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**Assessment of Combination of Kennan's
Sugarcane Baggase Activated Carbon and Natural
Zeolite for Removal of Lead (II) and Cadmium(II)
Metal Ions from Aqueous Solutions**

*A Thesis Submitted in the requirements for the Degree of Doctor
of Philosophy in Chemical Science (Analytical Chemistry)*

By

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December 2022

Certificate

This is to certify that the thesis entitled '**Combination of Kennan's Sugarcane Baggase Activated Carbon and Natural Zeolite for Removal of Lead (II) and Cadmium(II) Metal Ions from Aqueous Solutions**' submitted by **Safa Ebrahim Sulieman Hamad** is a record of an original research work carried out by her under my supervision and guidance in the requirements for the award of the degree of **Doctor of Philosophy in Chemical Science (Analytical Chemistry)** during the session July'2018 – December'2022 in the Department of Chemistry, Univesity of Nile Valley, River Nile State, Sudan. Neither this thesis nor any part of it has been submitted for the degree or academic award elsewhere.

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الآية

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

(رَبَّنَا لَا تُؤَاخِذْنَا إِن سَئِينَا أَوْ أَخْطَأْنَا)

صدق الله العظيم

سورة البقرة الآية (286)

DEDICATION

*To the soul of my dear Mother and Father, God give him
along life, and to all my brothers who supported me to
continue, to my dear husband who encourage me by all his
possession.*

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Abstract

This study investigates a comparative assessment of two adsorbents, prepared activated carbon, AC (KSCB)KOH and AC (KSCB)H₃PO₄ Combined with natural Natural Zeolite sample in the removal of lead(II) and cadmium(II) ions from their aqueous solutions. Maximum Pb(II)removal was observed at pH (5.0 - 6.0) when using KOH and H₃PO₄ , while it was showed a maximum removal for Cd(II) at pH (6.0 – 8.0) when using the same activators respectively. The Langmuir and Freundlich isotherm models were applied to the adsorption data. The coefficients of determination of the two models were high with Langmuir model providing the best description for the experimental adsorption data. The fitting of the adsorption data into Freundlich model shows that the mode of adsorption of the metal ions by both adsorbents follows physisorption. Investigation into the maximum adsorption capacity showed that Cd(II) was better adsorbed than Pb(II) on both adsorbents. Maximum adsorption capacities corresponding to monolayer coverage, obtained from the Langmuir plots were (714.29) mg/g and (588.24) mg/g respectively for Cd(II) and Pb(II) ions onto the AC (KSCB)KOH Combined with Natural Zeolite and (270.27) mg/g and (161.29) mg/g for their adsorption onto AC (KSCB)H₃PO₄ Combined with Natural Zeolite. The Langmuir adsorption coefficient, K_L which is related to the affinity of the adsorbents for the metal ions were (150.00) and (138.77) respectively for adsorption of Cd(II) and Pb(II) ions onto AC (KSCB)KOH Combined with Natural Zeolite and (34.33) and (92.39) for adsorption onto AC (KSCB)H₃PO₄ Combined with Natural Zeolite following the initial order. The carbonized AC (KSCB)KOH Combined with Natural Zeolite based - adsorbent was generally found to have an increased adsorption capacity for the metal ions than AC (KSCB)H₃PO₄ Combined with Natural Zeolite.

المستخلص

تبحث هذه الدراسة في تقييم مقارنة لاثنتين من الممتزات: الكربون المنشط المحضر من AC (KSCB) KOH و AC (KSCB) H₃PO₄ مع عينة من الزيوليت الطبيعي في إزالة أيونات الرصاص (II) والكاديوم (II) من محاليلها المائية. لوحظ ان الحد الأقصى لإزالة الرصاص (II) عند الأس الهيدروجيني (5.0 – 6.0) عند استخدام هيدروكسيد البوتاسيوم و حمض الفسفوريك، بينما لوحظت أقصى إزالة للكاديوم (II) عند الأس الهيدروجيني (6.0 - 8.0) عند استخدام نفس المنشطات على التوالي. تم تطبيق نماذج متساوي الحرارة لانغمير و فريندلخ على بيانات الامتزاز. كانت معاملات تحديد النموذجين عالية حيث قدم نموذج لانغمير أفضل وصف لبيانات الامتزاز التجريبية. يُظهر تركيب بيانات الامتزاز في نموذج فريندلخ أن طريقة امتزاز أيونات المعادن بواسطة كلا المادصتين يتبع عملية الادمصاص الفيزيائي. أظهر التحقيق في السعة القصوى للادمصاص أن الكاديوم (II) كان يمتاز بشكل أفضل من الرصاص (II) على كلا المادصتين. كانت ساعات الامتصاص القصوى المقابلة للتغطية أحادية الطبقة، التي تم الحصول عليها من قطع لانغمير (714.29) مجم جم⁻¹ و (588.24) مجم جم⁻¹ على التوالي لأيونات الكاديوم (II) والرصاص (II) المنشط بواسطة هيدروكسيد البوتاسيوم (KSCB) AC مع الزيوليت و (270.27) مجم جم⁻¹ و (161.29) مجم جم⁻¹ لادمصاصهما على حمض الفسفوريك (KSCB) AC متحداً مع الزيوليت. كان معامل امتزاز لانغمير K_L المرتبط بتقارب المواد الماصة للأيونات المعدنية (150.00) و (138.77) على التوالي لادمصاص أيونات الكاديوم (II) و الرصاص (II) المنشط بواسطة هيدروكسيد البوتاسيوم (KSCB) KOH متحداً مع الزيوليت و (34.33) و (92.39) لادمصاص على حمض الفسفوريك (KSCB) H₃PO₄ AC متحداً مع الزيوليت وفقاً للترتيب الأولي. تم العثور على هيدروكسيد البوتاسيوم (KSCB) KOH المتحد مع الزيوليت بسعة و قدرة ادمصاص متزايدة للأيونات المعدنية مقارنة بحمض الفسفوريك (KSCB) AC المتحد مع الزيوليت.

Chapter One

Introduction

1.1 Role of Activated Carbon for removal of metal ion

Generally activated carbon can be prepared from various raw materials including agricultural and forestry residues. Most of the precursors used for the preparation of activated carbon are rich in carbon[1]. Production of AC was achieved typically through two routes, physical activation and chemical activation[2]. Physical activation involves carbonization of raw material followed by the activation at high temperatures between (800 and 1100C^o) in the presence of oxidizing gases like carbon dioxide or steam [3] whereas chemical activation mixing of chemical agent with precursor and then followed by pyrolysis at moderate temperatures in the absence of air. Chemical activation on the other hand enjoys the benefit of development of better porous structure in single process route at low carbonization temperatures as compared to physical activation [4].

The sugar industry produces about 800 million tons of sugar annually on global scale which results in about 240 million tons of bagasse, some of which is used as fuel for mill boilers and electricity generation[5]. The unused bagasse is not readily biodegradable for composting and application in the farms and therefore, poses disposal problems for mill owners. Many efforts have been directed towards finding commercially viable applications of sugarcane bagasse[6]. For instance it has been applied in the manufacture of pulp and paper products, charcoal and building materials[7].

Bagasse is rich in lignocellulose and has abundant pores giving it a large internal surface area[8]. Due to this property, sugarcane bagasse has also been applied in removing some heavy metal ions from contaminated water. The degree of success in removing these ions from water differs from one metal to another, and depends on prevailing experimental conditions such as temperature, concentration and contact time[9]. These authors only used

bagasse but did not convert it to other possible forms like the ash and charcoal[10].

Water contamination is a worldwide challenge that is caused by dyes, pathogens, turbidity, oil and its derivatives and heavy metals from industries and agricultural effluents. Heavy metals in particular persist in the environment indefinitely and cause dangers to public health, with lead and cadmium being the most common heavy metals[11]. Lead poisoning causes low intelligent quotient, concentration disorders and behavioral changes in children. It causes degeneration of the axon, cerebral edema, infertility, menstrual disorders, abortions and stillbirths in adults[12]. Prolonged exposure to cadmium ions causes damage to kidneys, lungs, liver and it is carcinogenic[12].

Adsorption is one of the alternatives for purification of water and wastewater before disposal. The most popular adsorbent used in wastewater treatment is the coal-based activated carbon but it is relatively expensive especially for small scale application[13]. There is increasing research interest in use of alternative adsorbents of lower cost obtained from locally available materials and wastes that are environment friendly [13]. For example, agricultural wastes such as bagasse, banana and orange peels, rice and coffee husks, maize cobs and others can be effectively used in cleaning wastewater before disposal and in water treatment plants while curbing disposal challenges simultaneously [14].

The capacity of unprocessed sugarcane bagasse to adsorb cadmium (II) and zinc (II) ions has been investigated and found to be 31.11 and 6.79 mg/g respectively [15]. Converted bagasse fly ash into an efficient adsorbent by treating it with hydrogen peroxide and reported a capacity of 13.21mg/g for zinc ions in water[16]. Equilibrium results from Irfan and Umi, 2006, on adsorption of Cu^{2+} ions have shown that chemically treated sugarcane bagasse activated carbon increases the adsorption capacity by 50%, giving a capacity of 39.06mg/g for Cu^{2+} ions.

Different ions adsorb differently onto various adsorbents and diverse methods of activation also produce distinctive adsorption capacities. Therefore, this study set out to investigate and determine the adsorption capacities of non-activated bagasse, bagasse activated with sodium hydroxide, its charcoal activated with phosphoric acid and its ash, to remove Cd^{2+} and Pb^{2+} ions from ion spiked water under varying experimental conditions of pH, contact time, rate of shake, initial concentration, adsorbent dosage and temperature. Since removal of methylene blue and turbidity from water by bagasse adsorbents has not been studied, this study also sought to investigate the potential of these bagasse based adsorbents in also removing turbidity and methylene blue from simulated contaminated water.

1.2 Role of Natural Zeolites for removal of metal ions

Basically Natural Zeolites are a naturally occurring crystalline aluminosilicates consisting of a framework of tetrahedral molecules, linked with each other by shared oxygen atoms.

During 1970s, natural Natural Zeolites gained a significant interest among scientists due to their ion-exchange capability to preferentially remove unwanted heavy metals such as strontium and cesium[17]. This unique property makes Natural Zeolites favorable for wastewater treatment.

The price of Natural Zeolites itself is considered very cheap about US\$ 0.03 0.12/kg, depending on the quality of the Natural Zeolites itself [18].

Natural Zeolites consist of a wide variety of species such as clinoptilolite and chabazite. Clinoptilolite is most abundant in nature and is readily available from more than 40 natural Natural Zeolites species [18]. Among the most frequently studied natural Natural Zeolites, clinoptilolite was shown to have high selectivity for certain heavy metal ions such as Pb^{2+} , Cd^{2+} .

Research has been conducted to show the effectiveness of clinoptilolite to remove lead and cadmium as well [18]. It was indicated that clinoptilolite is more selective for Pb^{2+} , but Cd^{2+} is also exchanged at satisfactory level. Approximately 1.4 mg/g of Pb^{2+} and 1.2 mg/g of Cd^{2+} were removed.

Concerning the effect of temperature on the adsorption process, it was further mentioned that the metals uptake is favored at higher temperature[19] since a higher temperature activates the metal ions for enhancing adsorption at the coordination site of Natural Zeolites.

In 1992, a further investigation on the use of carbonized Natural Zeolites for removing lead from wastewater was also conducted [20]. The strategy behind creating carbonized Natural Zeolites is to combine lyophilic and lyophobic surfaces that can bind with organic and inorganic substances, which are found in waste streams. It was reported that the carbonized Natural Zeolites removed about 99% of 260 ppm lead solution.

The influence of pretreatment upon the cation exchange capacity (CEC) and selectivity of Natural Zeolites for metal ions was investigated by a number of researchers. It was demonstrated that the CEC of clinoptilolite depends on the pretreatment method and that conditioning improves its ion exchange ability and removal efficiency [21].

1.3 Heavy Metals

The heavy metals present in water are the main ecological concern due to their accumulation and non-degradability on their own [22]. Various sources like paper manufacturing units, fungicide, insecticide, lather industry, mining operations, and electroplating industries release heavy metals into the water resources which are highly toxic and cannot be destroyed on their own [23].

1.4 The Problem Statement

The performance of wastewater treatment processes in terms of heavy metals removal has great importance in determining their quantity discharged into receiving waters, especially in areas where waters, re-use is practiced. Therefore, recovery of these pollutants from wastewater became an important environmental issue. Water pollution has been a major challenge to the environmental researchers, due to the release of toxic heavy metals and dyes from various industries. Trace amounts ($\mu\text{g I}^{-1}$) of different heavy metals, lead and cadmium, are considered as highly toxic due to their carcinogenicity and

other health disorders. The sources of these pollutants include effluents from many industrial wastewaters such as automobile, finishing, leather thinning electroplating, petroleum and textiles dying are known to have toxic effects to the receiving environment.

