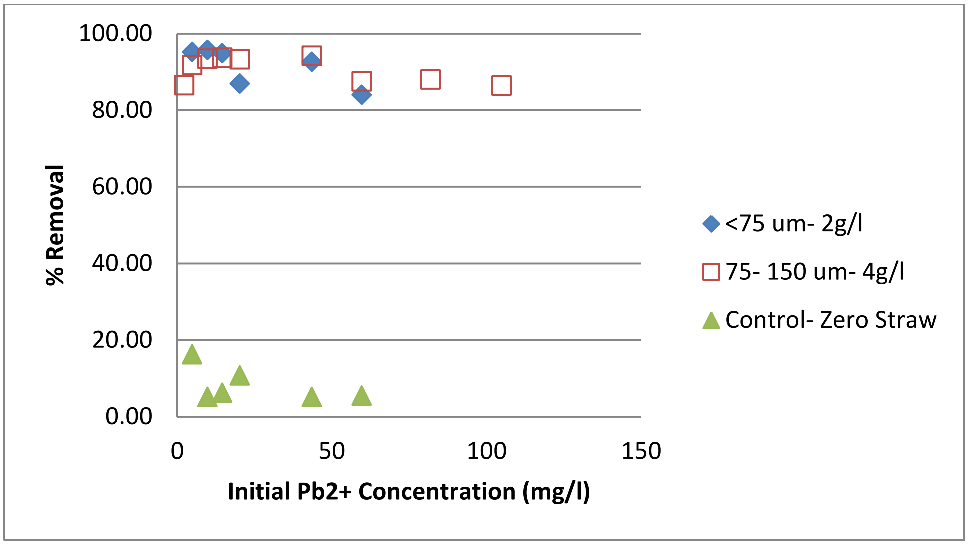


Figure 27: Impact of Initial Pb^{2+} Concentration at the optimum doses for specific particle sizes on % Removal of Pb^{2+} by Rice Straw (pH 5.5, contact time: 30 min)

ii Particle Size: 75-150 µm

As for the particle size in the range of 75-150 µm, the optimum dose used for the analysis was 4 g/l. The lead concentrations used for the batch study were 2, 5, 10, 15, 20, 40, 60, 80, and 105 mg/l. Figure 27 show that at very low initial concentration of lead the removal efficiency was relatively low. The initial concentration of heavy metals has an impact on the sorption capacity because it acts as a driving force to overcome the resistance of the metal or the mass transfer from the liquid phase to the solid phase (Ahmaruzzaman 2011). As the initial Pb^{2+} concentrations were increased, the uptake by rice straw has increased to reach 94.12% at initial Pb^{2+} concentration 40 mg/l, and went down to around 87% at 60 mg/l Pb^{2+}, and then almost reached a constant percent of removal in the tested range of initial Pb^{2+} concentrations. At elevated concentrations of heavy metals, the possibility of collisions between the metal ions is high; consequently, slowing down the sorption of the metal ions on the binding active sites on the surface of the bio-sorbent (Wong, et al. 2003a).

Both particle sizes, each at its optimum dose, have yielded very close % removals, as shown in Figure 27, yet it is recommended for industrial applications to use the 75-150 µm with an optimum dose of 4 g/l in order to save the cost and time needed for grinding rice straw into very fine particles. Besides, a very fine particle size of rice straw would be more difficult to remove by settling after treatment. Figure 28 shows that the adsorption capacity of rice straw increased by increasing the Pb^{2+} concentration using a constant rice straw dose. The adsorption capacity of particle size <75 µm is higher than the 75-150 µm size because its dose is half the dose of the latter.

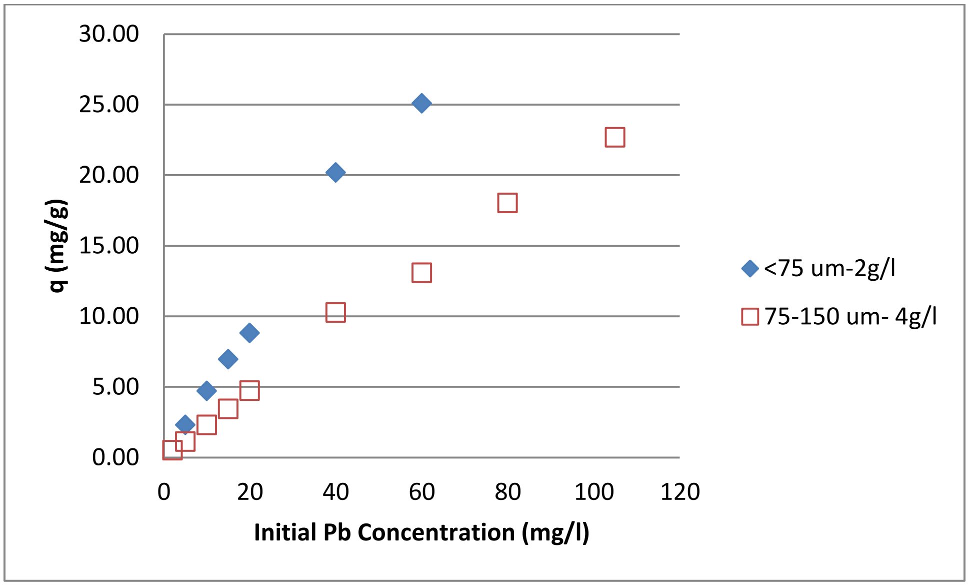


Figure 28: Impact of initial Pb^{2+} concentration at the optimum doses for specific particle sizes (<75 µm and 75-150 µm) on the adsorption capacity of Pb^{2+} by Rice Straw (pH 5.5, contact time: 30 min)

4.2.6 Effect of Pre- treatment of Rice Straw

Chemical treatment using Tartaric acid, one of the carboxylic acids, was applied in order to enhance the adsorption capacity by increasing the carboxylic groups on the surface area of the adsorbent (Wong, et al. 2003a). Two parameters of TA- RS have been studied, which are the optimum contact time and the optimum dose for 75 µm-150 µm particle size. The results are presented in the following sub-sections.

i Optimum Contact Time

Tartaric acid modified rice straw (TA-RS) exhibited more rapid kinetics compared to raw rice straw (Raw-RS). At a dose of 2 g/l of TA-RS, pH 5.5 and initial Pb^{2+} concentration around 40 mg/l, 92.6% of Pb^{2+} was removed in the first 15 min, and then the % removal stayed almost stable, as shown in Figure 29, due to the state of equilibrium reached between the adsorbent and the adsorbate, as explained before. TA-RS showed more enhanced performance compared to Raw-RS due to the carboxyl groups added to the rice straw resulting from the reaction with tartaric acid, as confirmed by FTIR spectrum of TA-RS, see Figure 47. At the optimum time 30 min, the % removal has increased by 7% and the adsorption capacity has increased by 2.12 mg/g of rice straw, compared to Raw-RS, as presented in Figure 29 and Figure 30. Several researchers have reported similar behaviors of agricultural wastes pre-treated using different kinds of carboxylic acids, such as Zhu, et al. (2008) who reported the same trend using soybean hulls pre-treated using another kind of carboxylic acids; citric acid, for adsorption of Cu^{2+}, Wong et al. (2003a), in using tartaric acid modified rice husk for adsorption of Pb^{2+} and Cu^{2+}, and Marshall, et al. (1999) in using citric acid modified soybean hulls for uptake of Cu^{2+} ions.

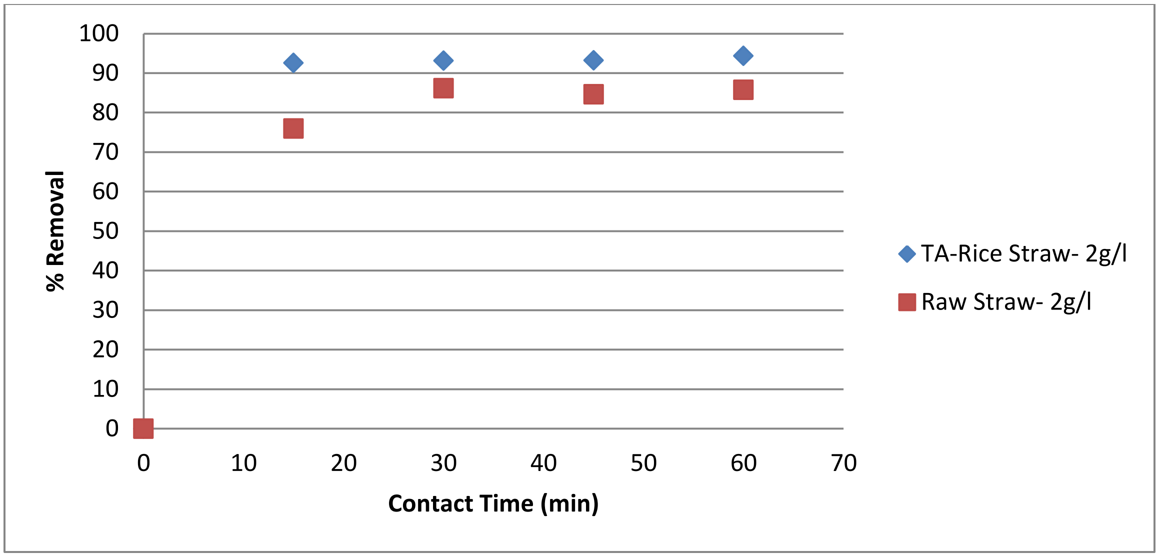


Figure 29: Impact of Tartaric Acid pre-treatment and contact Time on Pb^{2+} Uptake by Rice Straw (Dose: 2g/l, pH 5.5, 40mg/l Pb^{2+}, particle size: 75-150µm)

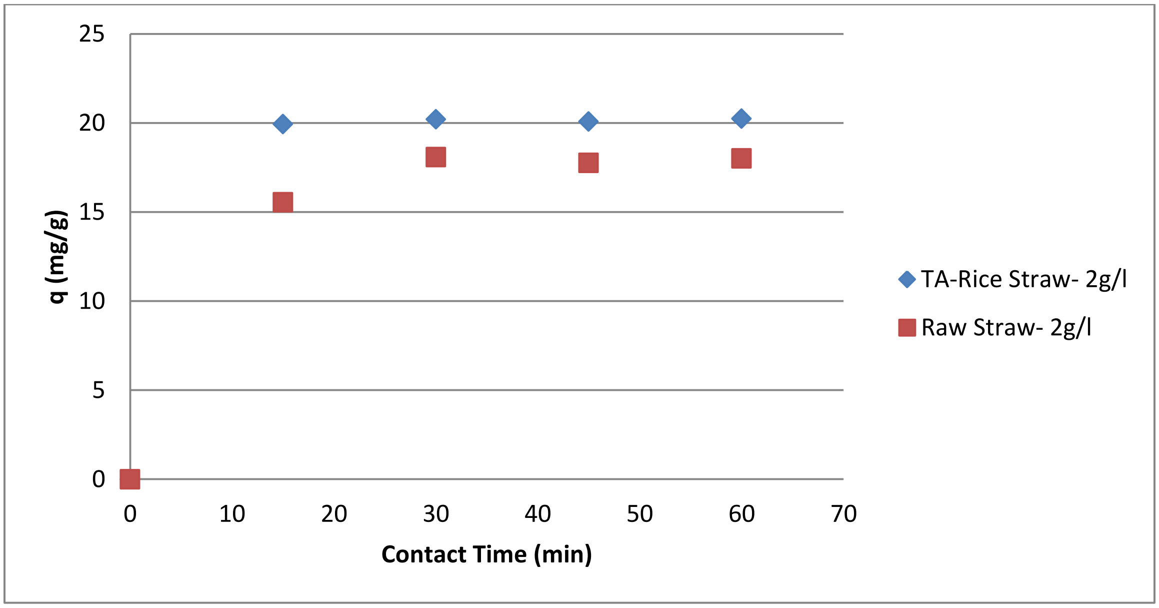


Figure 30: Impact of Tartaric Acid pre-treatment and contact Time on Adsorption Capacity of Pb^{2+} by Rice Straw (Dose: 2g/l, pH: 5.5, 40mg/l Pb^{2+}, particle size: 75-150µm)

ii Optimum Dose

The doses studied are 2, 4, and 6 g/l at an initial Pb^{2+} concentration around 40 mg/l. It was observed that the light yellow color resulting in the solution from large doses of rice straw has diminished after the chemical treatment, even if the dose has increased up to 6 g/l. Pre-treatment of agricultural wastes prevents the release of colors into the solution and enhances their adsorption capacity (Ngah and Hanafiah 2008). Based on the results presented in Figure 31, it is clear that the % removal is almost the same for the 4 g/l and 6 g/l doses; however, it is concluded that the optimum dose for TA- RS is 6 g/l in order to meet the limits of decree 44/2000 for the discharge of industrial wastewater in the public sewage network, which is 1mg/l. On the other hand, Figure 31 and Figure 32 show that the differences in % removal and adsorption capacity of TA-RS and Raw-RS are very small at high doses of 4 g/l and 6 g/l. Therefore, utilizing raw rice straw for Pb^{2+} uptake from aqueous solutions is more economic and eliminates the extra cost, time, and effort that will be exerted to prepare chemically modified rice straw.

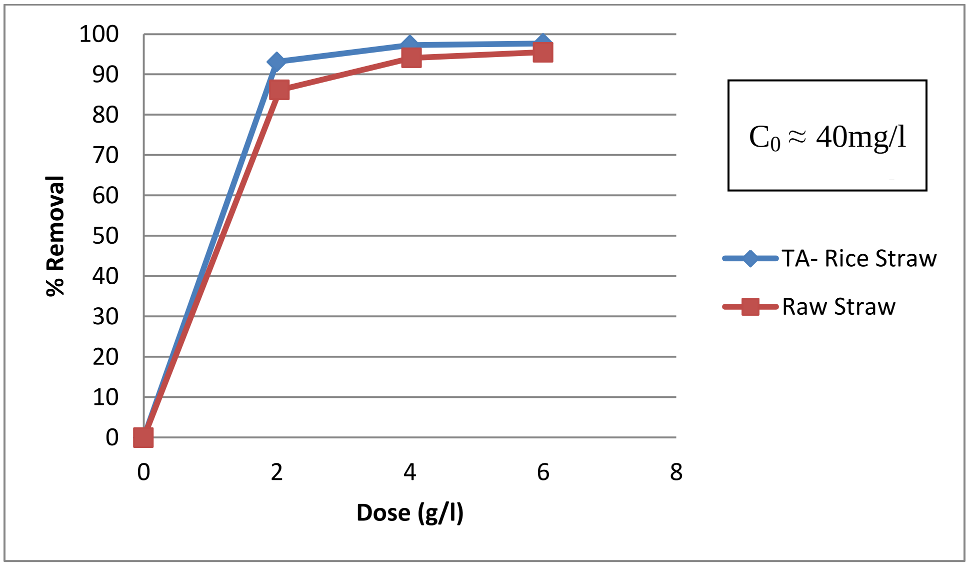


Figure 31: Impact of Tartaric Acid Pre-treatment and Rice Straw Dose on the percent Removal of Pb^{2+} by Rice Straw (C_o: 40 mg/l, Contact Time: 30 min, pH: 5.5, particle size: 75-150 μm)

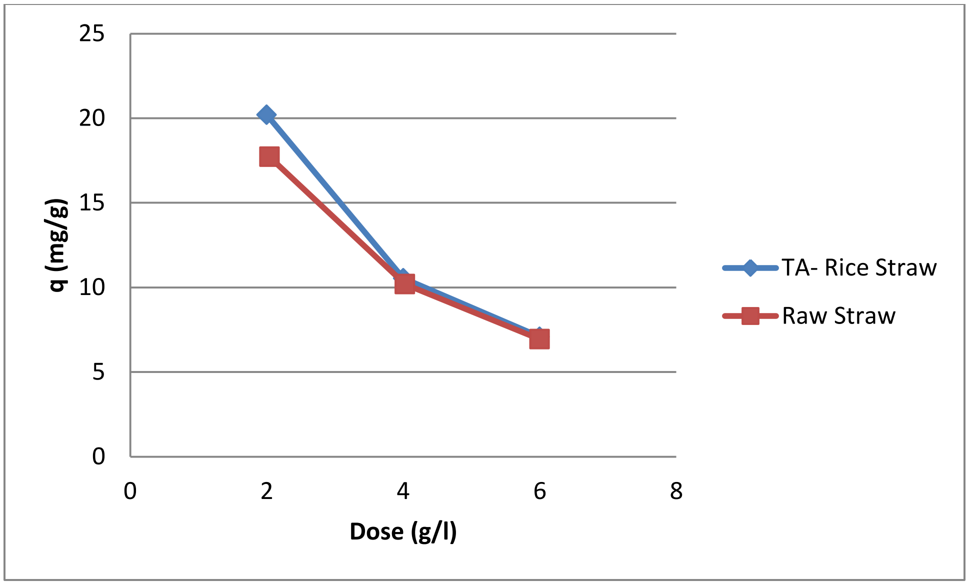


Figure 32: Impact of Tartaric Acid Pre-treatment and Rice Straw Dose on the Adsorption Capacity of Pb^{2+} by Rice Straw (Contact Time: 30min, C_o: 40 mg/l, pH: 5.5, particle size: 75-150 µm)

4.3 Sorption Isotherm Models

The batch equilibrium experimental data of raw rice straw were fitted and analyzed via the most two widely used models in the literature in the following sub-sections. The batch equilibrium data analyzed by Langmuir isotherm and Freundlich isotherm was acquired using the optimum rice straw dose; 4 g/l (0.2 g/50 ml) of a particle size 75-150 µm, over a wide range of initial Pb^{2+} concentrations; 10-105 mg/l, see Table C-1 and Table C-2 in Appendix C.

4.3.1 Langmuir Isotherm Model

Langmuir isotherm model assumes monolayer sorption via physical forces (Sarma, Kumar and Pakshirajan 2015). The Langmuir equation is presented by the equation below (Grassi, et al. 2012).

$$\frac{q_e}{q_m} = \frac{bC_e}{1+bC_e} \tag{4-4}$$

And the linear form of the equation is as follows (Ding, et al. 2012, Zhu, Fan and Zhang 2008):

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{4-5}$$

Or it can be presented in the following form (Wong, et al. 2003a):

$$\frac{1}{q_e} = \frac{1}{C_e q_m b} + \frac{1}{q_m} \tag{4-6}$$

Where,

q_e (mg/g): the amount of adsorbate per unit mass of adsorbent at equilibrium; adsorption capacity

C_e (mg/L): the equilibrium adsorbate concentration in a liquid-phase.

q_m (mg/g): the maximum adsorption capacity (monolayer capacity)

b (L/mg): the Langmuir constant related to the bonding energy of adsorption.

The parameters of Langmuir isotherm are presented in Table 13. Based on Langmuir isotherm, the maximum predicted adsorption capacity of Pb^{2+} using raw rice straw is 42.55 mg/g. As shown in Figure 33, the batch equilibrium data has perfectly fitted in the Langmuir model, with a correlation coefficient (R^2) 0.9889. The linearity of the plot suggests the creation of a homogenous monolayer of metal ions on the outer surface of the sorbent (Kardam, et al. 2014).

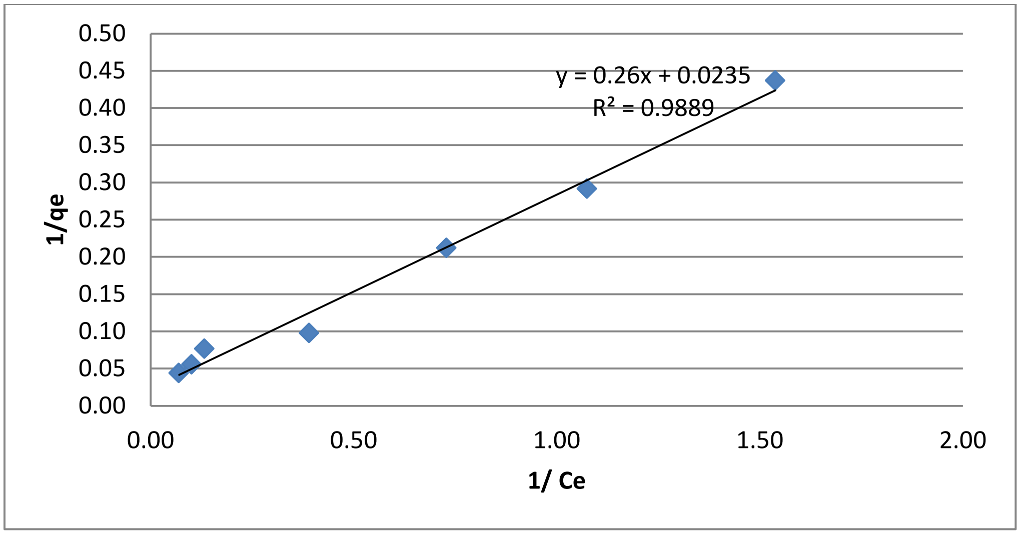


Figure 33: Langmuir isotherm for sorption of Pb^{2+} using rice straw (particle size: 75-150 µm)

Table 13: Parameters of Langmuir isotherm

q_{max} (mg/g)	b (l/mg)	R^2
42.55	0.09	0.9889

Table 14 presents the q_{max} achieved in several researches using agricultural wastes, mainly rice straw and rice husk, as well as commercial activated carbon as a benchmark for the effectiveness of adsorbents. The maximum adsorption capacity achieved by raw rice straw in the current research is considerably higher than the results reported in the literature for commercial activated carbon.

Table 14: Maximum sorption capacity of rice straw and rice husk for Pb^{2+} in various studies

Bio-sorbent	pH	q(mg/g)	Reference
Raw rice straw	5.5	42.55	The current study
Modified rice straw	6.5	9.42	(Kardam, et al. 2014)
Raw rice straw	6	23.35	(Soetaredjo, et al. 2013)
Raw rice husk	6	9.29	(Sarma, Kumar and Pakshirajan 2015)
Tartaric acid modified rice husk (TARH)	5.3	108	(Wong, et al. 2003a)
Commercial activated carbon (CAC)	4	15.625	(Jeyakumar and Chandrasekaran 2014)

4.3.2 Freundlich Isotherm Model

The basic assumption of Freundlich model is the heterogeneous surface energy of adsorption (Grassi, et al. 2012). The non- linear form of the model is the following (Grassi, et al. 2012):

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (4\text{-}7)$$

The linear form of the model is the following (EL Zayat 2014, Kumar and Bandyopadhyay 2006):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (4\text{-}8)$$

Where,

K_F (mg/g) (L/mg)$^{1/n}$: the Freundlich capacity factor, or the adsorption equilibrium constant. K_F is an indicator of the adsorption capacity when metal equilibrium concentration equals 1 (Zhu, Fan and Zhang 2008).

1/n: the Freundlich intensity parameter. According to Soetaredjo, et al. (2013), it is the extent of heterogeneity of the sorption system.

The constants in Freundlich isotherm can be calculated form the plot of log q_e versus log $C_{e.}$ (Metcalf & Eddy 2003). Figure 34 shows Freundlich isotherm plot. The isotherm parameters of the model are presented in Table 15.

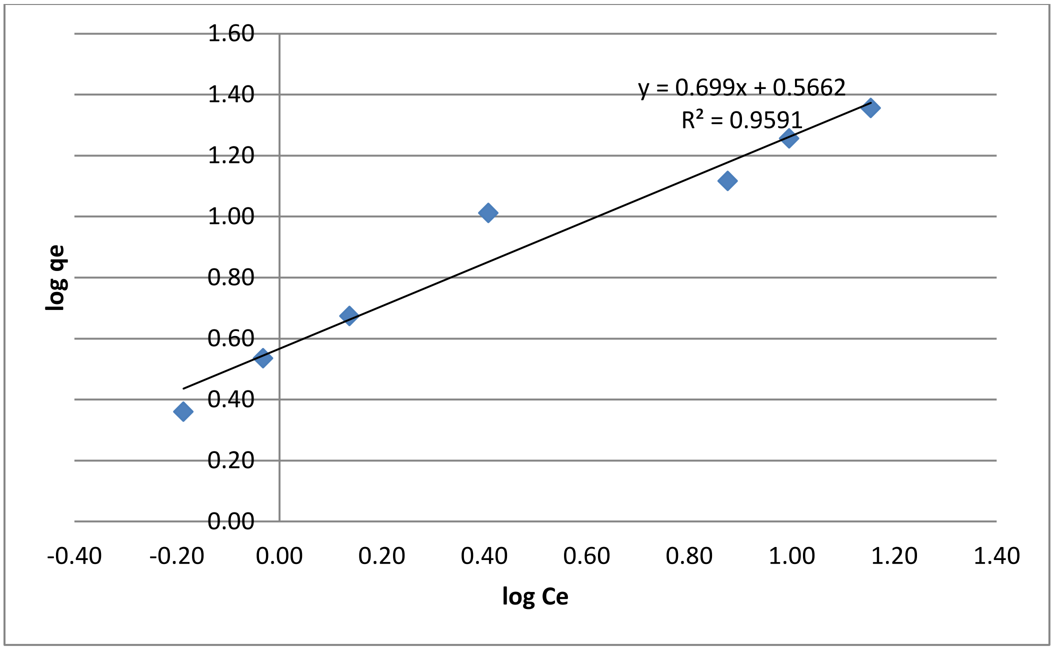


Figure 34: Freundlich isotherm for the sorption of Pb^{2+} using raw rice straw (particle size: 75-150 µm)

Table 15: Sorption Parameters of Freundlich isotherm

K_F	1/n	R^2
3.683	0.699	0.9591

4.4 Phase III- Fixed Bed Column Experiments

4.4.1 Overview

The third phase of this research, after the preliminary comparative study of several biosorbents and adsorbents, and the batch equilibrium tests of rice straw, is the fixed bed column tests. The results of the column tests are presented as breakthrough curves, which are the plots of either the effluent Pb^{2+} concentration versus service time (t) or bed volumes, or the plot of the ratio of the effluent Pb^{2+} concentration to the influent Pb^{2+} concentration (C/C_0) versus service time (t) or bed volumes. Bed volumes (BV) are the number of volumes of wastewater that pass through the column. One BV is equal to the product of the cross sectional area of the column and the bed depth. Breakthrough time (t_b) is the time when the effluent concentration reaches a critical point which is defined based on the specific application (Farooq, et al. 2013, Zakaria 2009). Breakthrough time was set in several researches as the time when the effluent concentration (C) reaches a certain percentage of the influent concentration of Pb^{2+} (C_0), usually in the range of 5%-10% (Chatterjee and Schiewer 2014, Chen, et al. 2012, Sarma, Kumar and Pakshirajan 2015, Farooq, et al. 2013). However, in this research it was found more practical to set the breakthrough time (t_b) when the effluent concentration (C) reaches the limits of the Egyptian law No. 93 for year 1962 for discharging liquid wastes in the public sewage network, amended by Ministerial decree No.44/2000, which is 1mg/l. Therefore, the effluent concentration at breakthrough (C_b) in the current research is 1 mg/l. That is because in practical applications when the effluent concentration reaches the limits of the law, it is essential to stop the system to replace or regenerate the packed biosorbent, or to run another column. Other important parameters are the exhaustion time (t_e) and exhaustion concentration (C_e) where the packed column reaches full saturation. At exhaustion, in the current research, the effluent concentration of Pb^{2+} reached a range of 89%- 95% of the influent concentration of Pb^{2+}, in other words C/C_0 was in the range of 0.89-0.95, based on the shape of the breakthrough curves. The time at which the breakthrough occurs and the shape of the breakthrough curve, normally S shape, are very vital for determining the operation conditions and dynamic of a sorption column (Farooq, et al. 2013, Chen, et al. 2012) .The shape of a breakthrough curve is a function of the sorbent geometry, and operating conditions (Farooq, et al. 2013). The area above the S curve is the amount of adsorbed Pb^{2+}, while the area under the curve is the amount of un-adsorbed Pb^{2+}.