1.5 Objectives

The overall objectives of this work is to prepare micro porous activated carbon (AC) Sugar Cane Bagasse, (SCB) combined with Natural Zeolite in different ratios to produce an optimum samples for an efficient removal of Lead and Cadmium metal ions from their aqueous solutions.

The specific objectives of this study include:

- To prepare microporous carbon from the biomass by carbonization.
- To activate carbonized carbon by chemical method using KOH or H₃PO₄ activation.
- To blend zeolite with activated carbon using different ratios.
- To characterize the blends of AC/SCB and zeolite.
- To characterize the blends of AC/SCB and zeolite using different techniques in order to find the optimum blend for adsorptions of metals.
- To use the optimum blend to remove heavy metals from aqueous solution under optimized conditions (pH, adsorbent dose, initial metals ions concentrations and contact time on the removal efficiency of ACs).

1.6 Study Scope

This study shall provide a better solution to Pb⁺² and Cd⁺² metal ions removal from aqueous phase by developing an efficient microporous adsorbent. It will also provide an ideal technology to utilize and convert sugar cane baggas waste (from Kenana's Sugarcane Company) to activated carbon, combined with Natural Zeolite into valuable product which can be commercialized for the removal of contaminants from aqueous phase.

1.7 Thesis Organization

The thesis is desired be organized in six chapters.

Chapter-1 is an introductory chapter.

Chapter -2 contains the detailed literature review on various topics related to this research study.

Chapter-3 includes all the materials and methods involved in this work.

Chapter-4 contains the preparation of activated carbon from raw material, sugar cane baggas waste (from Kenana's Sugarcane Company), at different operating conditions and its combination with commercial Natural Zeolite into valuable product and its characterization. AC will be prepared using different chemical activating agents such as KOH and H_3PO_4 . Also contains portrays the potential of prepared product for metals ions adsorption over a wide range of process parameters. In flounce of operating parameters such as pH, adsorbent dose, contact time and initial metal concentration on rate of adsorption will be explored.

Chapter -5 desired to contains conclusions and recommendations.

Chapter Two

Literature Review

2. Summary of Existing Information

Numerous studies on the production of AC from waste biomass materials have been conducted over the past decade. The study[24] conducted experiments using various types of waste biomass materials such as corn husks, cane bagasse, various peanut shells as well as several types of seeds. Their studies centred on finding the optimum process parameters for carbonization as well as activation. They also compared the different types of finished products against one another as well as with that of a commercial AC. Their studies conclude that ACs can be produced from waste biomass materials and the finished products obtain high adsorption capacities. The optimum carbonization temperature was found to be 600°C using phosphoric acid as the chemical activating agent. Research conducted by Thomauske et al. [25] focused on the physical activation of carbons produced from waste biomass materials. They found that the adsorption capacities of the produced ACs increased to a certain degree as the pyrolysis temperature increased, but once temperatures of 900°C were exceeded the quality of the AC deteriorated. The work done by these scientists and engineers, as well as others, have been reviewed and were used to form the basis of the experimental procedure related to this project. Although most of their testing was done with the aim of drinking water treatment, the ACs produced from this project will be used to treat textile effluent water with the main focus being on 520dye removal. The carbonization process will also be conducted under atmospheric conditions rather than in the presence of an inert gas. Although most literature reviewed mentioned the use of an inert gas, the effects of carbonization in the presence of oxygen have little effect on the quality of the AC produced[25].

2.1 Importance of Activated Carbon

Adsorption has gained significant importance as a purification, separation and recovery process on an industrial scale over the last few decades. AC is one of the most widely used adsorbents in industry for environmental applications. According to Bansal et al.[26] any material with a high carbon content and low inorganic content can be used as a raw material for the production of AC[26]. Global AC demands have increased due to the continuous intensification of the global environmental movement as well as rapid industrialization. The high adsorption capacities of ACs are related due to their unique properties such as pore volume, surface area and pore size distribution (PSD). The unique characteristics of ACs are dependent on the type of raw material used and the type of activation employed. Due to increasing demands of AC it is imperative to find a cost-effective and sustainable method of producing AC on a large scale. Although numerous studies have been conducted with regards to producing AC from agricultural waste materials, scientists are still trying to employ new methods in order to obtain ACs with application specific characteristics[27].

2.2 Activated Carbon

Activated carbon, also called activated charcoal, is an amorphous form of carbon that is specially treated to produce a highly developed internal pore structure and a large surface area[27]. AC forms a large and important class of porous solids, which have found a multitude of industrial applications such as decolourization, deodorization, and purification of liquid and gaseous media. The most common primary raw materials used for the production of AC are wood, coconut shell, bituminous coal etc. The charred remains can be easily activated to produce a relatively high quality AC. It is also during the carbonization and activation processes that the unique internal pore structure is created, which gives ACs their superior adsorptive properties[28].

2.2.1 History of Activated Carbon

There have been many well documented studies which depict the use of carbon in ancient times for their adsorbent properties in the purification of oils as well as medicinal uses. Although there is evidence that carbon was used in ancient times, it is almost impossible to pin its exact origin. For many centuries AC that was utilized was in the form of carbonized wood. The Ancient Egyptians and Sumerians were the first people documented to have made use of carbon in the form of wood chars in 3750 B.C. for the reduction of ores in manufacturing bronze and for medicinal purposes. The Ancient Hindus of India used charcoal and sand to filter drinking water and centuries later wood and bone charcoal were used to decolourize and purify cane sugar. However, activated carbon was first used in the 19th century by the English to purify drinking water on a large scale. Today, AC demand has rocketed to an all-time high and its application is no longer restricted to water treatment but many other industrial applications such as refining and recovery[29].

2.3 Preparation of Activated Carbon

Although most carbonaceous materials can be converted into AC, the final properties of the AC depend significantly on the nature of starting raw material. A large number of effective processes have been developed over the past century for making ACs. The general process consists of the pyrolysis of the starting material, followed by a stage of controlled oxidation in order to activate the carbon[30].

2.3.1 Pyrolysis

The pyrolysis step, also known as carbonization, involves heating of the source materials to temperatures ranging between 500°C - 900°C. This process is employed in order to eliminate most of the non-carbon elements such as hydrogen, nitrogen and oxygen as volatile gaseous products. The light volatile matters are first released, followed by the light aromatics and finally the hydrogen gas. The remaining product is referred to as the carbonaceous char. The residual carbon atoms are grouped into a condensed sheet of aromatic

rings with a cross-linked structure in a random manner [31]. The mutual arrangement of these aromatic sheets is irregular and leaves free space between the sheets which may be filled by tarry substances. The activation process is employed in order to remove these tarry substances. The activation process also widens the pores of the AC which were created during carbonization, hence changing the porosity[32].

2.3.2 Activation

The basic properties of a carbon are developed during the carbonization process. The ensuing oxidation step has to be designed to complement the pyrolysis step. During the oxidation process, the oxidizing agent gradually erodes the internal surfaces of the carbon and develops an extensive network of fine pores in the carbon. The oxidation step also changes the surface atoms of the carbon in order to produce specific adsorptive properties. The activation of carbon can be accomplished by two methods, namely physical activation and chemical activation[33].

2.3.2.1 Physical Activation

Physical activation is a two-step process which first involves the carbonization of the carbonaceous material followed by the activation of the resulting char material. The activation is carried out at elevated temperatures in the presence of a suitable gas such as steam, carbon dioxide or nitrogen. The carbonization temperatures usually range from 400°C up to 1100°C and these temperatures are dependent on the application of the desired AC as well as the starting raw material used for the production of the AC[34].

2.3.2.2 Chemical Activation

Chemical activation involves two steps which can be carried out simultaneously or separately, depending on the production requirements. Chemical activation is highly favoured as the process can be conducted in one step which saves valuable time. In chemical activation, the prepared raw material is mixed with chemical activating agents and carbonized at relatively low temperatures. These low temperatures mean that a better developed

porous structure is obtained which results in a superior AC. The chemical activating agents which are generally used are zinc chloride and phosphoric acid. The temperatures at which chemical activation occur are usually within the range of 400°C - 600°C [35].

2.3.2.3 Advantages of Chemical Activation over Physical Activation

The most important advantage of chemical activation is that the process occurs at lower temperatures and for a shorter period of time when compared to the processes employed in physical activation. Very high surface area ACs are obtained with a greater carbon content. The reason for these higher values is due to the chemical activating agents used. The chemical agents contain substances with dehydrogenation properties which inhibit the formation of tar and decrease the production of other volatile components. According to Bansal et al. (1988), the activation of wood can be carried out at temperatures of around 600°C using zinc chloride as the chemical activating agent. Another advantage of chemical activation is that the ratio of chemical agent to raw material can be modified to adjust the porosity of final produced AC[36]. Although there are significant advantages of chemical activation over physical activation, there are important disadvantages which need to be noted. The greatest disadvantage of chemical activation is the incorporation of impurities which are present in the activating agent, and these impurities affect the chemical properties of the AC. Another disadvantage is the high operating costs for the use of a recovery system for the chemical used for impregnation [37].

2.4 Structure of Activated Carbon

The adsorption capacity of a specific AC is highly dependent on its structure. Majority of literature refer to the structure of AC as a modified graphite-like structure. However, recent studies provide a better understanding of the AC structure and these are summarized below[38].

2.4.1 Porous Structure

The unique porous characteristics of AC which include surface area, pore volume and pore size distribution (PSD) are what give the AC its high adsorption capacities. According to Islam and Rouf (2012), all ACs have a porous structure with an ash content of up to 15%. The structure of the pores and the PSD are dependent on the nature of the raw material and activation procedure employed. The pore systems of ACs are complex and individual pores vary greatly in both size and shape. According to IUPAC, three different groups of pores have been identified and these are defined below[39]:

- Macropores (> 50nm diameter).
- Mesopores (2nm – 50nm diameter).
- Micropores (< 2nm diameter).

Majority of the internal surface area of an AC is credited to the micropores as they generally constitute up to 95% of the surface area (Brunauer, 1970). Mesopores are referred to as the transitional pores and contribute less than 5% to the surface area of the AC. Mesopores act as conduits which lead the adsorbate molecule to the microporous network. Macropores contribute very little to the surface area of the AC but they are nevertheless important as they act as transport channels which allow the adsorbate molecules to flow into the mesopore and micropore networks. Figure 1 below depicts the typical PSD of an AC[40].

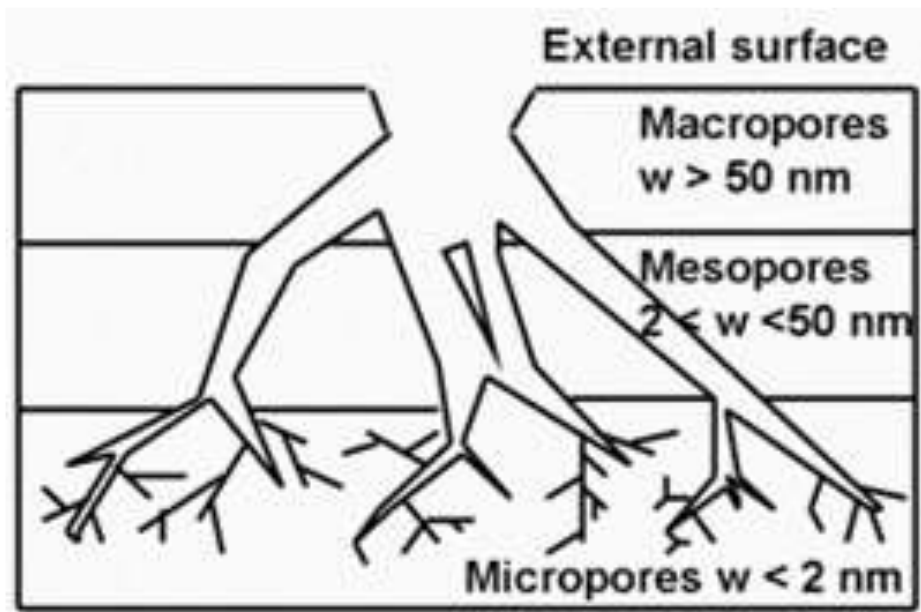


Figure (2.1) Graphical PSD of activated carbon [40]

2.4.2 Crystalline Structure

During the activation process, microcrystalline structures of ACs start to develop. The crystalline structures of ACs tend to differ to those of graphite in terms of interlaying spaces. However, the basic structural unit of the AC is closely approximated by that of the graphite structure.