Several important parameters have been calculated in order to analyze the performance of the column tests, such as the Bed Volumes (BV), which represents the number of volumes equivalent to the volume of the bed of rice straw packed in the column that passes through the column till breakthrough concentration (C_b) and exhaustion concentration (C_e) are reached. The bed volume is calculated as the treated volume of the solution per the rice straw bed volume as shown in the equation below (EL Zayat 2014).

$$\boldsymbol{Bed\ Volume = \frac{Volume\ Treated}{Volume\ of\ Packed\ Rice\ Straw} = \frac{Q\left(\frac{ml}{min}\right)*t\ (min)}{V}} \qquad (4\text{-}9)$$

Where;

Q (ml/min): flow rate

t (min): Service time

V (ml): Volume of packed rice straw = cross sectional area of the column * bed depth

The masses of Pb^{2+} adsorbed on the packed rice straw at both breakthrough and exhaustion times are calculated as a function of the influent and effluent masses of Pb^{2+} at t_b and t_e (Chatterjee and Schiewer 2014).

$$\boldsymbol{m_{ad} = m_{in,t} - m_{out,t}} \qquad (4\text{-}10)$$

$$\boldsymbol{m_{in,t} = C_0 * Q * t} \qquad (4\text{-}11)$$

$$\boldsymbol{m_{out,t} = C_0 * Q * \int_0^t \left(\frac{C}{C_0}\right) dt} \qquad (\ 4\text{-}12)$$

Where;

m_{ad}: Total mass of metal ions adsorbed on the rice straw packed in the column at time t (mg)

$m_{in,t}$: Influent mass of metal ions to the column at time t (mg)

$m_{out,t}$: Effluent mass of un-adsorbed metal ions at time t (mg)

C_0: Influent Pb^{2+} concentration (mg/l)

C: effluent Pb^{2+} concentration (mg/l)

Q: Flow rate (l/h)

t: Service time (h)

It was also of crucial importance to calculate the uptake capacity (mg/g), which is the mass of Pb^{2+} adsorbed per unit mass of sorbent, at breakthrough (q_b) and exhaustion (q_e), as shown in the equations blow (Chatterjee and Schiewer 2014).

$$q_e = \frac{m_{ad,t_e}}{M} = \frac{C_0 * Q * \int_0^{te}\left(1-\frac{C}{C_0}\right)dt}{M} \tag{4-13}$$

$$q_b = \frac{m_{ad,t_b}}{M} = \frac{C_0 * Q * \int_0^{tb}\left(1-\frac{C}{C_0}\right)dt}{M} \tag{4-14}$$

Where;

q_e: Adsorption capacity at exhaustion, nearly full saturation, of the rice straw column (mg/g)

$m_{ad,te}$: Total mass of metal ions adsorbed on the rice straw packed in the column at time of exhaustion (mg)

M: mass of rice straw in the column (g)

q_b: Adsorption capacity of rice straw at breakthrough (mg/g)

$m_{ad,tb}$: Total mass of metal ions adsorbed on the rice straw packed in the column at time of breakthrough (mg).

Mass transfer zone (MTZ) is the zone where the sorbent is actively adsorbing the metal ions and did not reach saturation, the MTZ moves through the column in the direction of the flow until it reaches the end of the column, then breakthrough takes place (Chatterjee and Schiewer 2014, Metcalf & Eddy 2003). Figure 35 shows the movement of the mass transfer zone inside the sorption column with respect to the throughput volume.

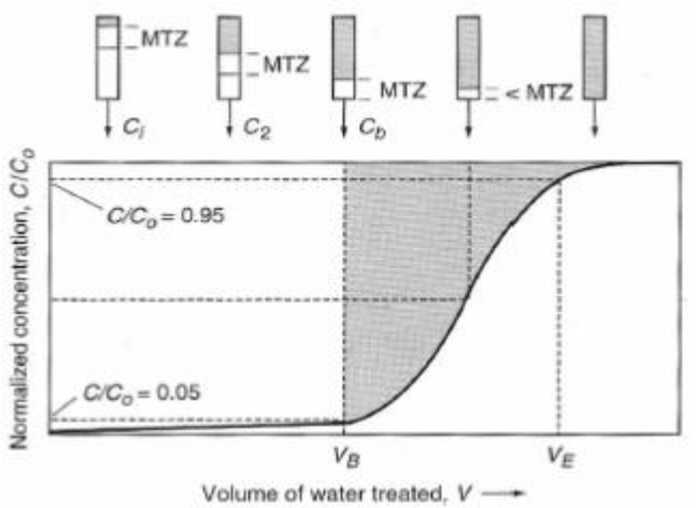


Figure 35: Typical breakthrough curve showing the transition of the mass transfer zone (MTZ) along the length of the column (Metcalf & Eddy 2003)

According to Chatterjee and Schiewer (2014), MTZ is calculated as per the equation below:

$$\boldsymbol{MTZ = \left(1 - \frac{t_b}{t_e}\right) * L} \qquad (4\text{-}15)$$

Where;

MTZ: length of the mass transfer zone (cm)

t_b: time when breakthrough occurs (h); $C/C_o = 5\%$

t_e: time when exhaustion occurs (h) ; $C/C_o \approx 95\%$

L: length of the adsorption column (cm)

Empty Bed Contact Time is the time spent by one drop of water inside the column if the column was empty of the sorbent material. EBCT is calculated according to the equation below (Chen, et al. 2012):

$$\boldsymbol{EBCT\ (min) = \frac{Bed\ Volume\ (ml)}{Flow\ Rate\ (ml/min)}} \tag{4-16}$$

The parameters studied in the continuous flow tests are:

1. Initial Pb^{2+} Concentration
2. Bed depth
3. Flow rate of the Pb^{2+} solution feeding the packed column

4.4.2 Effect of Initial Pb^{2+} Concentration

A stainless steel column with length of 8 cm and internal diameter of 0.75 cm was used. Dry rice straw was packed into the column; the bed depth was 3cm, weighing around 0.56 g, with some variations among the three runs that could result from the degree of manual tapping of the packed straw using a glass rod. The performance of the column was analyzed at Pb^{2+} concentrations of 15 mg/l, 40 mg/l, and 80 mg/l, at a flow rate 6 ml/min and pH 5.5. Using Equations (4-9) to (4-16), the following parameters were calculated as shown in Table 16.

Table 16: Parameters of fixed- bed column tests at various Pb^{2+} concentrations (bed depth 3 cm; Q 6 ml/min; pH 5.5)

Pb^{2+} Conc. (mg/l)	**Time (h)**		**Bed Volume**		**m_{ad} (mg)**		**q(mg/g)**		**MTZ (cm)**	**EBCT (min)**
	t_b	t_e	BV_b	BV_e	$m_{ad,\ tb}$	$m_{ad,te}$	q_b	q_e		
15	2.25	6.70	616.3	1809.9	11.90	20.00	19.9	33.5	1.92	0.22
40	0.76	4.00	207.35	1087.05	10.3	18.2	21.2	37.5	2.26	
80	0.27	1.15	73.23	312.53	7.71	19.07	12.8	31.7	2.30	

Figure 36 illustrates that both breakthrough and exhaustion occurred faster and the slope of the curves got steeper as the initial concentration of Pb^{2+} (C_0) was increased. In other words, the service time or the life span of the sorption column gets shorter with the increasing influent Pb^{2+} concentration, similar trends were reported by Chen, et al. (2012) in the removal of hexavalent chromium using modified corn stalk and Wong, et al. (2003b) in the removal of Pb^{2+} and Cu^{2+} using modified rice husk. To illustrate, at 15mg/l influent concentration the time needed for rice straw to reach breakthrough (C=1 mg/l, $C/C_0=0.07$) and full saturation ($C/C_0 \approx 0.95$) was the maximum; 2.25 h and 6.7 h, respectively, compared to the higher Pb^{2+} concentrations, as shown in Table 16 and Figure 36. Upon increasing the Pb^{2+} concentration to 80mg/l, the service time to breakthrough (t_b) dropped to 0.27h (16.2 min), and the service time to exhaustion (t_e) dropped to 1.15 h. Similarly, at 15 mg/l Pb^{2+} the bed volumes treated until breakthrough and saturation were the maximum compared to the bed volumes treated at 40 mg/l and 80 mg/l Pb^{2+} initial concentration, as presented in Figure 37 and Table 16. To illustrate, the number of treated bed volumes has drastically decreased with increasing influent Pb^{2+} concentration; from 616 and 1,810 at breakthrough and exhaustion, respectively at C_0=15 mg/l to 207 and 1087 at breakthrough and exhaustion, respectively at C_0=40 mg/l and down to 73 and 312 at breakthrough and exhaustion, respectively at C_0= 80 mg/l. It was observed that at Pb^{2+} concentration 40 mg/l, the service time of the column and the treated BV until the breakthrough point, where the effluent concentration reached the limits of the Egyptian regulations, were around 34 % of their equivalent values at Pb^{2+} concentration 15mg/l. That trend can be attributed to the fact that the increase in the influent Pb^{2+} concentration creates a stronger driving force that leads to faster mass transfer process; therefore, leads to faster saturation of the rice straw, in other words shorter t_b and t_e (Chen, et al. 2012).

In the same way, the mass of Pb^{2+} ions adsorbed (m_{ad}) by rice straw has slightly decreased with increasing influent Pb^{2+} concentration (C_0), this could be due to the shorter service time of the column as the Pb^{2+} concentration increases. Usually, the percentage of uptake decreases with increasing the heavy metals concentration (Wong, et al. 2003b). As the C_0 of Pb^{2+} increased from 40 mg/l to 80 mg/l, there was a notable decrease in the adsorption capacity from 21.2 mg/g to 12.8 mg/g at breakthrough and from 37.5 mg/g to 31.7 mg/g at exhaustion, this could be due to the very short service times t_b and t_e at C_0 80 mg/l; 0.27 h and 1.15 h, respectively. As for the length of the MTZ, it has slightly increased with the increase in the initial Pb^{2+} concentration.

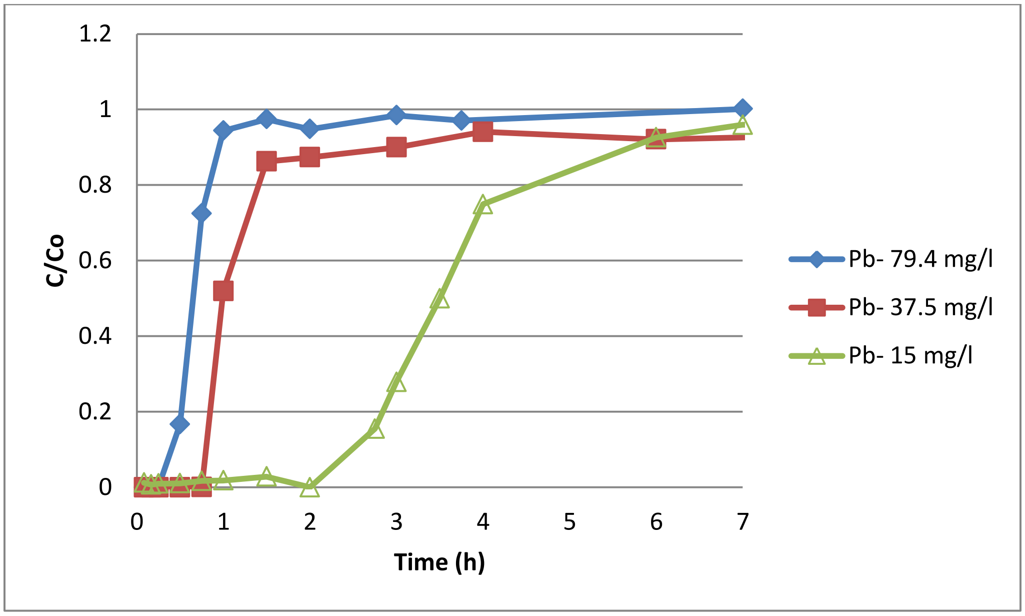


Figure 36: Breakthrough curves of Pb^{2+} biosorption by rice straw at various initial Pb^{2+} concentrations (bed depth 3cm; flow rate 6ml/min; pH 5.5)

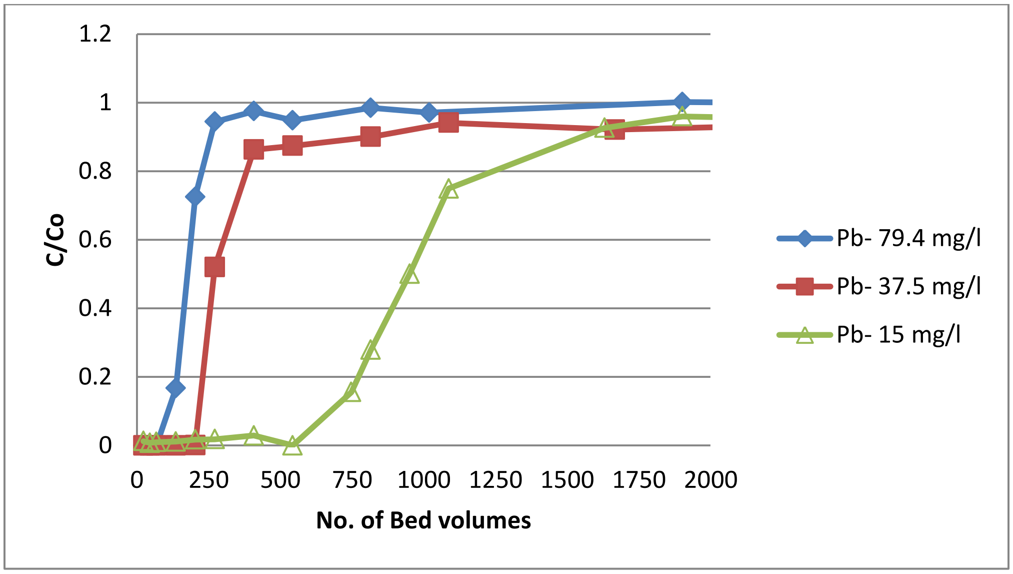


Figure 37: Impact of initial Pb^{2+} concentration on the number of treated bed volumes (bed depth 3 cm; flow rate 6 ml/min; pH 5.5)

4.4.3 Effect of Bed Depth

The impact of the bed depth on the breakthrough curves was analyzed. Column tests were run at a flow rate of 6 ml/min and 3 cm, 6 cm and 12.5 cm bed depths, corresponding to 0.49 g, 1.34 g and 2.41 g, respectively dry weight of rice straw packed in the column. A stainless steel column with diameter of 0.75 cm and length of 8 cm was used for the 3 cm and 6 cm bed depth; whereas, a stainless steel column with diameter of 0.7 cm and length of 16.5 cm was used for the 12.5 cm bed depth. The Pb^{2+} concentration in the three cases was almost 40 mg/l and the pH of the synthetic solution was adjusted to 5.5 prior to the experiment. The significant parameters were calculated and presented in Table 17, and the breakthrough curves are shown in Figure 38 and Figure 39.