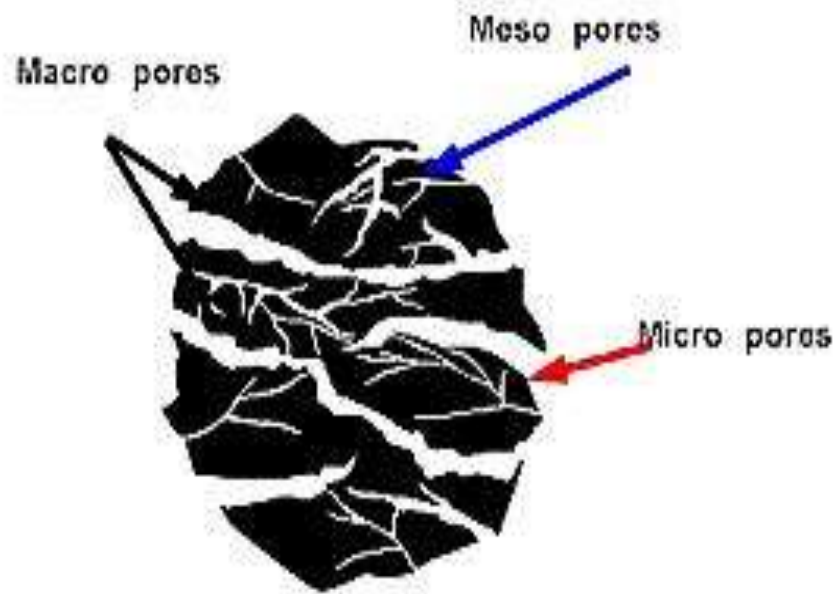


Figure (2.2) Layered structure of activated carbon [40]

2.4.3 Chemical Composition

Apart from having porous and crystalline structures, the surface of an AC also has chemical structure. Although the porous structure of the AC contributes to most of its adsorptive properties, its adsorption capacity is significantly influenced by the small amounts of chemically bonded hetero-atoms [41]. These hetero-atoms include oxygen, hydrogen, sulphur and nitrogen. Studies have shown that oxygen greatly influences the surface behaviour of the AC as well as its catalytic properties[41].

2.5 Classification of Activation Carbon

ACs are unique and complex products due to the nature of their preparation, the type of raw material used and the type of activation employed. It is therefore a complex task of classifying these products into specific groups based on their characteristics. However, a general form of classification has been devised based on the AC particle size. These are powdered activated carbon (PAC), granular activated carbon (GAC) and activated carbon fibres (ACF).

PAC has a typical particle size of less than 1 mm. PACs are generally used in industrial waste water treatment, decolourization in the food industry and various pharmaceutical applications.

GAC has a mean particle size between 1 mm and 4 mm. GACs have better micropore distribution and can be regenerated, hence they have a wider range of applications than PACs.

ACFs are non-graphitizable carbons which have been heat treated in an oxidizing agent. Many of the recent research have been dedicated to finding suitable precursors for the production of this carbon product[42].

2.6 Applications of activated carbon

AC is an effective purification and recovery agent which has gained much popularity in industry over the past few decades. The broad range of AC applications can be split into two categories; 1) liquid-phase applications and

2) gas-phase applications. These categories are explained in greater detail below.

2.6.1 Liquid-Phase Applications

In the water treatment and purification sectors, AC is used in its powdered form (PAC) as well as its granular form (GAC), depending on the specific application. AC was initially used in water treatment to remove colour and odours from water, but in more recent years the AC has been modified to such an extent that it has been used to treat effluent water containing pollutants in order to create potable water and even drinking water [43].

2.6.1.1 Textile Effluent Treatment

The term environment encompasses the whole range of diverse surroundings in which we experience and react to the changes in it. One of the main challenges facing the environment, which includes air, water and land, is pollution. Pollution is an unhealthy and undesirable change in the environment which is caused directly and indirectly by humans through the process of living or through industrial processes. The wastewater effluent generated by the textile industry is one of the largest contributors to water pollution in industry with the major pollutant released being dye. The dye is released during the manufacturing process and enters the wastewater stream where it is difficult to treat in high concentrations. The dyes are also toxic and not easily biodegradable. The textile industry currently employs three methods of treatment[44]:

- i. Primary Treatment: which removes colour and odours.
- ii. Secondary Treatment: involves aerobic and anaerobic treatment.
- iii. Tertiary Treatment: involves numerous processes to ensure the water is reusable.

2.6.2 Gaseous-Phase Applications

Gas phase applications include separation, gas storage and catalysis. The products treated are generally more expensive than those used in the liquid phase applications. Some of the popular applications include:

- Solvent recovery.
- Natural gas purification.
- Removal of pollutants in air conditioning and exhaust systems.
- Removal of odorous substances.
- Flue gas cleaning.

2.7 Adsorption Process

Adsorption is the desired separation of substances from liquid or gaseous media and involves the concentration of the substance onto the surface of a solid substrate. The adsorbing medium is the adsorbent and the substance removed/adsorbed is the adsorbate. The driving force of adsorption is the ratio of partial pressure to vapour pressure of the compound in gaseous phase adsorption and the ratio of concentration to solubility of the compound in liquid phase[45].

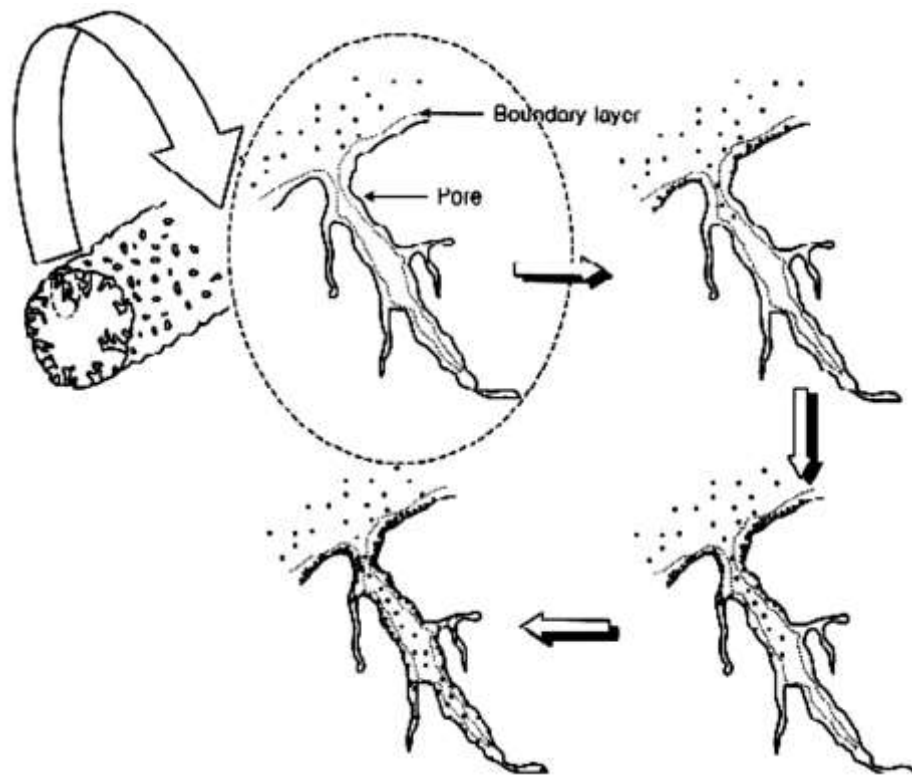


Figure (2.3) Conceptual diagram of dye adsorption on activated carbon fiber

2.7.1 Access to Clean Water

Water is a very important aspect in life and a treasure for any country aspiring for human civilization[46]. Provision of a suitable environment for economic and overall growth requires that clean water for consumption and other activities such as domestic and agriculture is easily available. Methods of providing clean water should also not be too expensive for the consumer. Unfortunately, there is evidence of decreased water per capita and it is foreseen that by 2025, water demand will be higher than the supply [47].

The 21st century is experiencing striking challenges of providing unpolluted and affordable water for human consumption. There is a water supply struggle evidenced in many countries worldwide to keep up with the increasing demand that is worsened by water pollution, high rate of population growth and global climate change[48]. Anthropogenic activities especially agriculture, sewage disposal, food processing and other industrial and land-use activities such as mining and ore-processing all contribute to water quality deterioration [49]. In Kenya, there is intermittent supply of water and its accessibility is still wanting in many of the low income areas [50]. This is especially common in urban slums and rural areas and it is worsened by rapid population increase.

2.7.2 Water Contaminants

Major water contaminants include turbidity, dyes, bacteria or pathogens in general, oil and its derivatives, pharmaceuticals, pesticides, personal care products, heavy metals and sediments[51]. Wasewar, 2010, emphasizes that heavy metals persist indefinitely in the environment and are hazardous to public health. Effluents from agricultural, mining, domestic and industrial activities are a major source of heavy metal contamination in water that causes health complications directly by consumption of the contaminated water or indirectly when the heavy metals accumulate through food chains. Some dyes released from textile industries also have heavy metals in their structure which are health hazards too [52].

Lead and cadmium are the most commonly bioavailable out of the known toxic heavy metals such as copper, mercury, chromium, arsenic, zinc and nickel [53]. The source of cadmium is attributed to its use in making anticorrosion protective coating for metals, in alloys and batteries [54]. Exposure to cadmium ions over a long time produces damage to kidneys, lungs, liver and respiratory system generally in addition to being carcinogenic[55]. Some industries use lead, for instance those manufacturing batteries, cables, pigments, metals, paints, steel and alloys, glass and plastics. Their discharge contaminates water making it unsafe for use[56]. Lead poisoning affects children more than adults and the affected show lower intelligent quotient, concentration disorders and behavioural changes. Generally, effects of lead poisoning are teratogenic and neurological in nature. It causes degeneration of the axon, cerebral oedema, infertility, menstrual disorders, abortions and stillbirths among other effects. Cadmium, lead and aluminium in drinking water hike the risk of hip fractures [57].

2.7.3 Common Techniques used to remove Heavy Metal Ions from Water

Various methods have been considered for removing heavy metal ions from wastewater and the common ones include reverse osmosis, electrochemical methods, ion exchange, electro-dialysis, chemical precipitation, flotation and membrane filtration [58]. Limitations accompanying these methods include incomplete removal, high energy and reagent requirements, generation of toxic sludge and other wastes that require disposal and are limited in decontaminating water with heavy metal ions in a low concentration range[59]. For example, chemical precipitation is simple and inexpensive but it is usually adopted to treat water containing high concentration of heavy metal ions. In ion exchange, resins are regenerated by chemical reagents on exhaustion which can cause substantial secondary pollution [60]. The high energy consumption is also a drawback for electro-dialysis process.

Batnagar and Mika, 2010, emphasize that selection of a water treatment process should take into account waste disposal constraints, desired water

quality, capital and operating costs in addition to space for construction of equipment. They further highlight that of the many methods employed, most require substantial input and cost factors override importance of pollution control hence their use is restricted to large scale applications [61].

2.7.4 Lead II

Lead is one of the most dangerous contaminants which is released to the environment by various anthropogenic activities[62]. In the air, lead is in the form of particles and is removed by rain or gravitational settling. The solubility of lead compounds in water is a function of pH, hardness, salinity, and the presence of humic material. Solubility is highest in soft, acidic water. The sink for lead is the soil and sediment. Because it is strongly adsorbed to soil, it generally is retained in the upper layers of soil and does not leach appreciably into the subsoil and groundwater. Lead compounds may be transformed in the environment to other lead compounds; however, lead is an element and cannot be destroyed. Anthropogenic sources of lead include the mining and smelting of ore, manufacture of lead-containing products, combustion of coal and oil, and waste incineration. Many anthropogenic sources of lead, most notably leaded gasoline, lead-based paint, lead solder in food cans, lead-arsenate pesticides, and shot and sinkers, have been eliminated or strictly regulated due to lead's persistence and toxicity. Because lead does not degrade, these former uses leave their legacy as higher concentrations of lead in the environment[62] .

Based on a survey of 900 public water supply systems, EPA in 1988 estimated that 99% of the 219 million people in the United States using public water supplies were exposed to drinking water with levels of lead $<5\text{mg/L}$ and approximately two million people are served by drinking water with levels of lead $>5\text{mg/L}$. A survey of 580 cities in 47 states indicated that the national mean concentration of lead in drinking water was 29mg/L after a 30s flushing period. However, it was estimated that in 1988 the average lead content of drinking water decreased to 17mg/L . In 1991, EPA examined the occurrences

of lead in source water and distributed water. By resembling at the entry point to the distribution system, few samples were found to contain lead at levels above 5mg/L. EPA now estimates that approximately 60 groundwater systems may have water, leaving the treatment plant, with lead levels above 5mg/L. Based on several data sets, it is estimated that <1% of the public water systems in the United States have water entering the distribution system with lead levels above 5mg/L. These systems are estimated to serve <3% of the population that receives drinking water from public systems[63].

Lead poisoning is a medical condition caused by increased levels of the metallic lead in the blood. Lead may cause irreversible neurological damage as well as renal disease, cardiovascular effects, and reproductive toxicity. Humans have been mining and using this heavy metal for thousands of years, poisoning themselves in the process due to accumulation, exposure and direct contact. These dangers have long been known, though the modern understanding of their full extent and the small amount of lead necessary to produce them is relatively recent; blood lead levels once considered safe are now considered hazardous, with no known threshold. The current EPA and WHO drinking water standard for Pb^{+2} is 0.05mg/L and 10mg/L, respectively. Pb^{+2} accumulates mainly in bones, brain, kidney and muscles and may cause many serious disorders like anemia, kidney diseases, nervous disorders and sickness even death[64].

Recently, the removal of Pb^{+2} ions from drinking water has been focused due to its high toxicity to humans in terms of nausea, convulsions, coma, renal failure, cancer and subtle effects on metabolism and intelligence. Different approaches to remove Pb^{+2} ions from wastewater, including chemicals precipitation, ion exchange, reverse osmosis, electro kinetic remediation, phytoremediation and adsorption have been used to reduce the concentrations to safe levels before discharge into fragile environments[64].

2.7.5 Cadmium II

Cadmium is a trace, extremely toxic metal. In nature it occurs in trace amounts and presents 0.00005% of the crust of the earth (Jankiewicz et al. 2000). In comparison with other heavy metals, it is an environmental pollutant, but easier than the others accumulated in the food chain.

Cadmium can get into the bloodstream by absorption from stomach or intestines after food or water ingestion or by absorption from lungs after inhalation. It mainly accumulates in the kidneys and at high levels it can lead to serious kidney failure. The major route for cadmium intake is its ingestion. This is largely due to the presence of trace levels of cadmium in foodstuffs of natural origin or use of phosphate fertilisers and sludge on agricultural soils. The metal in trace amount is very important industrially, it is widely used in special alloys, pigments, coatings stabilisers and in rechargeable nickel cadmium batteries [64].

2.8 Adsorption as an Alternative Method for Water Remediation

Adsorption implies the formation of a thin layer of molecules of some substance to the surface of a solid or liquid. The solute that accumulates is called adsorbate and the surface onto which it adheres is referred to as adsorbent[64]. Adsorption is among the alternatives for removing heavy metal from water. It is convenient, easy to operate and simple in design. Furthermore, since adsorption can sometimes be reversed, adsorbents may be renewed by suitable desorption procedures [64].

According to Batnagar and Mika [64], adsorption is an important purification method in industry particularly in wastewater treatment because it can remove a variety of pollutants. They compiled a report on materials that have been widely applied as adsorbents in water decontamination like activated carbon, silica gel, Natural Zeolites and activated alumina. From their report, they concluded that cost implications when selecting the adsorbent materials for use in water remediation is an important factor to consider [64]. The most widely used adsorbent is the coal-based activated granular carbon. It is

versatile and can remove different types of water contaminants but its application is limited due to its high cost and the fact that it is based on a non-renewable source [65].

2.9 Application of Biosorbents

Biosorbents are inactive non-living materials from biomass and cellular products such as cellulose and lignin that can be utilized in eliminating pollutants from water or any other solution. Metal biosorption occurs when there is high attractive force between the biosorbent and the dissolved metal ion. It may also be due to presence of functional groups like hydroxyl, carboxyl and amines among others [66]. The type of functional groups on the adsorbents determines the adsorption selectivity for heavy metals. For instance, carboxylic and amino groups have been reported to adsorb more lead (II) than cadmium (II) ions [67]. On the other hand, more sorption of cadmium (II) than lead (II) is observed on functional groups containing a sulfur atom bonded to a hydrogen atom [68]. Biosorption has the advantage of cost effectiveness in decontaminating water containing heavy metal ions [69]. Biomass wastes such as banana peels, sugarcane bagasse, orange peels and others contain high lignocellulose therefore numerous pores and large internal surface area [70]. Various low-cost biomasses have been studied for removing pollutants in water which include anaerobically digested sludge, algae, bacteria and fungi. Agricultural wastes which have also been investigated include soybean and cotton seed hulls, rice bran, crop milling waste, maize cob meal, groundnut husk sawdust and coconut shell. Activated carbon from agricultural byproducts is effective and relatively cheaper due to their abundance and ease of availability [71].

Minamisawa and coworkers studied adsorption of Cd^{2+} and Pb^{2+} onto the biomaterials namely aloe, green tea, chitosan, coarse tea, Japanese coarse tea and coffee. They reported blend coffee, coarse tea and green tea to have adsorptive capacities nearly equal to Natural Zeolite and activated carbon [72]. Agwaramgbo and coworkers investigated removal of Pb^{2+} from water using

charcoal, caffeine, un-brewed coffee, fishbone and tea reporting efficient removal of over 70% except for caffeine extract at 1% [73]. Studies by Demiral and coworkers indicated that hazelnut bagasse carbon activated with zinc chloride has high potential in removal of sandolan blue textile dye by adsorption. They reported adsorption capacities of 357.14, 370.37 and 450.25mg/g at 25, 35 and 45°C respectively [74].

With all these studies, it is important to note that pollutants adsorb differently onto the named adsorbents since each has unique properties. Studies must be done for specific pollutants and specific adsorbents before application to achieve maximum output. For instance, Kobya and coworkers proved that the efficiency of apricot stone activated carbon is dependent on the type of ion since it showed high efficiency in removing cadmium ions from water but was inefficient in removal of lead ions [75].

Sugarcane bagasse, the fibrous material that remains after sugarcane juice has been extracted, is of research interest in part due to its disposal challenges around sugar mills, around markets and homesteads and also because it has shown the potential as a bioadsorbent for metal ions [76]. Globally, about 240 million tons of bagasse results from production of approximately 800 million tons of sugar annually[77]. This bagasse is used as fuel for mill boilers in generation of steam and electricity, but this still remains in excess posing a disposal menace. In addition to other avenues of its utilization, sugarcane bagasse has been applied in adsorption of some metal ions from synthetic wastewater. The degree of success in adsorption differs from one metal to another and depends on prevailing experimental conditions [78].

For instance, Zn^{2+} ions were successfully removed by modified bagasse fly ash whereby at low concentrations there was 100% removal and 65% at higher concentrations[79]. Reza and others obtained 35% Zn^{2+} removal by charcoal ash at optimized conditions and the process was endothermic [80]. Mohan and Singh obtained 100% removal of cadmium ions at a pH value of 8. Ibrahim and coworkers investigated adsorption kinetics of unprocessed

bagasse towards cadmium ions and reported rapid adsorption rate and that cadmium ions adsorbed by chemisorption[81]. Gupta and Sharma[81], converted bagasse fly ash into an efficient adsorbent for zinc ions from water. Bagasse pith was studied by McKay and coworkers for the removal of two acidic dyes and two basic dyes from aqueous solutions [82]. Equilibrium results from Irfan and Umi, 2006, on adsorption of Cu^{2+} have shown that chemically treated sugarcane bagasse activated carbon increases the adsorption capacity by 50%. Krishnan and Anirudhan[82], worked on steam activated sulphurised carbon from bagasse pith for removal of cadmium(II) ions and reported high capacity of 149.9mg/g. Sugarcane bagasse was used to make activated carbon by Qureshi and coworkers to improve removal properties for sugar colourants and reported that steam activated carbon at 900°C had best potential for producing activated carbon for sugar decolourization[83].

All the above studies indicate that there is need to determine the best adsorbent for particular ions and/or pollutants in water and optimize operating variables for maximum output. Different methods of activation or preparation of adsorbents also produce different adsorption capacities. Various studies provide data for comparison, and the current study aimed at determining the capacity of bagasse activated with sodium hydroxide, unprocessed bagasse and its carbon activated after pyrolysis, towards cadmium and lead ions in water. A comparison with other adsorbents from other studies was also done.

2.10 Kenana Sugar

The Kenana Sugar Factory is a sugar cane factory located in the White Nile state that includes the Kenana Sugar Company Ltd. in Sudan. It is a partnership between the Government of Sudan and a number of other countries, the most important of which is Kuwait. The factory is located in the city of Kenana of the White Nile State in the southeastern side, 21 km from the city of Rabak in the White Nile State. And the factory produces more than 300 thousand tons to cover the local consumption of sugar in Sudan and is

one of the largest single factories that produce sugar in the world. The factory was named after the city of Kinana, which was named after the Kinana tribe that lives in it. Kenana Sugar Company has accumulated experience in the industry and production of sugar over a period of more than 30 years and is considered one of the world's leading companies in the sugar industry, and it has a presence in the global markets. In addition, it is always seeking and tending to diversify its investments to reduce potential risks, and diversify sources of income as Kanana is one of the companies Qualified to implement projects inside and outside Sudan with its high technical capabilities. Finally, Kenana is considered a member of international institutions and organizations of sugar manufacturers in the world.

2.11 Natural Zeolites (Clinoptililite)

Zeolites represent a family of hundreds of microporous mineral members known for their ion-exchange properties. The term “zeolite” coined in 1756 by the Baron Axel Fredrik Cronstedt, a Swedish mineralogist and chemist, derives from the Greek language ζέω (“zeo”, to boil) and λίθος (“lithos”, stone) meaning “boiling stone”. The structure of the zeolites mainly consists of alumino-silicates with SiO_4 and AlO_4 structures connected by shared oxygen atoms. Clinoptilolite is one of the most abundant natural zeolites, widely distributed throughout the world and used for its ion exchange and adsorbent properties. Thanks to its remarkable and unique ion-exchange properties in water, it has been employed for various medical, industrial and environmental uses, in particular, for sequestration of toxic pollutants from industrial effluent and wastes. At present, many positive effects are recognized due to the capacity of natural occurring zeolite clinoptilolite (ZC) to adsorb and therefore remove harmful substances like heavy metals, ammonia, or other small molecules in the gastrointestinal tract of humans. It is important to mention that this positive impact can improve through modifications of ZC due to micronization of ZC (M-ZC) or tribomechanical activation of ZC (TMAZ) or double tribomechanical activation of ZC (PMA-

ZC), known as Panaceo Micro Activation. This recently developed PMA (Panaceo Micro Activation)-technology is a special tribomechanical micronization process that causes self-collisions of zeolite particles and contributes to increasing the surface charge and the cation exchange of the individual particles, improving the overall therapeutic performance of ZC. The oral application of the specific PMA-zeolite in a randomized clinical trial in humans furthermore suggests having a positive impact on the intestinal tract as it positively influenced the intestinal wall integrity. Preclinical data furthermore suggest a positive impact on the intestinal microbiome. This connection might be interesting as recent studies have established a possible link between the gut microbiome and chronic neurological disorders. This possible link has been termed as the “Gut-Brain Axis”.

Natural zeolite is widely used in agriculture fertilizer, water filter, heavy metal absorption, animal feed additive, oil-gases absorbent, aquaculture ammonia removal, construction, aquariums, livestock farming, environmental protection, and in various industrial uses. Heavy metal and chemical toxicity can be the cause of many-body health trouble. Therefore, high pure, and safe zeolite powder as a molecular sieve can help detox heavy metals and many other pollutants of the environment, it can help to effectively improve more health of the soil, animal, plant, and body.

Chapter Three

Materials and Methods

Laboratory experiments presented in this chapter were carried out in order to evaluate the adsorption efficiency of the prepared activated carbon, produced from Kanan's Sugarcane Bagasse, combined with Natural Zeolite. Series of experiments were conducted to determine adsorption capacity of the optimum samples derived from this combination for heavy metals ions removal; Lead (II), and Cadmium (II). The chapter also describes in detail various materials, chemical reagents and equipments, and outlines the experimental procedures used in this work for preparing the raw materials, then the chemical activation and equilibrium studies.

3.1 Materials

3.1.1 Sample

Sugarcane bagasse is new alternatives as a replacement to existing product of activated carbon. Bagasse pitch is a waste product from sugar refining industry. It is the name given to the residual cane pulp remaining after sugar has been extracted. Bagasse pitch is composed largely of cellulose, pentose, and lignin. The carbonaceous precursor used for preparation of activated carbon (AC), was Sugar Cane Bagasse, collected from Kenana Sugar Company in White Nile State -Sudan. Prior to use, samples were washed gently with water to remove impurities present on the surface and then dried for one week. Burning is carried out in absence of oxygen in furnace at 600°C for one hour.