Table 17: Parameters of fixed- bed column tests at various bed depths (C_o= 40mg/l; flow rate 6ml/min; pH 5.5)

Bed depth (cm)	**Time (hr)**		**Bed Volume**		**m_{ad} (mg)**		**q(mg/g)**		**MTZ (cm)**	**EBCT (min)**
	t_b	t_e	BV_b	BV_e	$m_{ad,\ tb}$	$m_{ad,te}$	q_b	q_e		
3	0.8	4	207.35	1087.05	10.3	18.2	21.2	37.5	2.26	0.22
6	2.3	6	307.5	814.87	32.77	50.43	24.39	37.53	3.49	0.44
12.5	4.5	7	341.34	523.85	65.39	85.65	27.10	35.5	4.2	0.80

The increase in the bed depth has led to an increase in the service time to breakthrough and exhaustion of the sorption columns, as shown in Figure 38. The same trend was reported by several researchers (Sarma, Kumar and Pakshirajan 2015, Singh, Ali and Prakash 2014, Farooq, et al. 2013). Upon the increase in the bed depth from 3 cm to 12.5 cm, the service time at breakthrough and at exhaustion has increased from 0.8 h and 4 h, respectively up to 4.5 h and 7 h, respectively. This could be explained by the fact that as the amount of rice straw increases in the column and the bed depth is longer, the surface area, eventually the active sites on the surface of rice straw that are available for the sorption process increase as well (Sarma, Kumar and Pakshirajan 2015); therefore, it takes longer time to get them all saturated by metal ions. Similarly, the number of treated bed volumes at breakthrough has increased from 207 BVs at a bed depth of 3 cm, up to around 341 BVs at a bed depth of 12.5 cm. The same trend is observed for the adsorbed mass of Pb^{2+} on the surface of rice straw at breakthrough and exhaustion, see Table 17. Figure 40 demonstrates the impact of the bed depth increase on the significant increase in the treated volume of wastewater of an effluent lead concentration that meets the limits of the Egyptian regulations. This is attributed to the concept that for short bed depths, the residence time of the solution in the column is short; hence, not allowing the metal ions to completely diffuse into all the available sorbent packed in the column; however, when the column is longer the residence time increases giving a chance for the metal ions to get adsorbed on all the available binding sites on the surface of the sorbent (Singh, Ali and Prakash 2014). Such a justification demonstrates the impact of the EBCT, which has increased from 0.22 min to 0.80 min when the bed depth was increased from 3 cm to 12.5 cm, respectively.

Moreover, the length of the mass transfer zone (MTZ) has increased with the increase in the bed depth, which is logic because the MTZ is a function of the bed depth. Normally, a sharp slope of a breakthrough curve is an indication of smaller MTZ (Chen, et al. 2012). The length of the MTZ for the column with a bed depth of 12.5 cm was calculated based on 89% exhaustion because the slope of the breakthrough curve has started to become flat at C/C_0= 0.89 and it did not reach 95%. Likewise, all the exhaustion parameters for that specific column were calculated at 89% exhaustion.

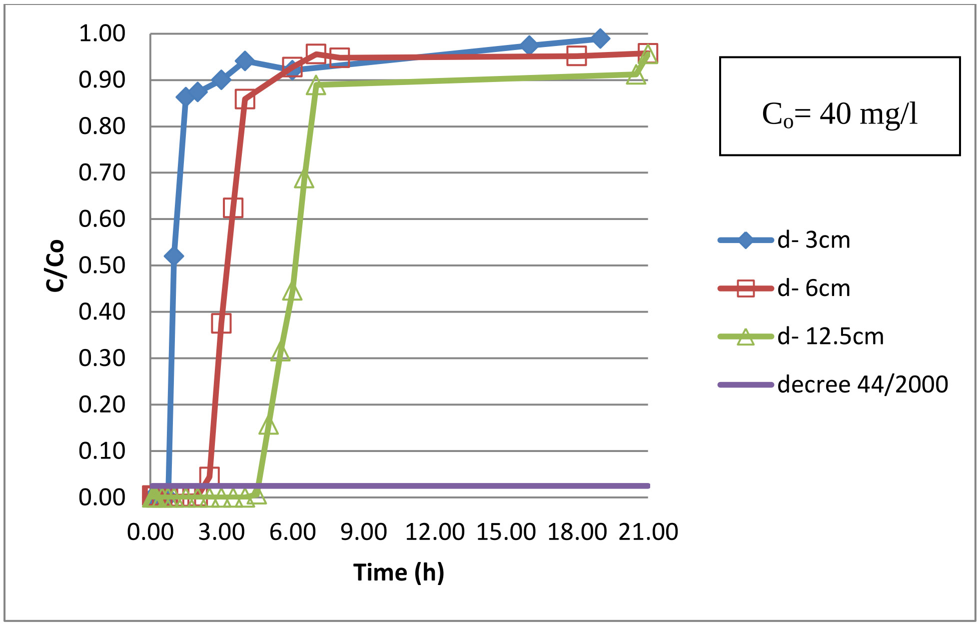


Figure 38: Breakthrough curves of Pb^{2+} bio-sorption by rice straw at various bed depths (C_0= 40mg/l; flow rate 6ml/min; pH 5.5)

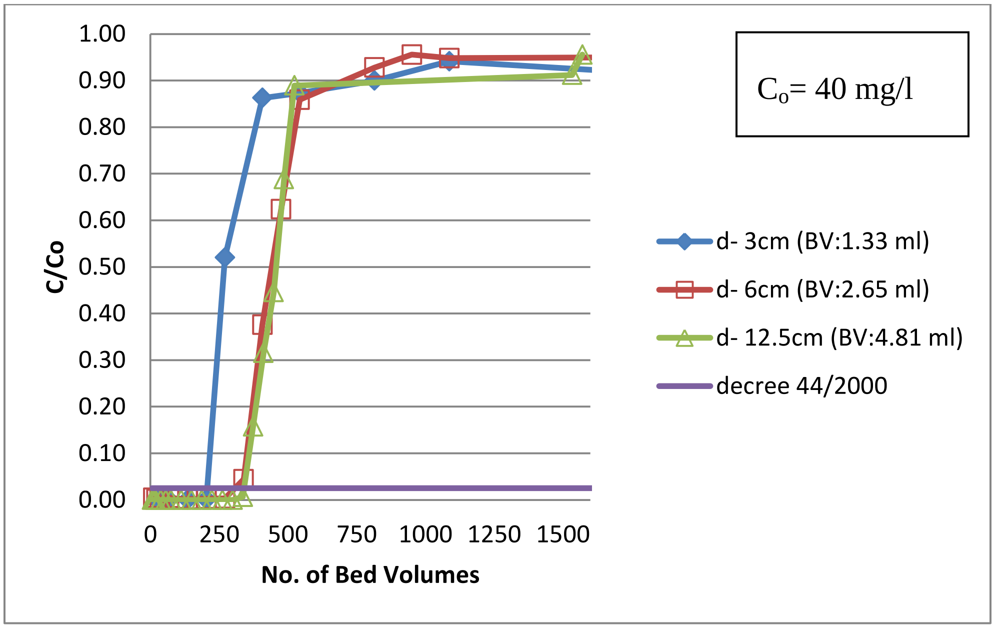


Figure 39: Impact of the bed depth on the number of treated bed volumes (C_0= 40mg/l; flow rate 6ml/min; pH 5.5)

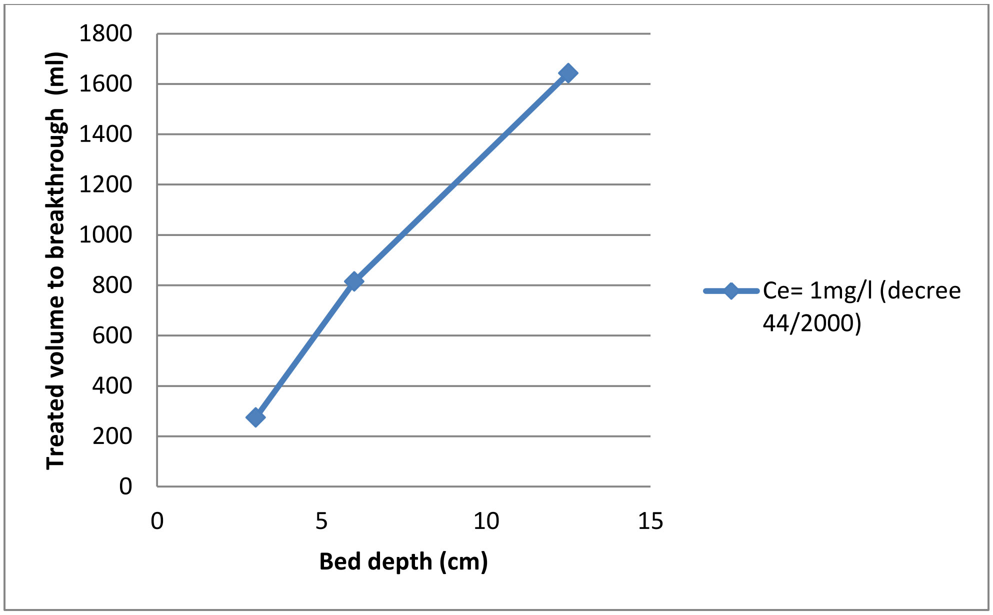


Figure 40: Impact of bed depth on the treated volume of wastewater up to the Egyptian regulatory limits; 1mg/l

4.4.4 Effect of Flow Rate (Q)

The impact of the solution flow rate on the shape and the parameters of the breakthrough curves were analyzed in this sub-section. The tests were run at 6 ml/min and 3 ml/min flow rates and the breakthrough curves were compared. The bed depth was 6 cm, corresponding to an average of 1.31 g dry rice straw, pH 5.5, and Pb^{2+} initial concentration was around 40 mg/l. The main parameters were calculated and presented in Table 18.

Table 18: Parameters of fixed- bed column tests at various feed solution flow rates (C_0= 40 mg/l; bed depth=6cm; pH 5.5)

Q (ml/min)	Time (h)		Bed Volume		m_{ad} (mg)		q (mg/g)		MTZ (cm)	EBCT (min)
	t_b	t_e	BV_b	BV_e	$m_{ad,\,tb}$	$m_{ad,te}$	q_b	q_e		
6	2.3	7	307.70	951.17	32.77	51.27	24.39	38.16	3.85	0.44
3	5.5	21.8	751.42	2962.21	40.55	113.5	31.69	88.67	4.46	0.88

As shown in Figure 41, the service time of the sorption column at breakthrough (t_b) has increased from 2.3 h at a flow rate of 6 ml/min to 5.5 h at a flow rate of 3 ml/min. The breakthrough is the point when C/C_0 reaches 2.5%, at C_0 around 40 mg/l. Similarly, the exhaustion time was increased from 7 h at Q= 6 ml/min to 21.8 h at Q= 3 ml/min. The same trend was observed for the number of treated bed volumes, which has increased from 307.7 at Q= 6 ml/min to 751.4 at Q= 3 ml/min, and from 951.17 at Q= 6 ml/min to 2,962.2 at Q= 3 ml/min at breakthrough and exhaustion, respectively, as presented in Figure 42 and Table 18. The slope of the breakthrough curve at 6 ml/min is much steeper than at 3 ml/min flow rate. Also the mass of adsorbed Pb^{2+} ions (m_{ad}) and the adsorption capacity (q) exhibited the same increasing trend with the decreasing flow rate of the feed solution. At 2.5% breakthrough, the adsorption capacity at 3 ml/min has increased to 31.69 mg/g compared to 24.39 mg/g at 6 ml/min flow rate. The same trend was reported by several researchers (Sarma, Kumar and Pakshirajan 2015, Singh, Ali and Prakash 2014, Chen, et al. 2012). As for the EBCT, it was definitely affected by the flow, as it increases with the decrease in the flow rate; therefore, it was doubled from 0.44 min to 0.88 min when the flow rate was reduced to the half.

The prolonged service time and the improved performance which the column test has demonstrated at reducing the flow by 50% could be attributed to the longer contact time (EBCT) of each drop of the influent solution on the surface of the sorbent. Consequently, allowing a larger portion of the heavy metal ions to get chelated by the binding sites on the surface of the straw; inevitably, leading to enhanced Pb^{2+} removal. At higher flow rates, the residence time is shorter; hence, not allowing full saturation of the active sites by the metal ions and leading to a decrease in the amount of metal ions adsorbed (Chen, et al. 2012). The contact time is increased at lower flow rates enabling more interaction of metal ions with the sorbent, allowing inter-particle diffusion to take place; in other words, allowing diffusion of a larger number of ions into the pores of the sorbent resulting in slower breakthrough (Sarma, Kumar and Pakshirajan 2015, Singh, Ali and Prakash 2014). The MTZ has increased from 3.85 cm to 4.46 cm. The MTZ changes with the variation in the flow rate because dispersion, diffusion and channeling of the metal ions in a granular medium are mainly affected by the flow rate of the solution (Metcalf & Eddy 2003).

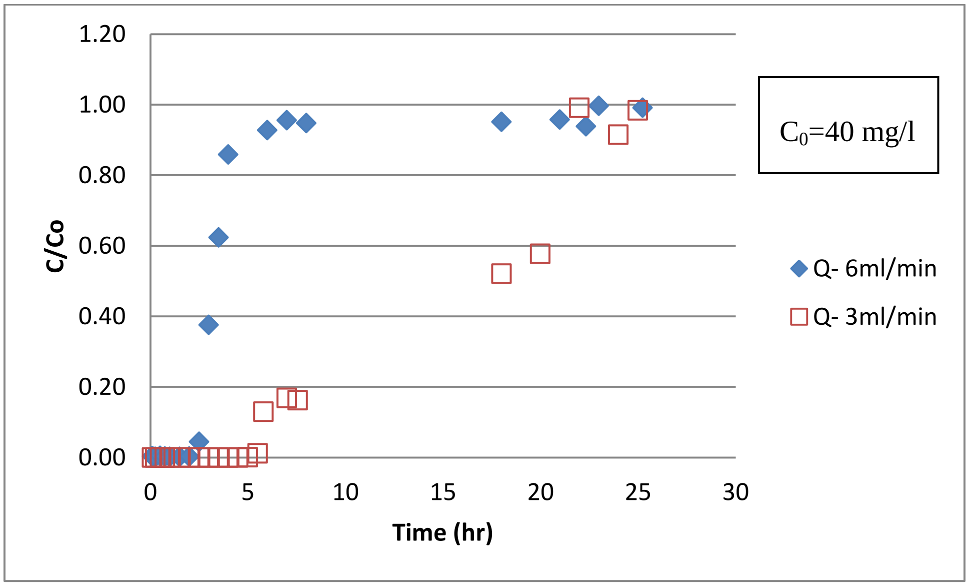


Figure 41: Breakthrough curves of the biosorption of Pb^{2+} by rice straw at various flow rates (C_o= 40 mg/l; bed depth=6 cm; pH 5.5)

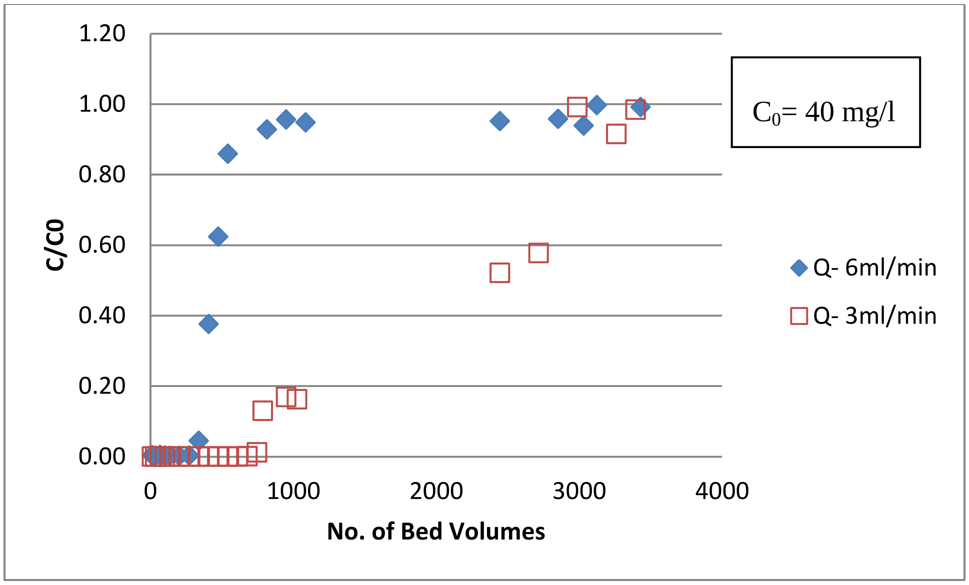


Figure 42: Impact of flow rate on the number of treated bed volumes (C_o= 40 mg/l; bed depth=6 cm; pH 5.5)

4.5 Rice Straw Sample Characterization

Rice straw characterization was carried out in order to define the BET surface area, pore volume, average pore size, predominant functional groups, shape of the cell wall, and the chemical composition. The density and the bulk density of rice straw were measured in the Engineering laboratory of the American University in Cairo; the average values are 1.251 g/cm3 and 0.2245 g/cm3, respectively.