3.1.2 Chemicals

All chemical reagents used in this work were analytical grade (Merck, Germany) or (Fluka, Germany), used without further purification.

Pb(II) and Cd(II) ion aqueous solutions were prepared by dissolving respective amount of the metal nitric salts, $\text{Pb}(\text{NO}_3)_2$ (Merck-Germany), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Fluka, Germany), in double distilled water. The initial

metal ions concentration used in the adsorption equilibrium experiments were in the range between 10-150 mg/L. (KOH and H₃PO₄). Natural Zeolite (Clinoptililite) was brought from Khartoum State Water Authority.

3.1.3 Equipements:

Scanning Electron Microscopy (SEM), Energy Dispersive X-ray spectroscopy (EDX), Fourier Transform Infrared Spectroscopy(FTIR), Iodine number and Atomic Adsorption Spectrophotometer (AAS).

3.2 Methodology

3.2.1 Preparation of Inactivated Carbon

Sugar Cane Bagasse was dried. Crushed and grinded in ball mill. The grinded samples were sieved to obtain particles of uniform (90 μm).

3.2.2 Preparation of Activated Carbon

Cleaned and dried bagasse samples were burned in absence of oxygen in furnace at 600°C for one hour. The carbonized materials obtained from Sugar Cane Bagasse was cooled to room temperature, crushed and grinded in a ball mill. The grinded sample was sieved to obtain particles of uniform. The precursor obtained was washed to remove surface bounded impurities and dried at 105°C for 24h. Two 100g of the precursor were impregnated with Phosphoric Acid H₃PO₄ and Potassium Hydroxide, KOH for 24 h in ratio of 1: 1.5 at 50°C to achieve well penetration of the chemical into the interior of the precursor. To remove the residual chemical agents until the pH value of the rinsed water was neutral. The adsorbents prepared were denoted as AC(KSCB) H₃PO₄ and AC(KSCB) KOH throughout the work, and shown in Figure (3.2).

3.2.3 Combination of activated carbon and natural zeolite

A series of activated carbon prepared from sugar cane bagasse, abbreviated AC/SCB, and natural zeolite, abbreviated NZ, were prepared using different ratios as illustrated at table 3-1:

Table 3-1. AC/SCB and NZ blends

Sample no.	AC (KSCB) (KOH)	Zeolite
1	0.9	0.1
2	0.8	0.2
3	0.7	0.3
4	0.6	0.4
5	0.5	0.5
6	0.4	0.6
7	0.3	0.7
8	0.2	0.8
9	0.1	0.9
10	1.0	0.0

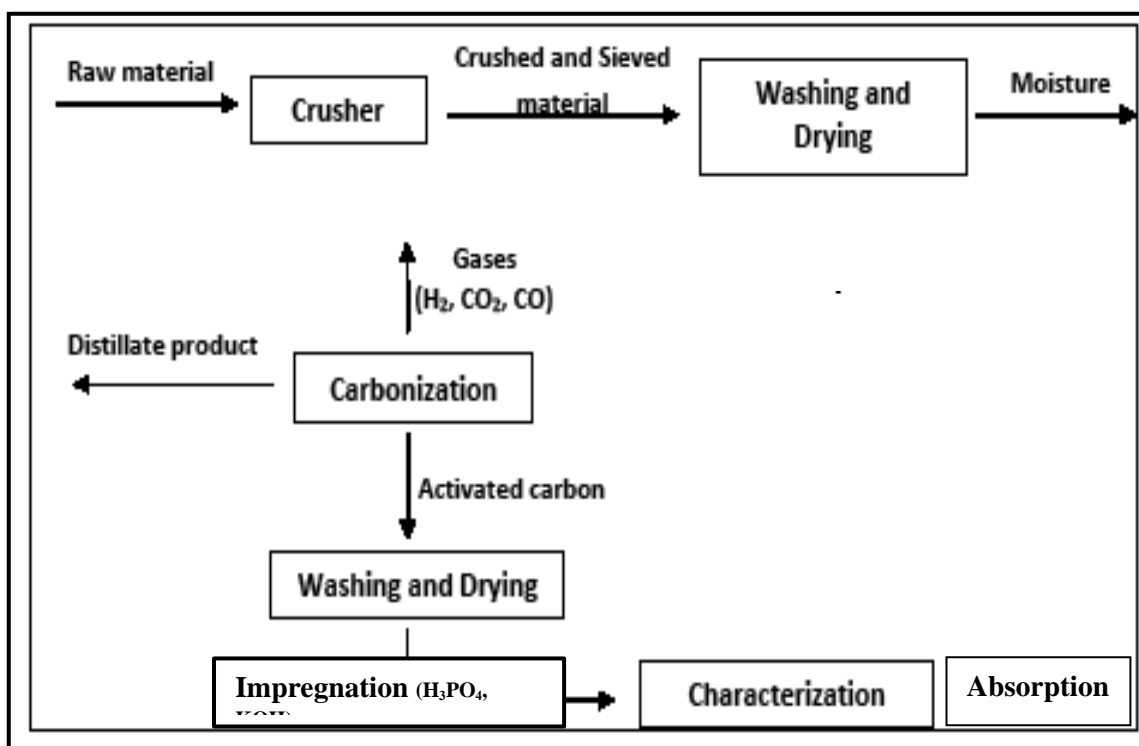


Figure (3.1) Schematic diagram for preparation of activated carbon



(A)



(B)



(C)



(D)

Figure (3.2) Images of activated carbon obtained from Sugar Cane Bagasse (A) before, (B) after carbonization process, and Natural Zeolite (C) before and (D) after combination with carbonized Sugar Cane Bagasse

3.2.4 Characteristics of Adsorbents

The activated carbon samples were evaluated four ways:

3.2.4.1 Scanning Electron Microscopy (SEM)

SEM analysis of all activated and inactivated samples were performed by using (JSM-6380LA) scanning electron microscope. The SEM instrument was operated at 5kV/SE(Accelerating Voltage Machine),and 50°C inclination. Before analysis, all samples were ground and coated in a sputter coating unit (Edwards Vacuum Components Ltd., Sussex, England) to reduce charging and improve the secondary electron signals for imaging. The micrographs were recorded using photographic techniques.

3.2.4.2 Energy Dispersive X-ray spectroscopy (EDX)

EDS detector is a self-enclosed vacuum system (called cryostat) with liq. N₂, or a cryogenic pumping. The crystal and FET are mounted on cold finger within cryostat to reduce the noise by cooling. The cooling is necessary as the detector produces small charge pulses. At low voltages, the resolution of the detector depends upon the noise. The X-ray peaks are typically 2-10 eV wide (FWHM). However, due to noise, this width can increase by at least an order of magnitude. The vacuum level should be maintained such that the condensation of molecules on crystal can be avoided. In detector crystal material used is silicon (Si), drifted with lithium (Li) [around 3mm thickness] for small levels of impurity compensation. When X-rays are incident on the crystal of detector then its energy gets absorbed by a series of ionizations within the semiconductor to generate electron-hole pairs. The absorption of every 3.76eV of X-ray radiation generates an electron-hole pair. Therefore, 1,966 electrons are generated by a Ni K α X-ray photon (7,471 eV). The electrons promoted to the conduction band can freely move in the crystal lattice. Every excited electron leaves behind a 'hole' in the valence band, which acts as a free (positive) charge carrier within the crystal. When the front and back face of the crystal are biased with high voltage, these electrons and

holes are swept towards the opposite poles, thereby generating a charge signal, whose size is proportional to the incident X-ray energy.

3.2.4.3 Fourier Transform Infrared Spectroscopy (FTIR)

The surface of the all samples were estimated by Fourier Transform Infrared (FTIR) spectroscopy (Shimadzu, Japan). The transmission spectra of the sample were recorded using the KBr pellet. About 1.0-2.0% of each sample was mixed with dry KBr and grinded in mortar. Then the sample were dried overnight at 100 °C and then inserted into the FTIR sample holder for the analysis which were recorded within 400 – 4000 cm⁻¹.

3.2.5 Atomic absorption spectroscopic analysis

The AA-6880F Series automatically optimizes the gas flow rate by measuring the changes in absorbance between a blank and a standard sample.

At least 1 mL (1000 µL) volume of a liquid sample is required for the continuous intake of sample during normal flame analysis. With micro sampling, however, approximately 50 to 90 µL of sample is injected in one shot into the flame and quantitation is based on the height and area of the peak signal obtained. This method offers the advantages listed below.

Examples of the measured waveforms (overlaid) and calibration curve for micro sampling analysis are shown to the right. A 2-ppm Cu standard solution was prepared by auto-dilution using the autosampler. The autosampler can also be used to conduct dilution measurements of the sample. (Injection volume: 90 µL).

Pb(217.0nm) CSye

Analyst: Munir, O
File Comment:

Comment:
pb sol = 0.07ug/L

Optics Parameters

Element:	Pb
Socket #:	10
Lamp Current Low(mA):	217.0
Wavelength(nm):	0.5
Slit Width(nm):	BGC-D2
Lamp Mode:	

Atomizer/Gas Flow Rate Setup

Fuel Gas Flow Rate(L/min):	2.0
Flame Type:	Air-C2H2
Burner Height(mm):	7
Burner Lateral Pos.(pulse):	0
Burner Angle(degree):	0

Measurement Parameters

Order:	1st
Zero Intercept:	No
Conc. Unit:	mg/L
Repetition Sequence:	SM-M-M...
Pre-Spray Time (sec):	3
Integration Time (sec):	5
Response Time:	1

	Num.Reps.	Max.Reps.	RSD Limit	SD Limit
Blank	1	1	3.00	0.00000
Standard	1	1	3.00	0.00000
Sample	3	4	3.00	0.00000
Reslope	1	1	3.00	0.00000

QA/QC Parameters
QC Type: _____ Judge Calc: _____ Standard Value: _____

Cd(228.8nm)

Analyst:
File Comment:

Comment:
Flame

Optics Parameters

Element:	Cd
Socket #:	1
Lamp Current Low(mA):	8
Wavelength(nm):	228.8
Slit Width(nm):	1.0
Lamp Mode:	BGC-D2

Atomizer/Gas Flow Rate Setup

Fuel Gas Flow Rate(L/min):	1.8
Flame Type:	Air-C2H2
Burner Height(mm):	7
Burner Lateral Pos.(pulse):	0
Burner Angle(degree):	0

Measurement Parameters

Order:	1st
Zero Intercept:	No
Conc. Unit:	mg/L
Repetition Sequence:	SM-M-M...
Pre-Spray Time (sec):	3
Integration Time (sec):	5
Response Time:	1

	Num.Reps.	Max.Reps.	RSD Limit
Blank	1	1	3.00
Standard	1	1	3.00
Sample	1	1	3.00
Reslope	1	1	3.00

QA/QC Parameters
QC Type: _____ Judge Calc: _____ Standard Value: _____

3.3 Effect of Process Parameters

3.3.1 Effect of pH

Effect of pH on metals adsorption was monitored over a pH range of 2 to 10, using electronic. In this study, 25 ml of separate solutions 75 mg/L metal was transferred into pH metals 100 ml conical flasks shaking well for 30 min with 0.25g Adsorbents each modified with Natural Zeolite, at 25°C. The mixture was filtered and the filtrate analyzed for residual metal ion concentration using Atomic Adsorption Spectrophotometer (AAS).

3.3.2 Effect of Contact Time

In order to study the effect of contact time on the percent removal of Pb(II) from aqueous solution, experiments were carried out at initial concentration of 75 mg/L using (0.25g) Adsorbents each modified with Natural Zeolite dose and different contact times from (15-180) minutes. The mixtures were filtered, centrifuged and residual metal ions in filtrate analyzed spectrophotometrically, (AAS).

3.3.3 Effect of Adsorbent Dosage

To determine the optimum adsorbent dosage, experiments were carried out by adding different weights of Adsorbents each modified with Natural Zeolite ranging from 0.05 to 1.50 g to 75 ml of desired the optimum concentration of metal ions in 250 ml conical flask at the optimum pH for Pb(II) and Cd(II) metal ion solutions. Aliquots concentration was analyzed to determine the extent of adsorption of each metal ions at equilibrium[85].

3.3.4 Effect of Initial Metals Concentration

25 ml solutions of metal ions with different initial concentrations between(10.0 – 150.0 mg/L) of each Pb(II) and Cd(II) were contacted with optimized adsorbent dosage 0.25 g at their optimum pH. The mixtures were shaken well for the optimum time at 25C°. The mixtures were filtered, centrifuged and the concentrations of the metal ions adsorbed were determined.

3.4 Equilibrium Adsorption Studies

The adsorption isotherms for the adsorption of Pb(II) and Cd(II) metal ions on Adsorbents each modified with Natural Zeolite, at 25°C were investigated by varying initial concentration from concentrations between (10.0–150.0 mg/L) of each Pb(II) and Cd(II), at optimized adsorbent dose, contact time, pH, temperature, and stirring speed (established after optimization of working parameters). The equilibrium data were investigations using Langmuir and Freundlich Isotherms models. The data obtained in the batch modes were used to calculate the equilibrium metal ion adsorptive amounts (mg/g) using the following expressions[86]:

$$q_e = (V/w) (C_0 - C_e) \quad (3.1)$$

$$\% \text{ Removal} = 100 (C_0 - C_e) / C_0 \quad (3.2)$$

Where q_e is the amount of the heavy metal ion adsorbed by the Adsorbents sample, each modified with Natural Zeolite in (mg/g), C_0 and C_e are the initial and equilibrium concentrations of the metal ion respectively in (mg/L), V is

the volume of the solution treated in (L) and w is the adsorbent mass of (Adsorbents sample, each modified with Natural Zeolite in (g) [87].

Chapter Four

4. Result and Discussion

4.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy images of the modified activated carbons with natural zeolite when using KOH and H_3PO_4 as activators are shown in Figs 4.3.1. and 4.3.2. The SEM scans show that the optimum prepared samples of the modified activated carbons { Samples No. 7 the best optimum one when using KOH activator (85% KSCB + 15% Zeolite)} and {Sample No. 4 the best optimum one when using H_3PO_4 activator (40% KSCB + 60% Zeolite)} has a more developed porous structure than the other prepared ones when using other different fractions from KSCB/ KOH modified with zeolite and KSCB/ H_3PO_4 modified with zeolite. The scans further show that the treatment (post and pre) enhanced the porous structure of the modified activated carbon leading to the development of channels and pores. Although, the enhancement also lead to great increase in the surface area. The enhancement in surface area, in the case of the post treated modified samples, is likely due to the interaction of zeolite and ashes due to the acidic and basic nature of the KOH and H_3PO_4 activators. Nevertheless, the scans showed that zeolite has deposited on the surface of the post treated activated carbon samples. On the other hand, the increase in the surface area of the pre-treated KSCB activated carbons is likely due to the opening of the structure of the biomass due to the acidic and basic digestion in the KOH and H_3PO_4 solution. The deposition of the zeolite is observed to be more thoroughly distributed through the ridges, channels and pores of the pre-treated KSCB activated carbons.

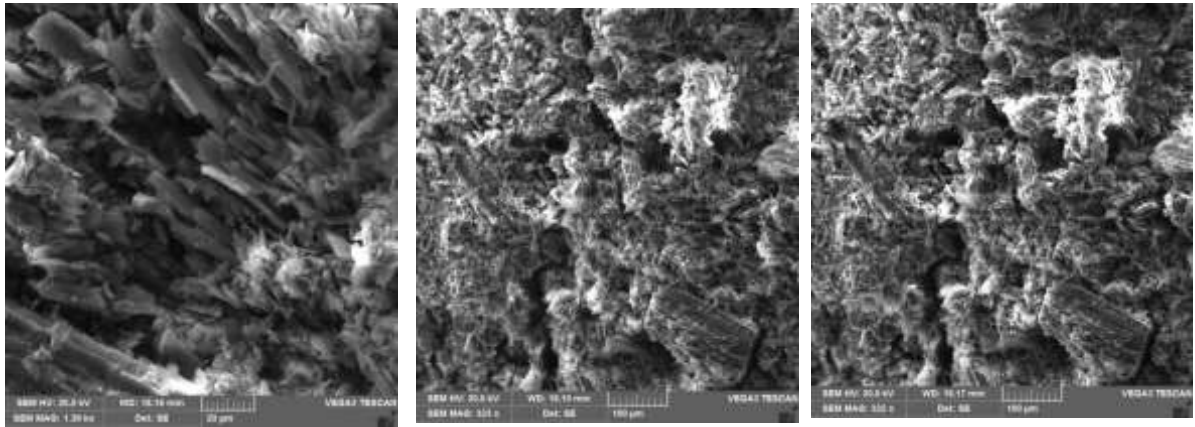


Fig.(4.1) Sample No. 7 the best optimum one when using KOH activator
(85% KSCB + 15% Natural Zeolite)

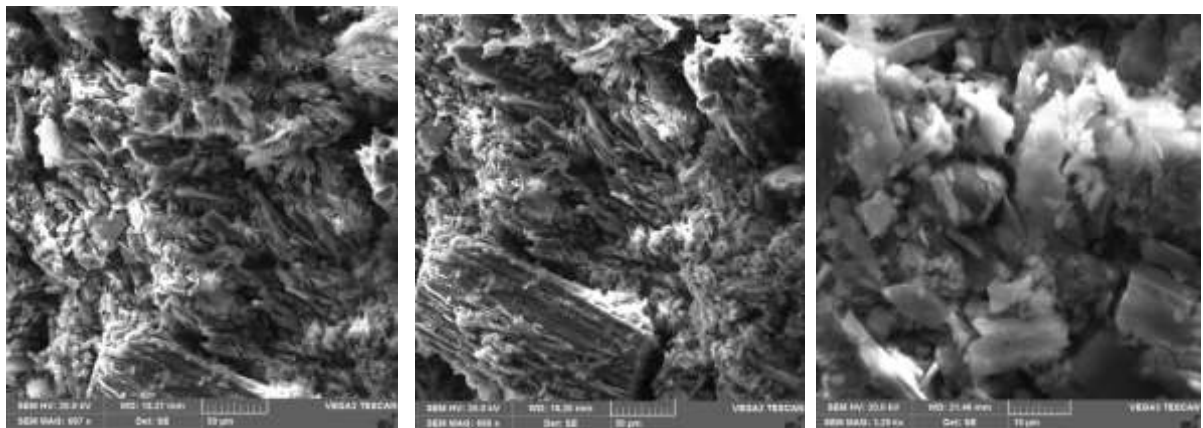


Fig.(4.2) Sample No. 4 the best optimum one when using H_3PO_4 activator
(40% KSCB + 60% Natural Zeolite)

4.2 Energy Dispersive X-ray spectroscopy (EDX)

the modified activated carbons { Samples No. 7 the best optimum one when using KOH activator (85% KSCB + 15% Zeolite)} and {Sample No. 4 the best optimum one when using H₃PO₄ activator (40% KSCB + 60% Zeolite)}. In this analysis, several elements appeared: potassium and phosphorus, due to the activation of (KOH) and (H₃PO₄). Silicon, calcium and iron elements also appeared, and this is a result of zeolite.

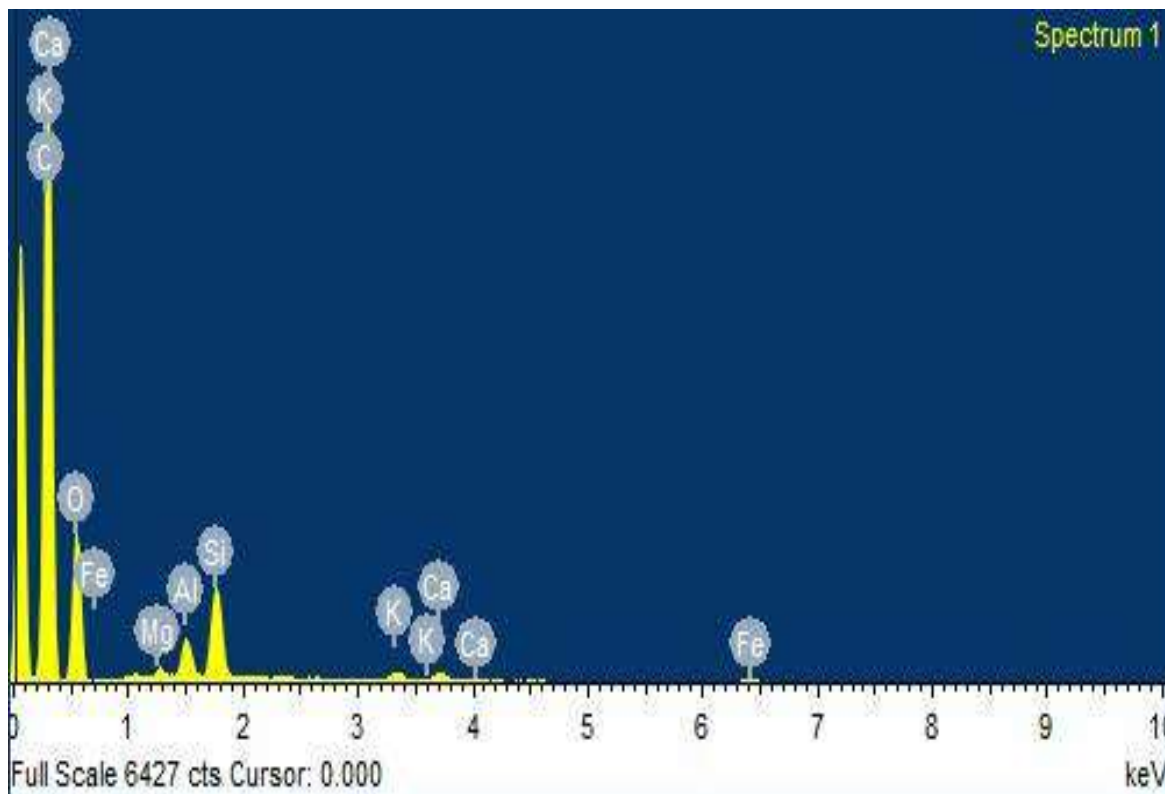


Fig.(4.3) Sample No. 7 the best optimum one when using KOH activator
(0.85g KSCB + 0.15g Natural Zeolite)

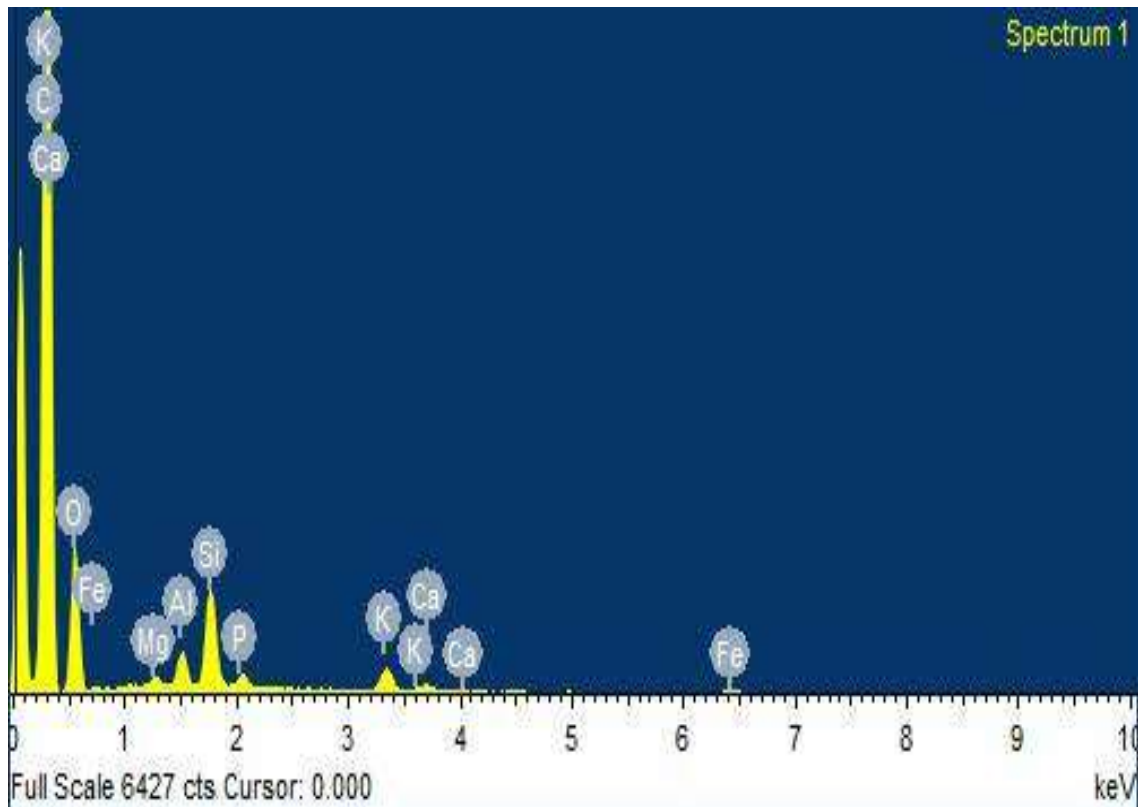


Fig.(4.4) Sample No. 4 the best optimum one when using H₃PO₄ activator
(40% KSCB + 60% Natural Zeolite)