4.5.1 BET Surface Area and Pore Volume

The specific surface area of rice straw of particle size 75-150 µm measured using the BET method at 77 k was 1.9475 m^2/g, the total pore volume was 0.006 cm^3/g at STP, and the average pore size was 12.14660 nm. The BET surface area is very low compared to the reported BET specific surface area of 40.7 m^2/g for un-modified rice straw (Soetaredjo, et al. 2013); however, it is relatively high compared to the BET specific surface area of un-modified soybean straw of 0.66 m^2/g (Zhu, Fan and Zhang 2008).

4.5.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was carried out for raw rice straw samples pre and post biosorption of Pb^{2+} in order to determine the main functional groups responsible for the biosorption. The FTIR spectra, shown in Figure 43 through Figure 47, were analyzed and the wave numbers of the peaks and their corresponding functional groups are presented in Table 19 and Table 20. According to the illustration of Singh, Ali and Prakash (2014) of the functional groups corresponding to a range of wave numbers, the largest peak of wave number 3435 cm^{-1} shown in Figure 43, corresponds to either free or H-bonded O-H groups that could be present in carboxylic acids on the surface of rice straw. The peak at 1626.5 cm^{-1} wave number corresponds to the C=O that could exist in the carboxylic acids. As for peaks of wave numbers in the range of 1383.6 to 1066.8 cm^{-1}, are an indication of C-O bond, and bands of wave number 2900 cm^{-1} are an indication of C-H bond. C-O bond may be due to carboxylic acids, aloxy groups or fiber carbonaceous that are present in the structure of rice straw that is composed of lignin and cellulose (Soetaredjo, et al. 2013). Those groups probably act as proton donors that once get deprotonated, the hydroxyl group or the carboxyl group adsorbs the heavy metal ions (Singh, Ali and Prakash 2014).

Table 19: Peaks wavenumbers and corresponding functional groups (particle size: 75-150 µm)

Wave number (cm^{-1})	**Functional Group**
3435.0	O−H
2900	C−H
1626.5	C=O
1383.6- 1066.8	C−O

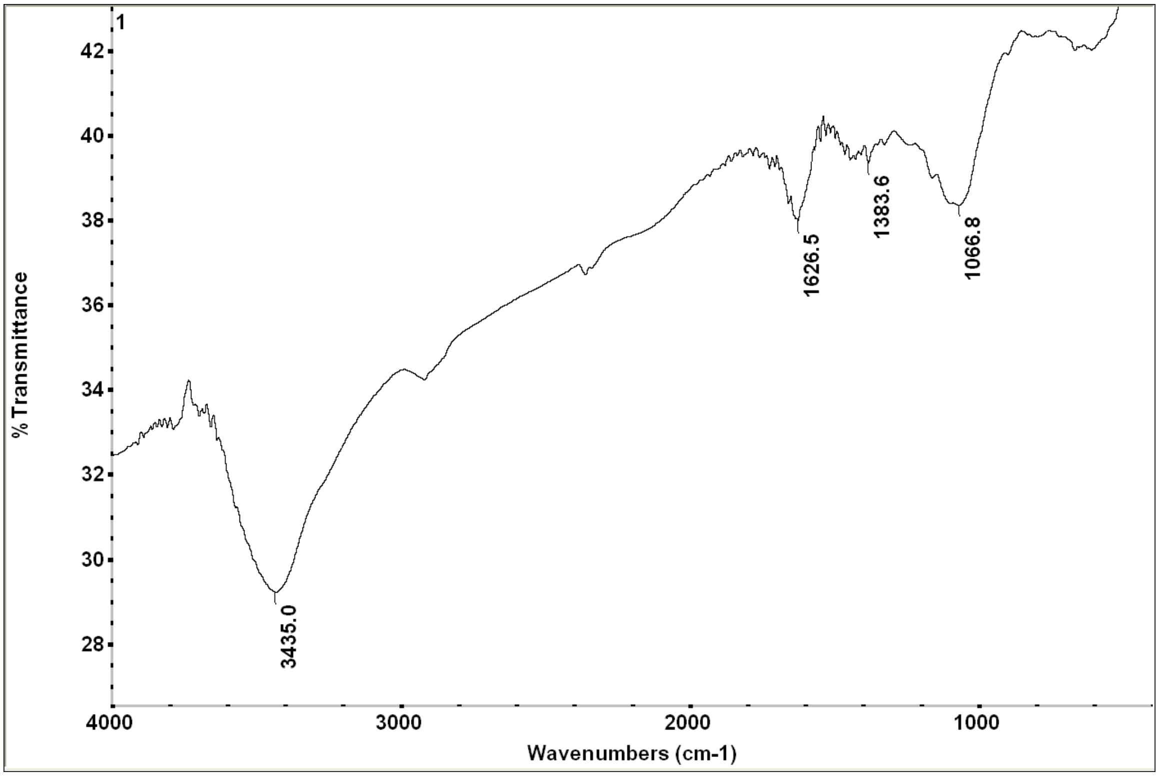


Figure 43: FTIR spectrum of raw rice straw (particle size: 75-150 µm) before biosorption of Pb^2

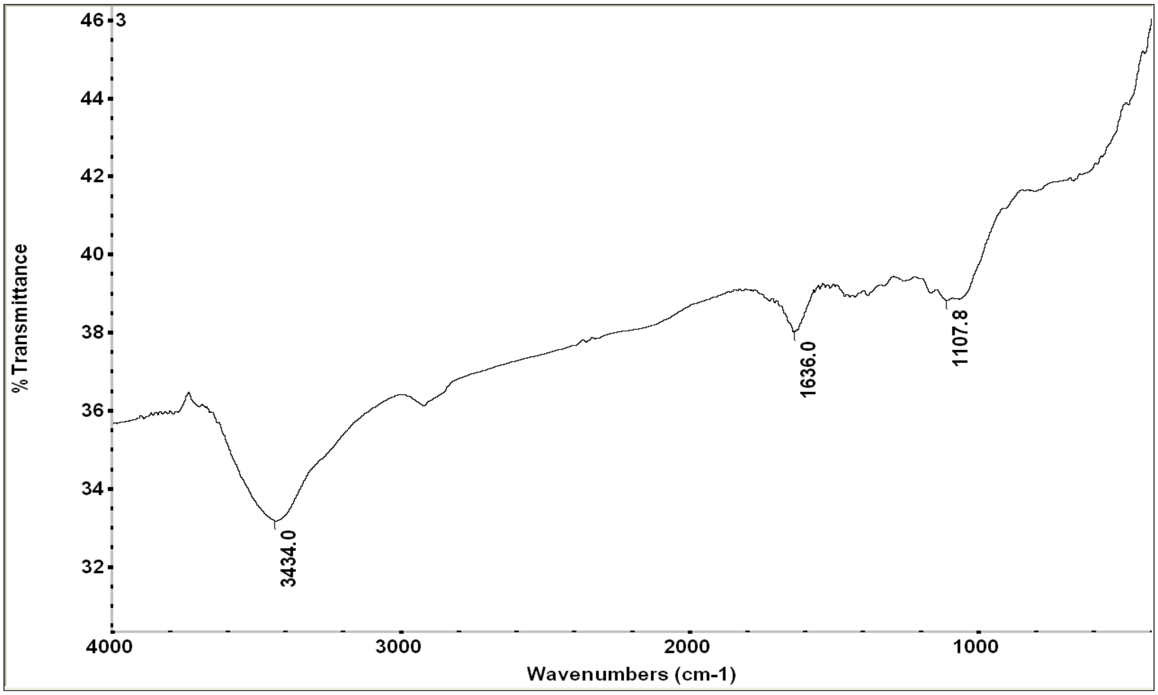


Figure 44: FTIR spectrum of raw rice straw (particle size 75-150 µm) after biosorption of 60 mg/l Pb^{2+}

As illustrated in Figure 43 and Figure 44, the peak representing the O-H bond was only shifted from 3435 cm^{-1} to 3434 cm^{-1}, which is an insignificant change. Whereas, the peak of the C=O bond was shifted from 1626.5 to 1636.0 cm^{-1}, and the peak of the C-O bond was shifted from 1066.8 to 1107.8 cm^{-1}. Those shifts can be attributed to the surface complexation created between Pb^{2+} and the carboxylic acids functional groups; hence, it is an indication that chemical complexation between Pb^{2+} and the carboxyl groups could be one of the mechanisms partially responsible for the biosorption of Pb^{2+} via rice straw.

As for the FTIR analysis of rice straw of particle size <75 μm, presented in Figure 45 and Figure 46, the peaks at 3435.8, 1638.4, 1426.4 and 1057.8 cm^{-1} before sorption of Pb^{2+} were shifted to 3430.7, 1635.7, 1425.2, 1058.5 cm^{-1}, respectively, after sorption of 60 mg/l Pb^{2+}. The shifts in the wavenumbers of the peaks, which indicate the strength of the bonds, were minor. In other words, the impact of the biosorption of Pb^{2+} on the chemical bonds representing the carboxylic acids was insignificant. Table 20 shows the peaks and the corresponding functional groups for a rice straw sample of particle size <75 μm. As a comparison of the impact of the particle size on the strength of the chemical bonds representing the carboxylic functional groups, it is noted from Figure 43 and Figure 45 that the C=O bond was shifted from 1626.5 to 1638.4 cm^{-1} and the C-O bond was shifted from 1383.6 to 1426.4 cm^{-1}, in particle sizes 75- 150 μm and < 75 μm, respectively; hence, the particle size has an impact on the bond order.

Table 20: Peaks wavenumbers and corresponding functional groups (particle size: <75 μm)

Wave number (cm-1)	**Functional Group**
3435.8	O−H
2920.6	C−H
1638.4	C=O
1426.4- 1057.8	C−O

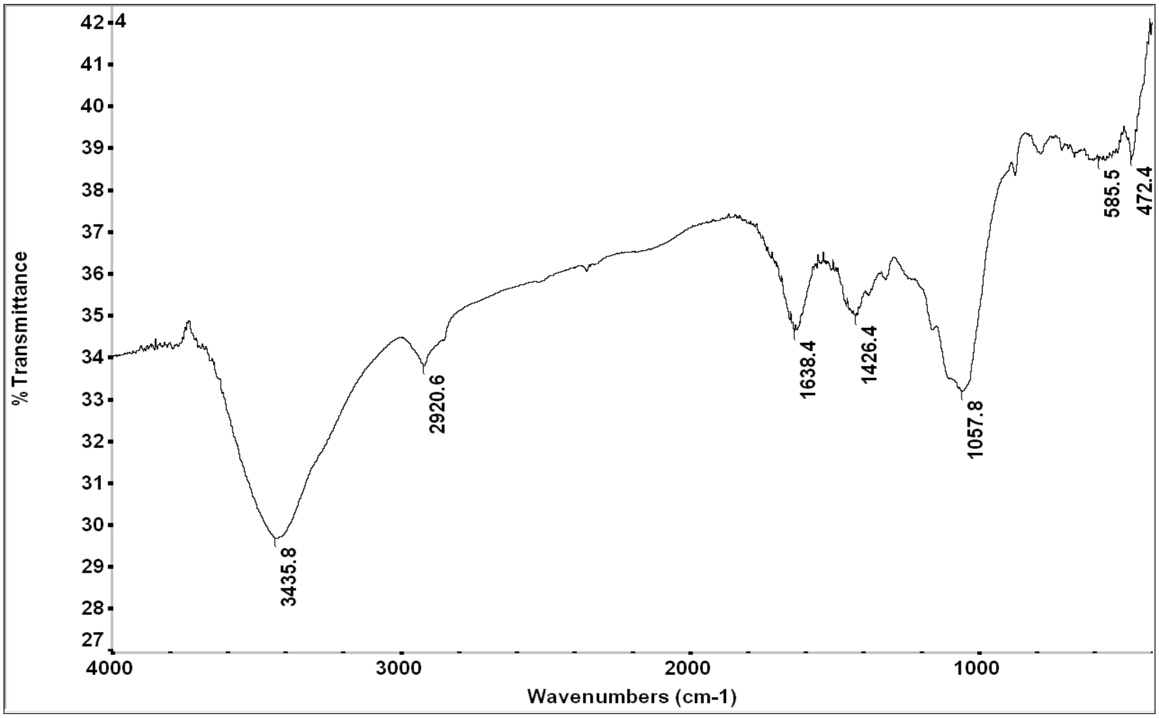


Figure 45: FTIR spectrum of raw rice straw of particle size <75 µm before biosorption of Pb^{2+}