4.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FT-IR spectra of the two adsorbents, prepared activated carbon AC (KSCB)KOH and AC(KSCB)H₃PO₄ Combined with Natural Zeolite, were performed in order to explore the surface characteristics of the biosorbents (Figs.1and 2). The spectra display a number of absorption peaks, indicating the possible functional groups present on these biosorbents that may be responsible for the removal of the two metal ions from their aqueous solutions. The peak positions were observed at 3564.45, 1435.12, 1597.06, 1207.44, 1161.15 cm⁻¹ for AC (KSCB)KOH and 3442.13, 1458.18, 1338.60, 1093.67, 1033.85, 802.39 and 1685.79 cm⁻¹ for AC (KSCB)H₃PO₄. The bands at 3564.45 and 3442.13 cm⁻¹ are due to N-H stretch (mainly primary and secondary amines) present on the adsorbents. The band observed at 1458.18, 1597.06 cm⁻¹ are assigned to C=C bond (from alkenes), the bands at 1068.56

and 1161.15 cm^{-1} are assigned to C-O stretch (alcohols, ethers, acids, esters), 11701.62 and 1685.79 cm^{-1} corresponds to N-H bend of amines and amides, 1033.85 cm^{-1} is due to C-H bend of $\text{CH}_2=\text{CH}_2$ - from vinyl groups. These peaks which correspond to different functional groups are possible sites for adsorption of these metal ions by the adsorbents. The peak intensities indicate that especially the OH groups, the C-O stretch of either alcohols, ethers, carboxylic acids or esters, the N-H stretch of the primary or secondary amines, N-H bend of the amine or amides and the C=C stretch of the alkenes may play a major role in the adsorption of Pb(II) and the Cd(II) ions from the aqueous solutions.

The bands at 1050 and 706 cm^{-1} represent the asymmetric and symmetric stretching vibrations, which respectively correspond to the SiO_4 or AlO_4 structure. The band at 550 cm^{-1} is assigned to the deformation vibration of the Al-O-Si group. The broad peak from $3400\text{--}3700\text{ cm}^{-1}$ has been associated with the stretching of hydroxyl groups of the zeolitic structure[88].

These functional groups contain either - electron which is electron - rich or lone pairs on nitrogen or oxygen, with which they can coordinate with the metal ions leading to their adsorption. Comparing (Figs.1 and 2), one can conclude that, some of these peaks are either absent or new ones detected. This may be due to surface variation resulting from the combination of the AC (KSCB) H_3PO_4 with Natural Zeolite waste.

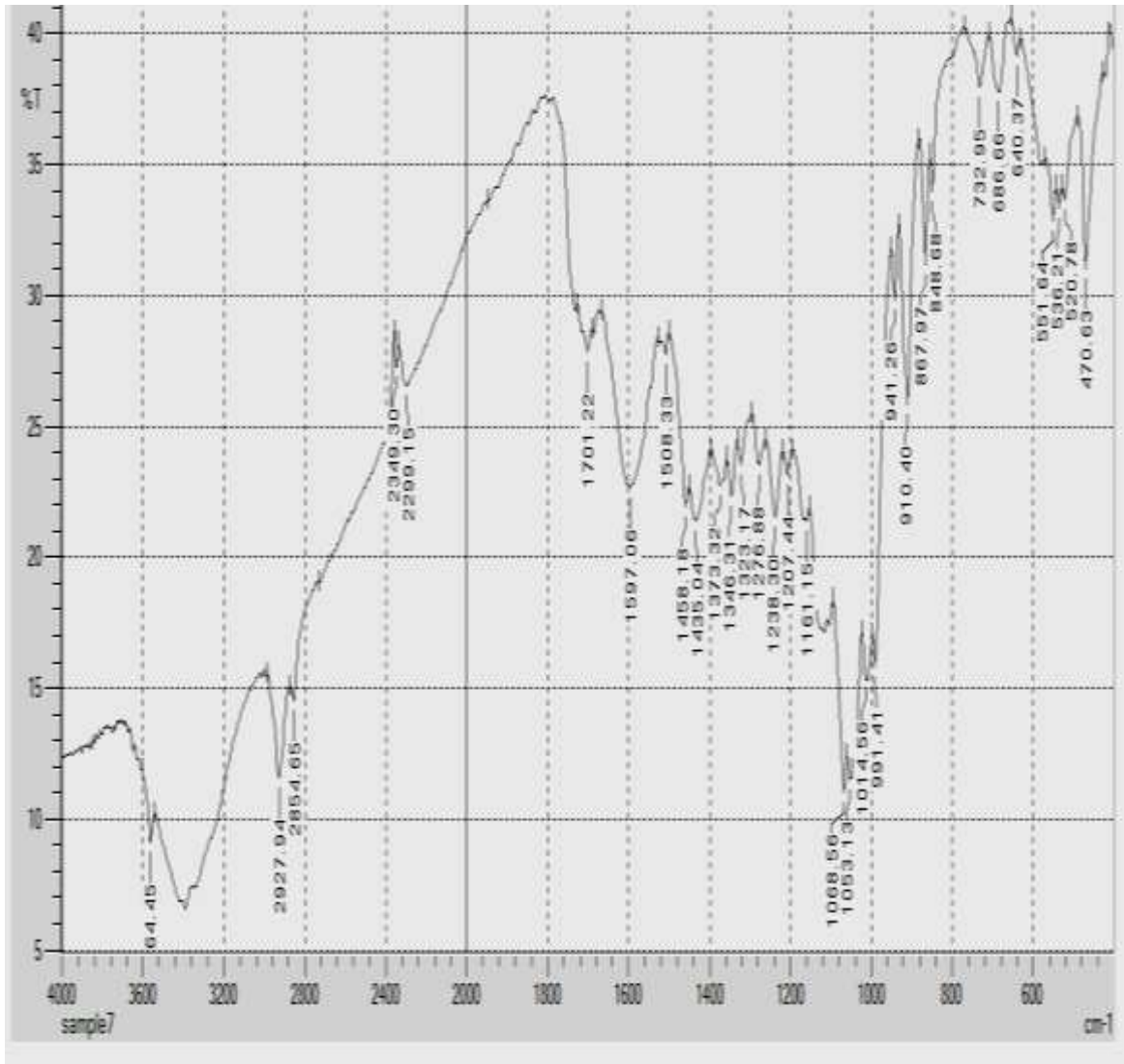


Fig.(4.5) Sample No. 7 the best optimum one when using KOH activator (85% KSCB + 15% Natural Zeolite)

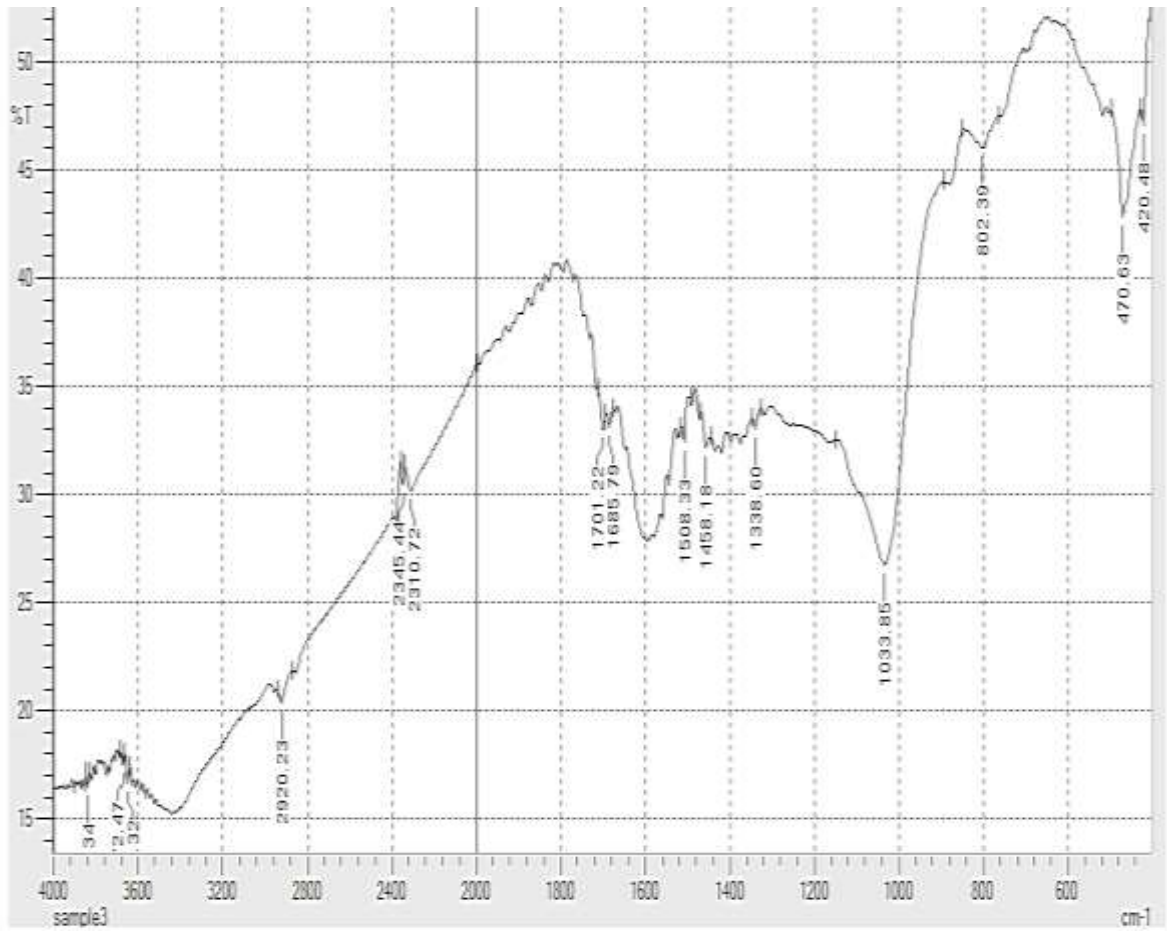


Fig.(4.6) Sample No. 4 the best optimum one when using H₃PO₄ activator
(40% KSCB + 60% Natural Zeolite)

4.4 Effect of Process Parameters

Lead (II) and Cadmium (II) ions removal using the prepared activated carbon AC (KSCB)KOH/ H₃PO₄ Combined with Natural Zeolite was affected by the following process parameters. Significance of these parameters on adsorption from their aqueous phase has been well established.

4.4.1 Effect of pH

Solution pH is one of the important process parameters that significantly influences the adsorption of Pb(II) and Cd(II) on adsorbent[100]. Kenanans bagasse AC (KSCB)KOH/ H₃PO₄ prepared by chemical activators(KOH and H₃PO₄) Combined with Natural Zeolite were employed for Pb(II) and Cd(II) removal at different pH values (2–10). The preliminary experiments were performed at definite experimental conditions (initial Lead and Cadmium concentrations –75.0 mg/L, adsorbent dose – 0.25 g/100ml, contact time – 60 min, and temperature – 25 ± 0.50 °C). The removal of the two ions under consideration was affected by changes in pH as observed from [Table(4.1) and Figure(4.1)]. It is evident from the figure that Pb(II) percentage adsorption is higher at acidic pH (5 & 6).The removal of Pb(II) was high as close to 87.58% when using KOH activator, while it was 96.83% when H₃PO₄ activator was used. On the other hand the highest average removals of Cd(II), observed at pH(7-8) and (6-8), was 83.72% and 88.49% when using KOH and H₃PO₄ activators respectively. Generally, metal ions are more soluble at lower pH values and this enhances their adsorption. Removal of metal ions at higher pH values could be attributed to the formation of their hydroxides which results in precipitates, this is consistent with the observation. The results obtained are in close agreement with previously reported studies[98]. Therefore, removal of metal ions at higher pH values is due to the formation of precipitates rather than adsorption [89].