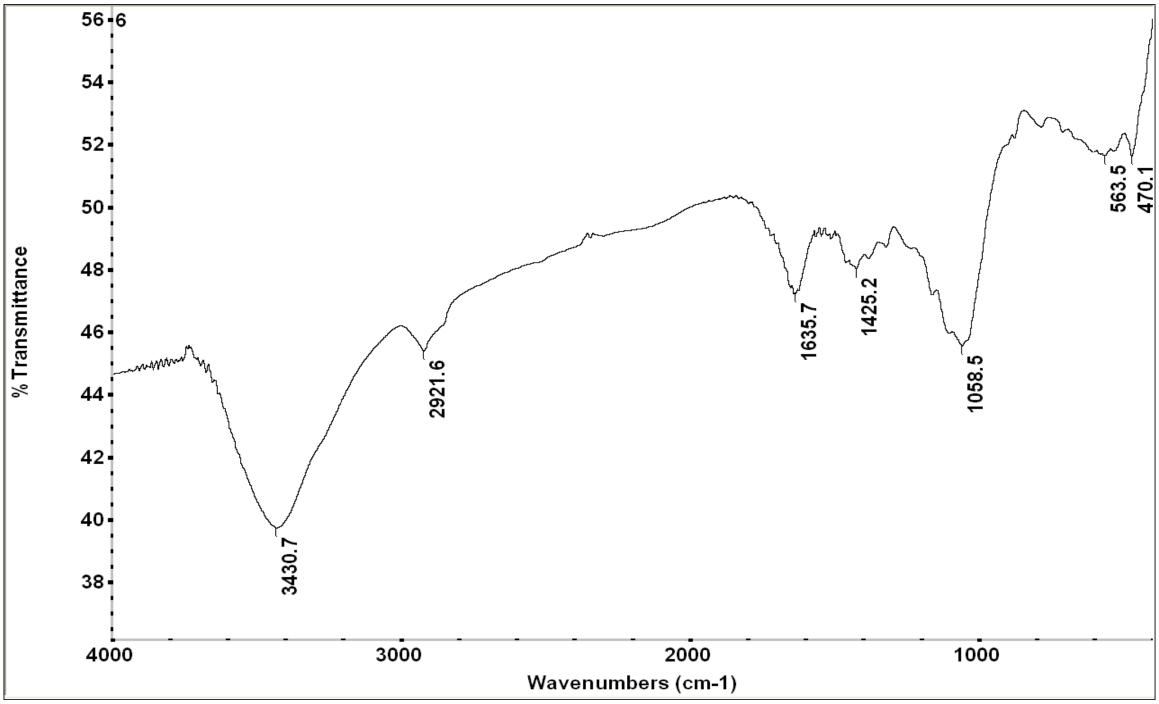


Figure 46: FTIR spectrum of raw rice straw of particle size <75 µm after biosorption of 60mg/l Pb^{2+}

Figure 47, shows the impact of the chemical modification using tartaric acid on the intensity of the peaks, the area enclosed by the peak, representing the carboxylic acids functional groups in comparison to the equivalent peaks in a raw rice straw sample, such as the peak corresponding to the O-H bond of 3434.7 cm^{-1} wave number, the C=O bond of 1634.8 cm^{-1} wave number, and C-O bond of 1383.2 cm^{-1} wave number. It is obvious that the intensity of the peaks has increased after treatment via tartaric acid. Moreover, the wave number of the C=O was shifted from 1626.5 cm^{-1} to 1634.8 cm^{-1}. Finally, this infers that pre-treatment of rice straw via tartaric acid has slightly increased the carboxylic acid functional groups on the surface of rice straw.

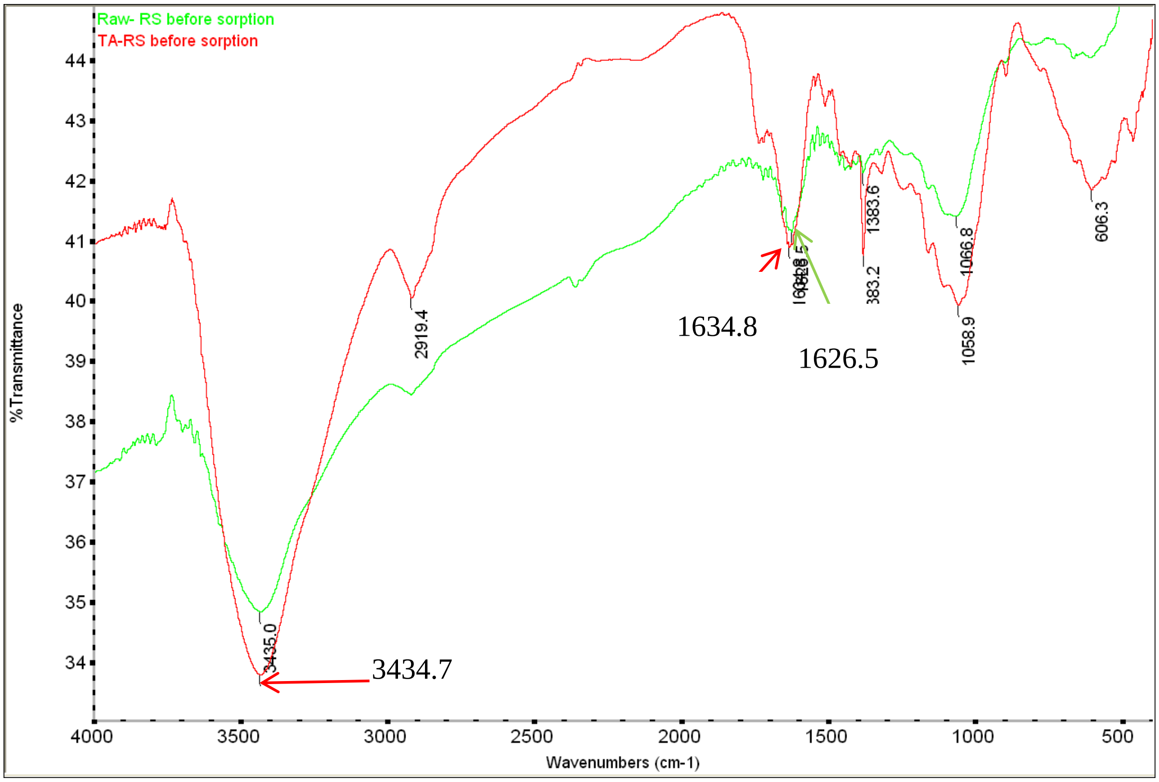
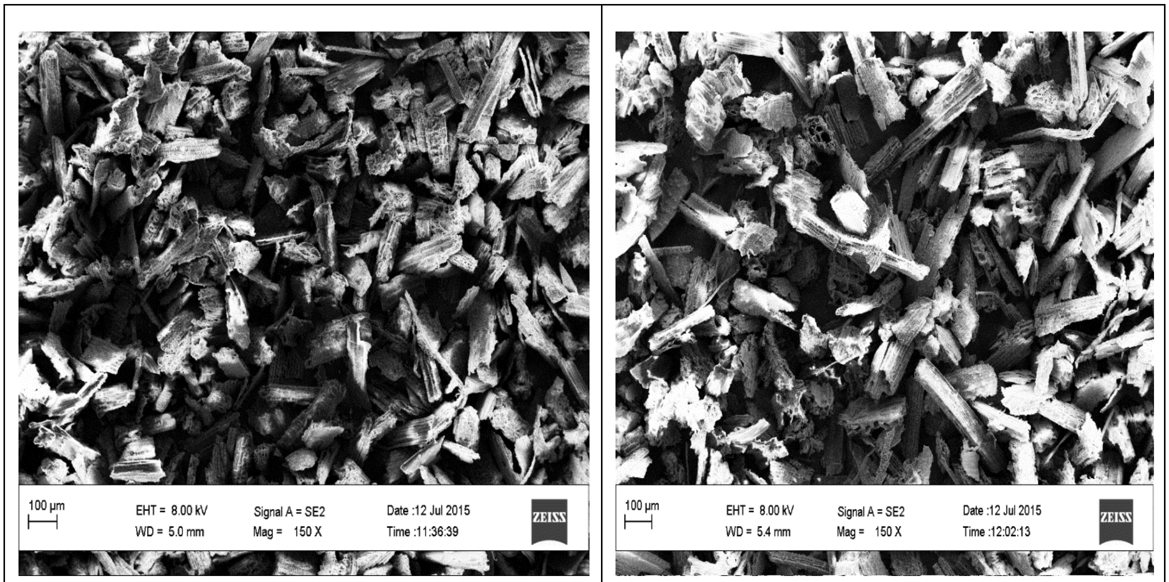


Figure 47: FTIR spectrum of tartaric acid modified rice straw (TA- RS) Vs. Raw rice straw (Raw- RS)

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

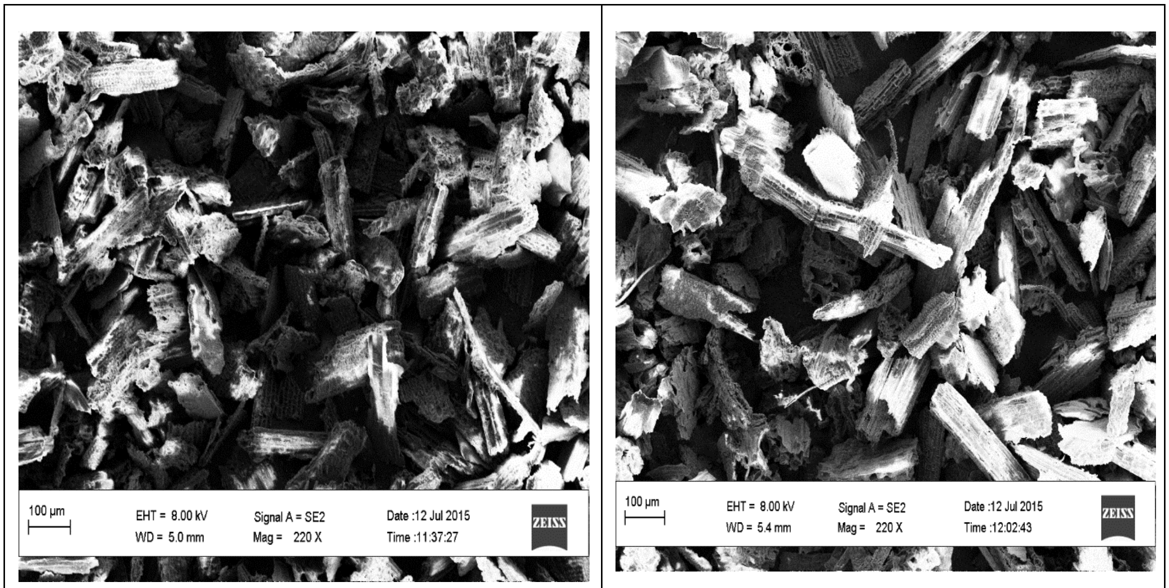
Scanning electron microscope analysis was conducted at various magnifications for fresh rice straw samples and Pb^{2+} loaded samples of particle size 75-150 µm, in an attempt to observe the surface structure of rice straw and any changes that could occur to the surface structure due to Pb^{2+} sorption on its surface. The SEM micrographs, Figure 48 through Figure 52, reveal that rice straw has an irregular rough surface.



Fresh Rice Straw

Pb^{2+} Loaded Rice Straw

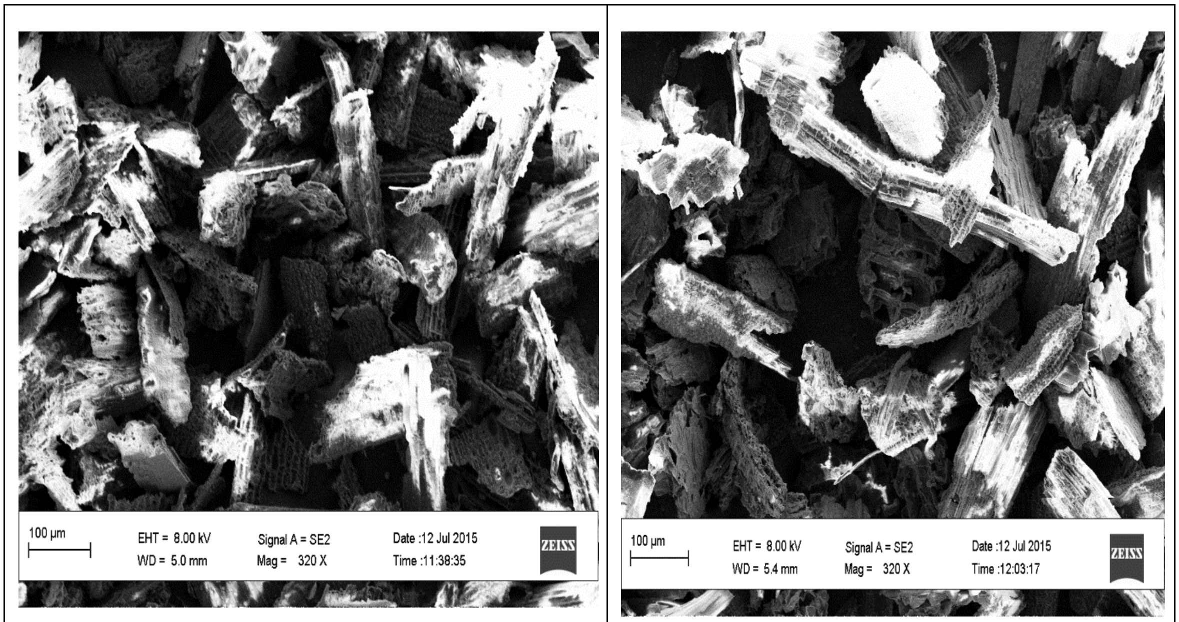
Figure 48: SEM micrographs of rice straw (75-150 µm) before and after sorption of Pb^{2+} at 150X magnification



Fresh Rice Straw

Pb^{2+} Loaded Rice Straw

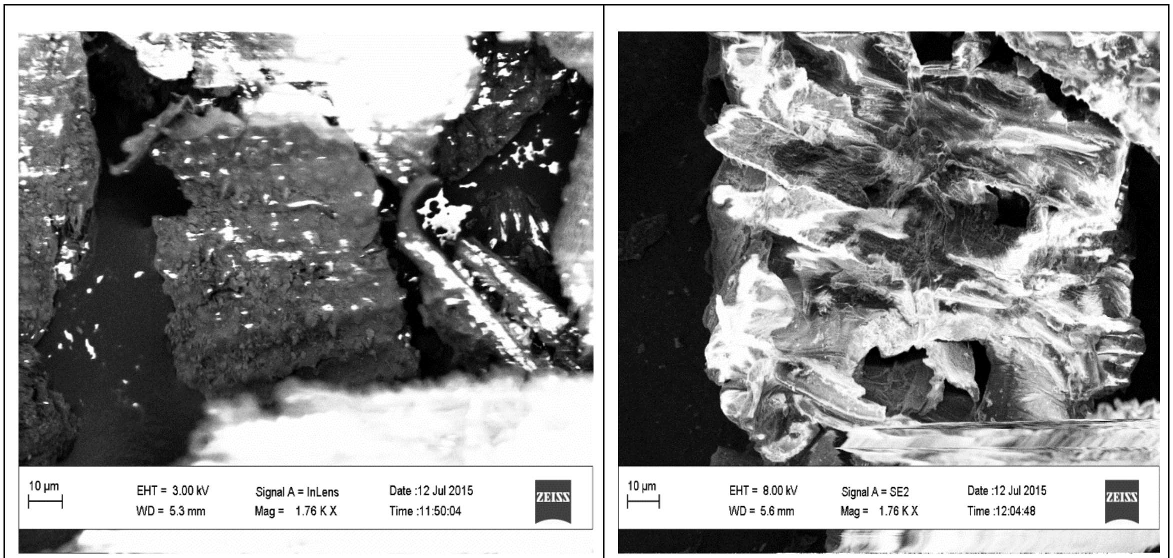
Figure 49: SEM micrographs of rice straw (75-150 µm) before and after Pb^{2+} sorption at 220X magnification



Fresh Rice Straw

Pb^{2+} Loaded Rice Straw

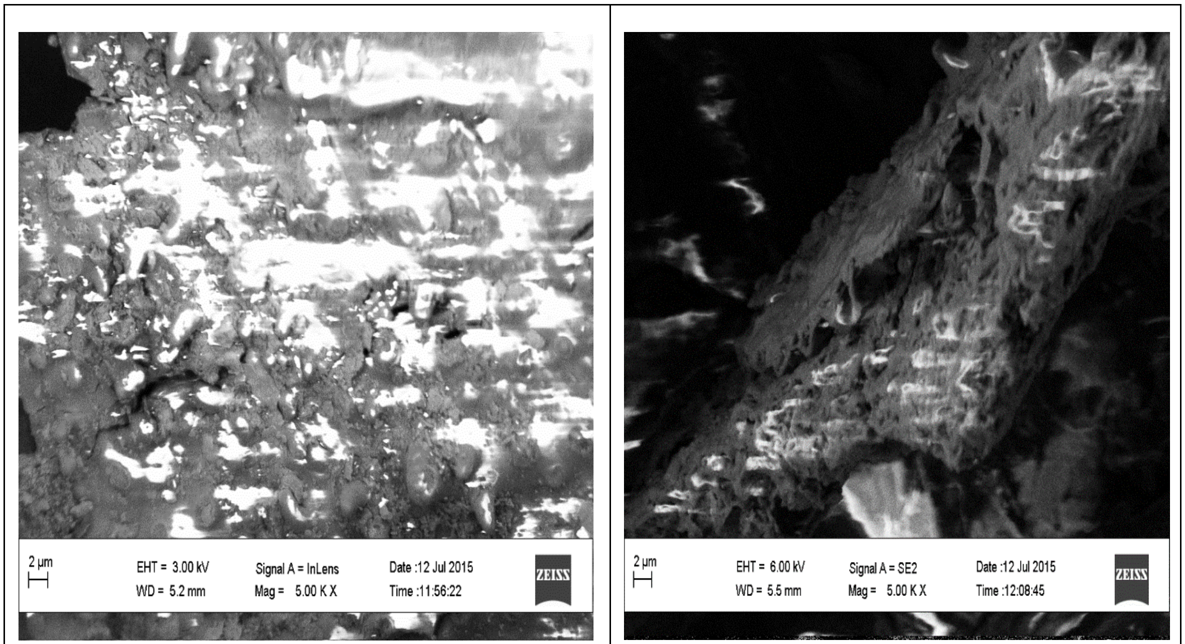
Figure 50: SEM micrographs of rice straw (75-150 µm) before and after sorption of Pb^{2+} at 320X magnification



Fresh Rice Straw

Pb^{2+} Loaded Rice Straw

Figure 51: SEM micrographs of rice straw (75-150 µm) before and after sorption of Pb^{2+} at 1.76 K X magnification



Fresh Rice Straw

Pb^{2+} Loaded Rice Straw

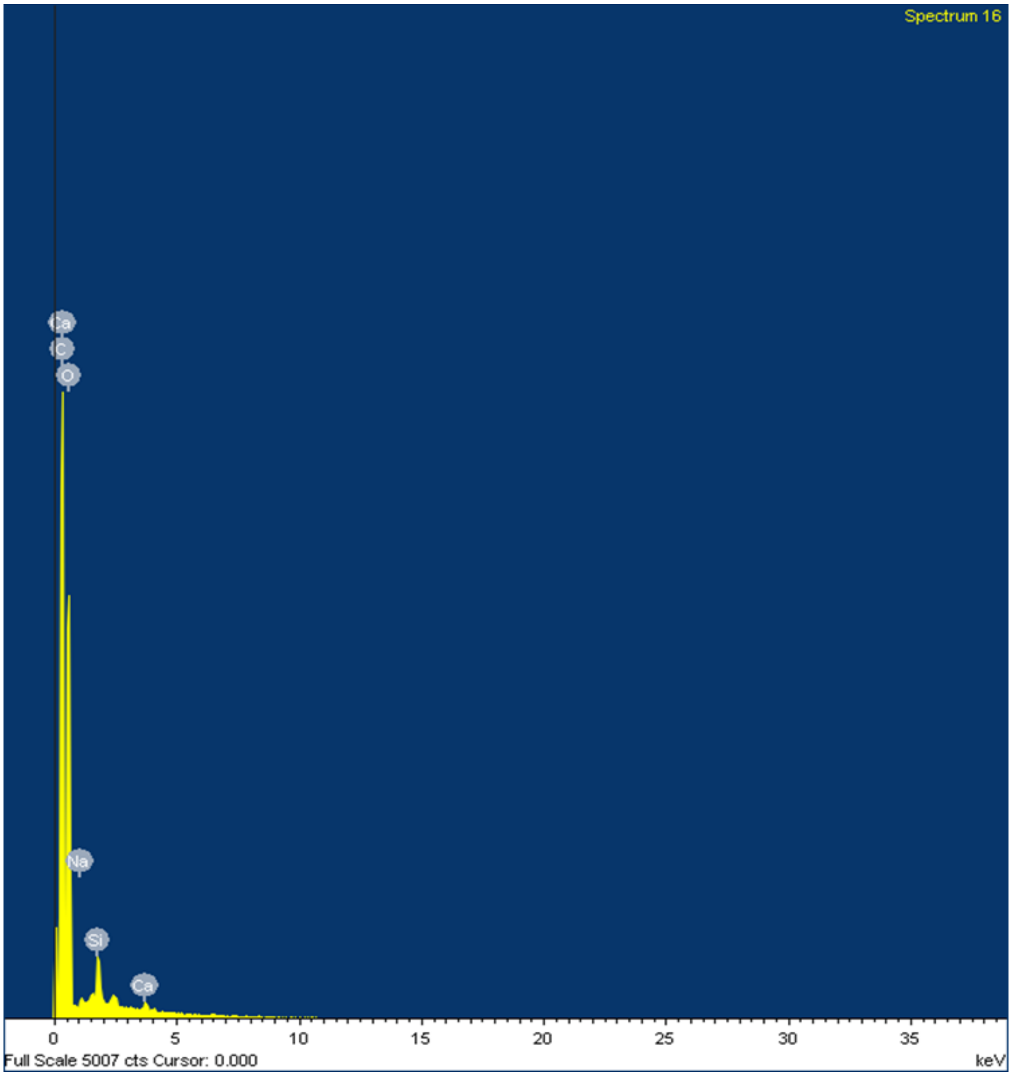
Figure 52: SEM micrographs of rice straw (75-150 µm) before and after sorption of Pb^{2+} at 5.00 K X magnification

Energy dispersive X-ray was carried out in order to analyze the chemical composition of rice straw. In an attempt to decide whether ion exchange is one of the predominant mechanisms of Pb^{2+} sorption by rice straw, the chemical composition of inorganic elements, such as Na, Ca, Mg, and Fe was measured by EDX in fresh rice straw and Pb^{2+} loaded rice straw samples, and any reduction was detected. Since rice straw is a non-homogenous material, EDX was applied to several samples and some variations in the percent by weight of the chemical constituents appeared as shown in Table 21.

Table 21: Chemical composition of fresh rice straw samples based on EDX results

Element	Weight %
C	48.16-49.89
O	43.36-50.65
Si	0.7-2.35
Ca	0.34-1.13
Mg	0-0.18
Na	0.36-0.66
Fe	0-0.5

Figure 53 demonstrates the results of the EDX analysis of Sample I; a raw rice straw sample of particle size 75-150 µm pre-sorption of Pb^{2+}, while Figure 54 presents the EDX analysis of Sample II; a rice straw sample of particle size 75-150 µm after biosorption of 60 mg/l Pb^{2+}. The EDX results of the fresh sample in Figure 53 show that the main constituents of rice straw are carbon (48.84%) and oxygen (49.31%), other inorganic elements are Na (0.36%), Si (1.14%) and Ca (0.34%). Lead appeared in the EDX spectrum of rice straw after sorption, which proves that Pb^{2+} sorption on the surface of rice straw has taken place. After sorption, the amount of Ca in rice straw has decreased from 0.34% to 0.18% as shown in Figure 54. That reduction in Ca implies that ion exchange is probably one of the mechanisms responsible for the uptake of Pb^{2+} by rice straw. Singh, Ali and Prakash (2014) have concluded that sorption of Pb^{2+} by agricultural wastes are mostly due to ion exchange processes. However, Soetaredjo, et al. (2013) reported that the main mechanism responsible for the uptake of Pb^{2+} by rice straw is surface complexation, or chalation; whereas, ion exchange had a minor impact on the process. The increase in the percent by weight of Si and Oxygen in Sample II could be due to the presence of sand particles in the sample, which in turn has caused a decrease in the percent by weight of carbon. The increase in the amount of Na in Sample II from 0.36% to 0.51% could be due to sorption of Na ions by rice straw from the $NaNO_3$ present in the Pb^{2+} synthetic solution that was used to adjust the ionic background of the solution (Zakaria 2009).

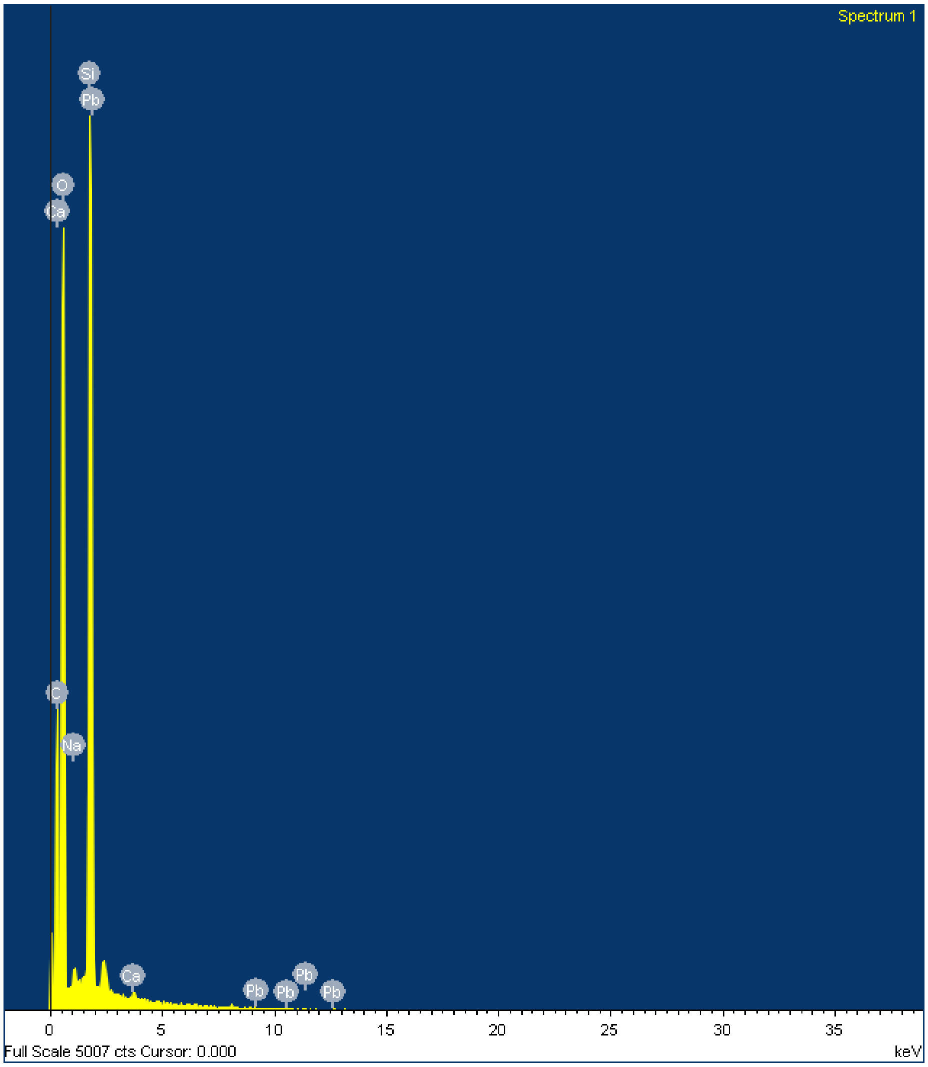


(a)

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	13.40	1.1533	48.84	0.59	56.37
O K	7.73	0.6587	49.31	0.59	42.73
Na K	0.07	0.8392	0.36	0.09	0.22
Si K	0.25	0.9225	1.14	0.08	0.56
Ca K	0.08	0.9672	0.34	0.07	0.12
Totals			100.00		

(b)

Figure 53: Sample I: EDX analysis results of rice straw (75-150 µm) before sorption (a) EDX spectrum, (b) chemical composition table of fresh rice straw



(a)

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	6.36	0.5511	32.25	0.58	41.65
O K	14.63	0.7863	51.87	0.53	50.29
Na K	0.16	0.8733	0.51	0.08	0.34
Si K	4.62	0.9464	13.63	0.19	7.53
Ca K	0.06	0.9558	0.18	0.05	0.07
Pb M	0.42	0.7490	1.56	0.18	0.12
Totals			100.00		

(b)

Figure 54: Sample II: EDX analysis results of rice straw (75-150 µm) after sorption of 60 mg/l Pb^{2+} (a) EDX spectrum, (b) chemical composition table of lead loaded rice straw

CHAPTER 5 : CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The aim of the current research is to study the feasibility and the efficiency of low cost waste materials in the removal of Pb^{2+} ions from wastewater. The research consisted of three phases; a preliminary comparative study, batch equilibrium tests and fixed- bed column tests. The main concluded points from the three phases of the research are summarized below:

- Regarding the removal efficiency of Pb^{2+} by the three raw biomasses utilized in Phase I of the research, Raw-RS has yielded the highest removal of 89.95%, followed by Raw-RH; 54.80%, and finally Raw-SB; 44.51%, at a dose of 2g/l and pH 5.5.

- Treatment using tartaric acid has increased the removal efficiency of Raw-SB from 44.51% to 98.50%, which was the highest percent removal achieved among all the studied biomasses.

- Treatment using NaOH prior to tartaric acid treatment did not prove any enhancement in the removal of Pb^{2+}, as TA-N-SB has only yielded 66.14% uptake, compared to 98.50% by TA-SB. Therefore, NaOH treatment is considered a dispensable step in the treatment process.

- Lime and cement kiln dust achieved very high removal efficiency; however, their high alkalinity would limit their industrial applications.

- Raw rice straw is considered the most promising sorbent for the uptake of Pb^{2+} due to its high efficiency, economic feasibility, and simplicity of preparation.

- In Phase II of the research, it was manifested that at pH values >6, Pb^{2+} removal was mainly due to precipitation.

- In the batch equilibrium experiments, PhaseII, raw rice straw (Raw-RS) demonstrated rapid kinetics of adsorption.

- Batch equilibrium experiments have proved that for raw rice straw (Raw-RS) the optimum particle size is 75-150 µm of a dose 4 g/l, contact time 30 min and pH 5.5. The maximum removal achieved at the optimum conditions is 94.12% and the equilibrium concentration of Pb^{2+} is 2.56 mg/l with an initial Pb^{2+} concentration of 40 mg/l.

- At initial Pb^{2+} concentrations in the range 2- 15mg/l, the final lead concentration in the treated effluent using Raw- RS complies with the limits of the Egyptian law No. 93 for year 1962 of discharging liquid wastes in the sewage network, amended by Ministerial decree No.44/2000; 1mg/l.

- For initial Pb^{2+} concentrations > 15 mg/l-40 mg/l, the treated effluent using Raw-RS does not comply with decree 44/2000 for discharging on the public sewers. Yet, it complies with the limits of the same decree for irrigation purposes, as well as FAO (1985) regulations for irrigation; 5 mg/l. However, if meeting the limits of the discharge on the public sewers is the main objective, then it is suggested either to apply a multi- stage treatment process; in other words, to operate two batch reactors in series, or to utilize TA-RS of a dose 6g/l.

- TA-RS has yielded higher percent removal efficiency (93.13%) compared to Raw-RS (86.15%) at 2 g/l dose; however, upon raising the dose to 4 g/l the difference was insignificant; 97.3% for TA-RS and 94.12% for Raw-RS. Therefore, utilizing raw rice straw for Pb^{2+} uptake from aqueous solution is considered more practical as it eliminates the extra cost, time, and effort that will be exerted to prepare chemically modified rice straw.

- The Batch equilibrium data was perfectly described by Langmuir model. The linearity of the plot suggested the creation of a homogenous monolayer of metal ions on the outer surface of the sorbent.

- The maximum adsorption capacity (q_{max}) derived from Langmuir model for the sorption of Pb^{2+} via raw rice straw is 42.55 mg of Pb^{2+}/g of rice straw. This value is higher than several other values reported in the literature for raw and pre-treated rice straw. Confirming that utilizing raw rice straw is more feasible than pre- treated rice straw since it is a very promising biosorbent, economically viable and easily prepared.

- It is concluded from the SEM and EDX analysis that rice straw possesses an irregular rough surface, and the main constituents are Carbon and Oxygen, followed by inorganic constituents, which are Ca, Na, Mg, Fe and Si.

- Biosorption of Pb^{2+} via rice straw is basically due to several mechanisms, which are:
    1. Surface complexation with carboxylic functional groups on the surface of rice straw, as illustrated by the FTIR analysis.
    2. Ion exchange with Ca ions, as illustrated by the EDX results
    3. Physical forces of attraction, as manifested by Langmuir isotherm

- In fixed- bed column tests, Phase III, the service time of the column and the volume of wastewater treated up to breakthrough and exhaustion are directly proportional to the bed depth; on the other hand, they are inversely proportional to the initial Pb^{2+} concentration and the flow rate of the feed solution.

- Raw rice straw managed to treat a significant number of bed volumes to breakthrough and exhaustion at lower flow rates. Rice straw sorption column of small bed depth (3cm) was not efficient in treating high concentrations of Pb^{2+}; 40mg/l and 80mg/l; therefore, for high concentrations larger depths are required.

- The increase in the bed depth has significantly increased the volume of treated effluent that complies with the Egyptian regulations.

Finally, utilizing rice straw as a biosorbent of $Pb2^+$ ions is perceived as a sustainable wastewater treatment technology for the following reasons:

1. Economic feasibility because of the utilization of a low cost waste material in the treatment process.
2. High efficiency of lead removal.
3. Abundant availability of rice straw in Egypt.
4. Re-use of an unused resource, rice straw; thus, conserving a natural resource.
5. Contribution to solving the problem of the solid waste sector by reducing the amount of waste that normally causes serious disposal problems.
6. Utilization of rice straw will reduce its quantity as a waste. As a result, this will mitigate the seasonal air pollution problem in Egypt of the black cloud, which is generated due to open field burning.
7. Treatment of wastewater to be suitable for re-use in purposes that do not require very high water quality; hence, conserving and sustainably managing the water resources and achieving the cradle to cradle concept.

5.2 **Recommendations**

Recommendations for future research and investigations are the following:

1. More extensive research on the efficiency of tartaric acid modified rice husk and tartaric acid modified sugarcane bagasse, considering the high results achieved in Phase I.
2. Investigating other simple pre-treatment methods for various agricultural residues.
3. Studying the removal efficiency of raw rice straw for other heavy metals, such as cadmium, chromium and mercury due to their adverse health impacts as explained in Chapter 1.

4. Conducting a research on the impact of agricultural wastes on the organic content in wastewater; BOD and COD.
5. Investigating the feasibility of regenerating metal loaded rice straw and heavy metals recovery.
6. Investigating the applicability of the research outcomes on real industrial wastewater.
7. Carrying out an economic feasibility study for the utilization of rice straw in wastewater treatment.

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APPENDIX A: PHASE I- DATA ANALYSIS

Table A-1: Biosorption of Pb^{2+} using various raw and modified agricultural wastes (pH 5.5, dose 2 g/l, contact time: 2h)

Biosorbent	**Final pH**	**C_e (mg/l)**	**% Removal**
Control	5.81	37.33	6.67
Raw-SB	5.85	22.20	44.51
N-SB	5.61	18.24	54.41
TA-N-SB	5.18	13.54	66.14
TA-SB	5.14	0.60	98.50
Raw-RH	5.49	18.47	54.80
TA-N-RH	5.01	8.04	79.91
Raw-RS	6.14	4.14	89.95
TA-N-RS	_	_	_

Table A-2: Adsorption of Pb^{2+} using CKD, lime & marble powder waste (pH 5.5, dose 2 g/l, contact time: 2h)

Adsorbent	**Final pH**	**C_e (mg/l)**	**% Removal**
Control	5.14	38.106	9.12
CKD	7.09	0.7245	98.27
Lime	7	0.5535	98.68
Marble powder waste	6.43	0.399	99.05

APPENDIX B: PHASE II- DATA ANALYSIS

Table B-1: Impact of pH on the equilibrium Pb^{2+} concentration, % removal of Pb^{2+} and adsorption capacity of rice straw

Rice straw Samples					Control Samples		
Initial pH	**Final pH**	**C_e (mg/l)**	**% Removal**	**q (mg/g)**	**Final pH**	**C_e (mg/l)**	**% Removal**
2.12	2.06	37.164	12.13	2.57	2.14	39.717	6.10
2.96	3.52	22.903	45.85	9.70	3.11	39.77	5.97
4.09	5.32	8.646	79.56	16.83	4.02	39.268	7.16
4.92	5.21	11.288	73.31	15.50	5.17	39.173	7.38
5.48	6.31	4.109	90.29	19.09	5.76	39.29	7.11
6.14	6.65	3.091	92.69	19.60	5.86	38.133	9.84
7.05	7.64	1.174	97.22	20.56	6.6	3.968	90.62

Table B-2: Impact of Contact Time on equilibrium Pb^{2+} concentration, % removal and adsorption capacity of rice straw

Time (min)	C_e (mg/l)	%Removal	q (mg/g)
1	15.026	63.29	12.952
2	10.466	74.43	15.23
5	8.9625	78.59	16.50

Time (min)	C_e (mg/l)	%Removal	q (mg/g)
7	9.9825	75.61	15.47
10	7.4935	82.06	17.23
15	9.8425	75.95	15.54
20	5.9855	85.71	17.99
30	5.8065	86.15	18.08
45	6.46	84.58	17.75
60	5.958	85.76	18.00
120	5.232	87.83	18.88
180	4.3405	89.65	18.81
240	4.458	89.55	18.75

Table B-3: Particle Size: 75-150 µm- Impact of Rice Straw Dose on 40 mg/l Pb^{2+} Uptake in an Aqueous Solution at pH 5.5 and Contact Time 30 min

Dose (g/l)	C_e (mg/l)	% Removal	q (mg/g)
0.116	35.595	18.32	68.84
0.206	38.67	11.27	23.83
0.51	25.535	41.41	35.66
0.71	25.87	40.64	25.08

1.02	18.155	58.34	25.02
2.04	5.81	86.15	17.72
4.03	2.561	94.12	10.19
6.00	1.964	95.49	6.94

Table B-4: Particle Size: <75 µm- Impact of Particle Size and Rice Straw Dose on Pb^{2+} Uptake and Adsorption Capacity (contact time: 30min, pH: 5.5, 40 mg/l Pb^{2+})

Dose (g/l)	C_e (mg/l)	% Removal	q (mg/g)
0.12	32.88	24.55	92.24
0.20	26.63	38.89	83.09
0.50	21.115	51.55	44.75
0.70	17.795	59.17	36.63
1.01	12.86	70.49	30.42
2.01	3.246	92.55	20.05
4.04	1.405	96.78	10.45
6.01	1.182	97.21	6.86

Table B-5: Particle Size: 300-600 μm- Impact of Particle Size, Rice Straw Dose and Contact Time on Pb^{2+} Uptake and Adsorption Capacity (pH: 5.5)

Dose (g/l)	**Contact Time: 30 min**			**Contact Time: 60 min**		
	C_e (mg/l)	**% Removal**	**q (mg/g)**	**C_e (mg/l)**	**% Removal**	**q (mg/g)**
0.50	19.54	53.88	45.49	23.62	44.27	37.37
1.01	19.88	53.09	22.23	18.07	57.35	23.87
2.02	15.84	63.64	13.76	12.63	71.03	15.35
4.01	6.86	83.81	8.87	4.473	89.45	9.44
6.01	4.19	90.09	6.35	3.85	90.91	6.40

Table B-6: Impact of Initial Pb^{2+} Concentration on the Percentage Removal of Pb^{2+} and Adsorption Capacity of Rice straw- particle size: < 75 μm

Initial Pb^{2+} Concentration C_o(mg/l)	**Ce (mg/l)**	**% Removal**	**q (mg/g)**
5	0.232	95.19	2.30
10	0.422	95.70	4.69
15	0.759	94.82	6.94
20	2.649	86.92	8.80
40	3.246	92.55	20.17
60	9.605	83.93	25.08

Table B-7: Impact of Initial Pb^{2+} Concentration on Percentage Removal and Adsorption Capacity of Pb^{2+} by Rice Straw- particle size: 75-150 µm

Initial Pb^{2+} Concentration C_o (mg/l)	**C_e (mg/l)**	**% Removal**	**q (mg/g)**
2	0.305	86.50	0.49
5	0.397	91.77	1.11
10	0.65	93.37	2.29
15	0.93	93.65	3.43
20	1.372	93.22	4.72
40	2.561	94.12	10.25
60	7.509	87.43	13.06
80	9.893	87.93	18.02
105	14.281	86.39	22.67

Table B-8: Impact of Contact Time on Pb^{2+} Uptake by TA-RS ($C_0 \approx$ 40 mg/l, Dose: 2 g/l, pH: 5.5)

Contact Time(min)	C_e (mg/l)	% Removal	q (mg/g)
15	3.23	92.59	19.92
30	3.00	93.13	20.20
45	2.96	93.22	20.08
60	2.46	94.36	20.25

Table B-9: Impact of Sorbent Dose on the Percent Removal of Pb^{2+} by TA-RS and the Adsorption Capacity (Contact Time: 30 min, $C_0 \approx$ 40 mg/l, and pH: 5.5)

Dose (g/l)	C_e (mg/l)	% Removal	Increase Vs. Raw-RS (%)	q (mg/g)	Increase Vs. Raw-RS (mg/g)
2	2.997	93.13	6.98%	20.2005	2.49
4	1.178	97.30	3.18%	10.54225	0.35
6	1.007	97.69	2.2%	7.082308	0.14

APPENDIX C: SORPTION ISOTHERM MODELS

Table C-1: Input data of Langmuir isotherm model for the sorption of Pb^{2+} using raw rice straw

Dose (g/50ml)	Initial concentration C_0 (mg/l)	Equilibrium concentration C_e (mg/l)	Adsorption capacity q_e (mg/g)	$1/C_e$ (l/mg)	$1/q_e$ (g/mg)
0.2	9.81	0.65	2.29	1.54	0.44
0.2	14.64	0.93	3.43	1.08	0.29
0.2	20.25	1.37	4.72	0.73	0.21
0.2	43.58	2.56	10.25	0.39	0.10
0.2	59.76	7.51	13.06	0.13	0.08
0.2	81.98	9.89	18.02	0.10	0.06
0.2	104.96	14.28	22.67	0.07	0.04

Table C-2: Input data of Freundlich isotherm model for the sorption of Pb^{2+} using raw rice straw

Dose (g)	Initial concentration C_0 (mg/l)	Equilibrium concentration C_e (mg/l)	Adsorption capacity q_e (mg/g)	Log C_e	Log q_e
0.2	9.81	0.65	2.29	-0.19	0.36
0.2	14.64	0.93	3.43	-0.03	0.54
0.2	20.25	1.37	4.72	0.14	0.67
0.2	43.58	2.56	10.25	0.41	1.01
0.2	59.76	7.51	13.06	0.88	1.12
0.2	81.98	9.89	18.02	1.00	1.26
0.2	104.96	14.28	22.67	1.15	1.36