Table(4.1)Effect of pH on Pb(II) and Cd(II) removal by AC(KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite (C₀=75mg/ L, Dose = 0.25 g,Contact Time = 60 min., T = 25C⁰ ± 0.50)

pH	Metal ion removal % by AC (KSCB)KOH Combined withNatural Zeolite		Metal ion removal % by AC (KSCB)H ₃ PO ₄ Combined withNatural Zeolite	
	Pb(II)	Cd(II)	Pb(II)	Cd(II)
2	27.3	18.2	64.18	37.13
3	45.68	33.35	68.22	45.11
4	66.16	42.15	85.24	51.81
5	85.23	56.17	96.83	66.63
6	86.44	70.89	96.2	88.75
7	87.58	82.52	87.13	89.55
8	85.74	84.92	77.91	87.17
9	84.91	79.51	75.14	71.32
10	75.94	74.16	73.44	69.54

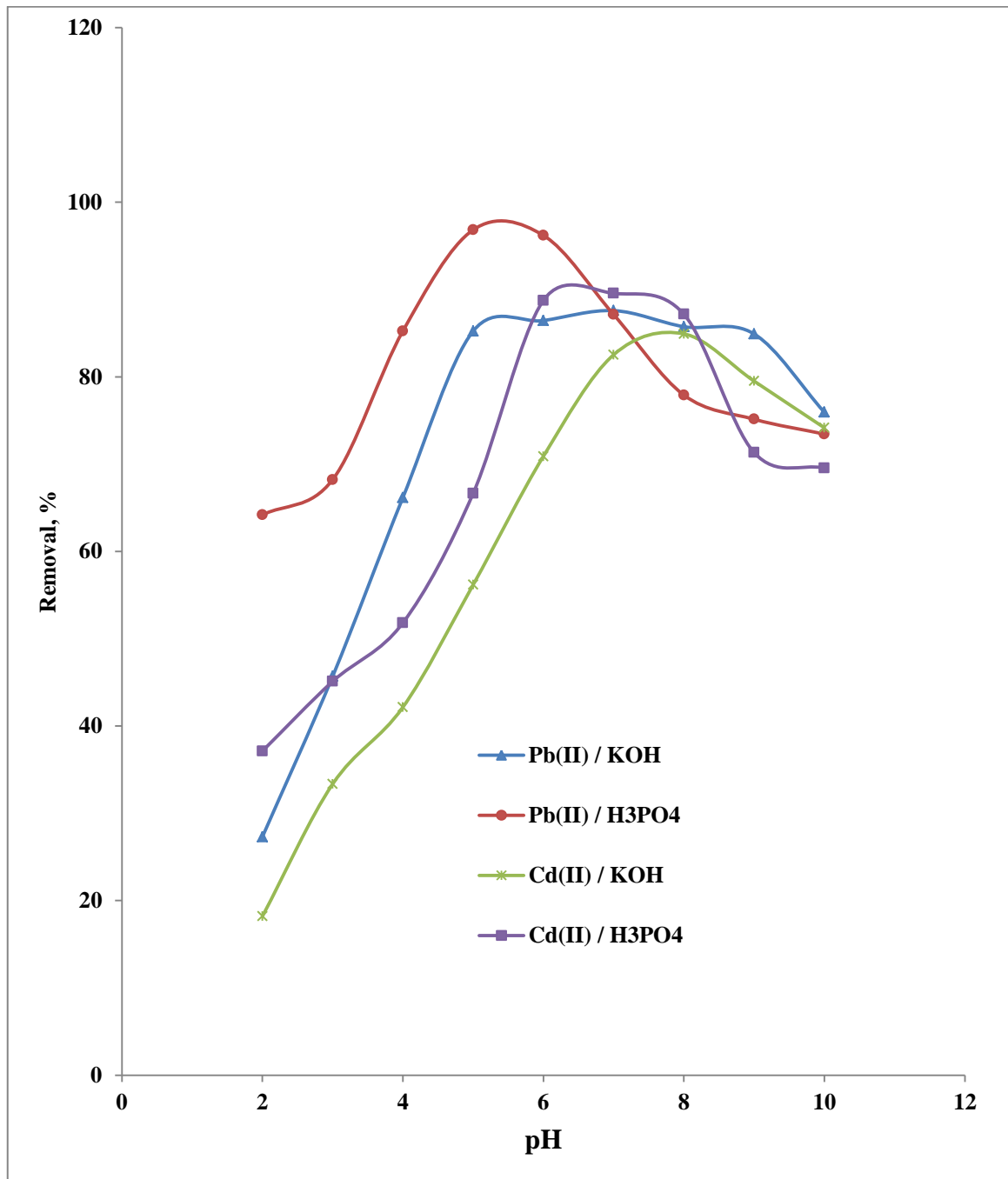


Figure (4.7) Effect of pH on Pb(II) and Cd(II) removal by AC (KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite (C₀= 75mg/ L, Dose = 0.25 g ,Contact Time = 60 min., T = 25C⁰ ± 0.50)

4.4.2 Effect of Adsorbent Dose

The effect of adsorbent dose on removal percentage of Pb(II), Cd(II) using the prepared activated carbon AC (KSCB)KOH/ H₃PO₄ Combined with Natural Zeolite was illustrated in [Table(4.2) and Figure (4.2)]. Different doses of adsorbent ranging from (50–1500mg) were considered and other process parameters were maintained constant, (pH=5&6 for Pb(II) removal, and 6&8 for Cd(II) respectively, using a concentration of 75 mg/L, contact time–60 min, at=25C⁰±0.50). An increase in adsorption capacity with increasing adsorbent dose up to a maximum of 0.25g/ml giving the corresponding optimum percentage removal of 88.24% and 91.26% for Pb(II) at pH=5 and 6, While it was 99.10 % and 94.60 % for Cd(II) respectively. On the other hand, it was found that any further addition over the above mentioned weight (1.50g) will not make any enhancement in the adsorption process, where almost negligible increase of removal efficiency over the specific adsorbent dose. The initial increase in adsorption capacity with increasing adsorbent mass is explained by the increase in the number of exchangeable sites for metal ion adsorption, after which equilibrations was attained [90].

Table (4.2) Effect of adsorbent dose on Pb(II) and Cd(II) removal by AC (KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite (C₀=75mg/ L, pH={5& 6 and 6&8}, Contact Time= 60 min., T=25C⁰ ± 0.50).

Dose, g	Heavy metal ion removal % using KOH Activator		Heavy metal ion removal % using H ₃ PO ₄ Activator	
	Pb(II)	Cd(II)	Pb(II)	Cd(II)
0.05	29.60	36.51	24.77	25.16
0.10	44.41	52.88	39.34	44.97
0.15	64.28	65.04	67.22	77.14
0.20	73.88	78.19	81.13	88.17
0.25	88.24	99.1	91.26	94.6
0.50	89.61	99.6	92.17	93.2
0.75	84.27	99.7	94.23	95.4
1.00	85.99	99.8	95.11	96.6
1.50	98.17	99.60	96.01	95.4

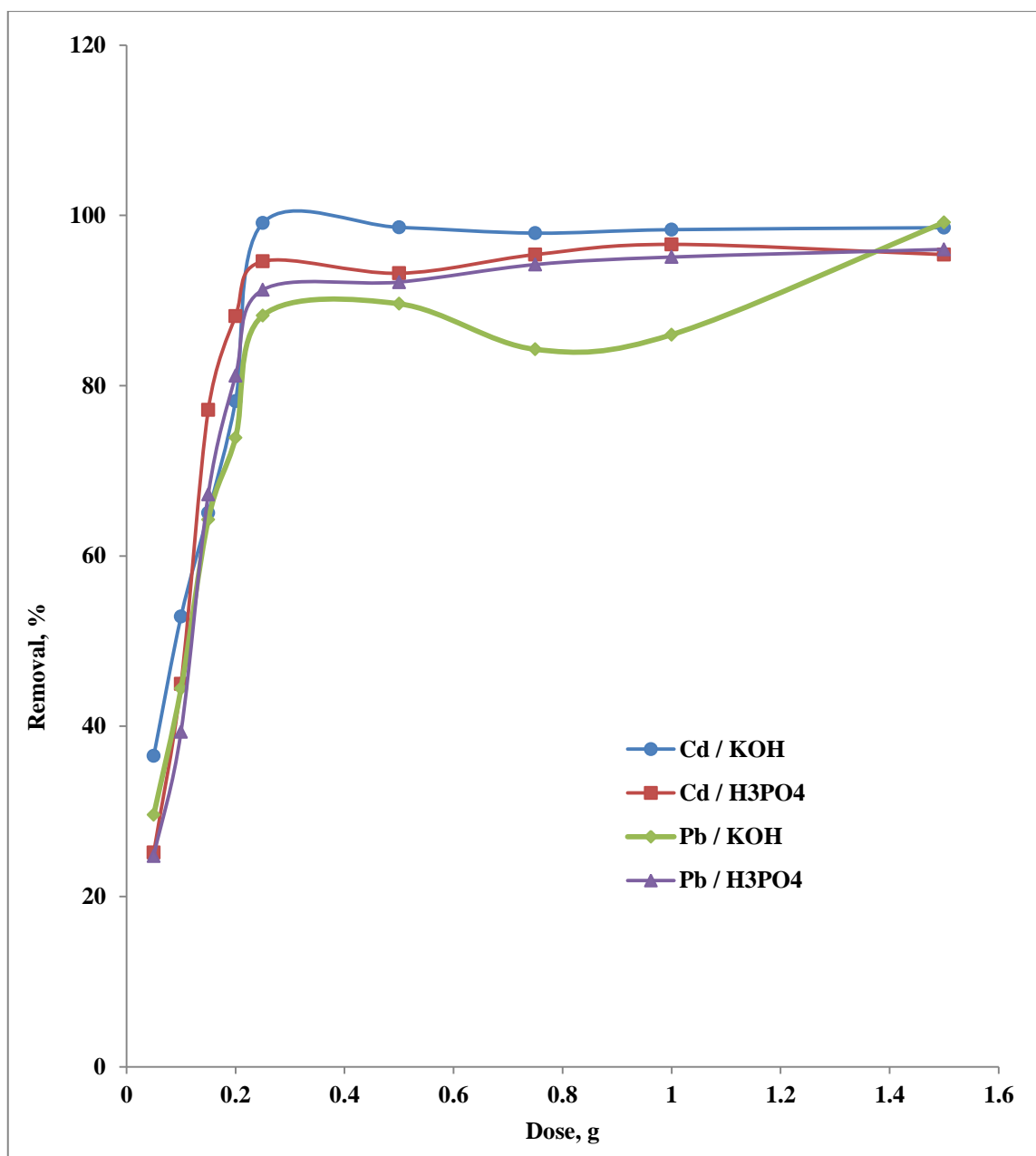


Figure (4.8) Effect of adsorbent dose on Pb(II) and Cd(II) removal by AC (KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite (C₀=75mg/ L, pH = {5& 6 and 6& 8}, Contact Time = 60 min., T = 25C⁰ ± 0.50)

4.4.3 Effect of Contact Time

The effect of contact time on the removal of Pb(II) and Cd(II) using AC (KSCB)KOH/ H₃PO₄ Combined with Natural Zeolite is shown in [Table (4.3) and Figure(4.3)]. The adsorption capacity of metal ions increased by a nearly even dynamic trend with increasing time, reached equilibrium after approximately 60 minutes; the adsorption capacity sequence was consistent with the result obtained in initial concentration tests. A constant adsorption is indicative of equilibration due to saturation of adsorption sites. Rapid adsorption of metal ions during the initial stages was due to the large initial concentration gradient between the adsorbate in solution and the number of available vacant sites on the adsorbent surface. The removal of Pb(II) was high under acidic condition, (pH = 5), as close to 90.60% when using KOH activator, while it was 86.13% under slight acidic conditions, (pH = 6), when H₃PO₄ activator was used. On the other hand the corresponding optimum percentage removal of 82.36% and 79.41% for Cd(II) at pH = 6 and 8, was obtained respectively.

Table (4.3) Effect of Contact Time on Pb(II) and Cd(II) removal by AC (KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite, (C₀=75 mg/L, pH = {5& 6 and 6& 8}, Dose = 0.25g, T = 25C⁰ ± 0.50).

Dose, g	Heavy metal ion removal % using KOH Activator		Heavy metal ion removal % using H ₃ PO ₄ Activator	
	Pb(II)	Cd(II)	Pb(II)	Cd(II)
0.05	29.60	36.51	24.77	25.16
0.10	44.41	52.88	39.34	44.97
0.15	64.28	65.04	67.22	77.14
0.20	73.88	78.19	81.13	88.17
0.25	88.24	99.1	91.26	94.6
0.50	89.61	99.6	92.17	93.2
0.75	84.27	99.7	94.23	95.4
1.00	85.99	99.8	95.11	96.6
1.50	98.17	99.60	96.01	95.4

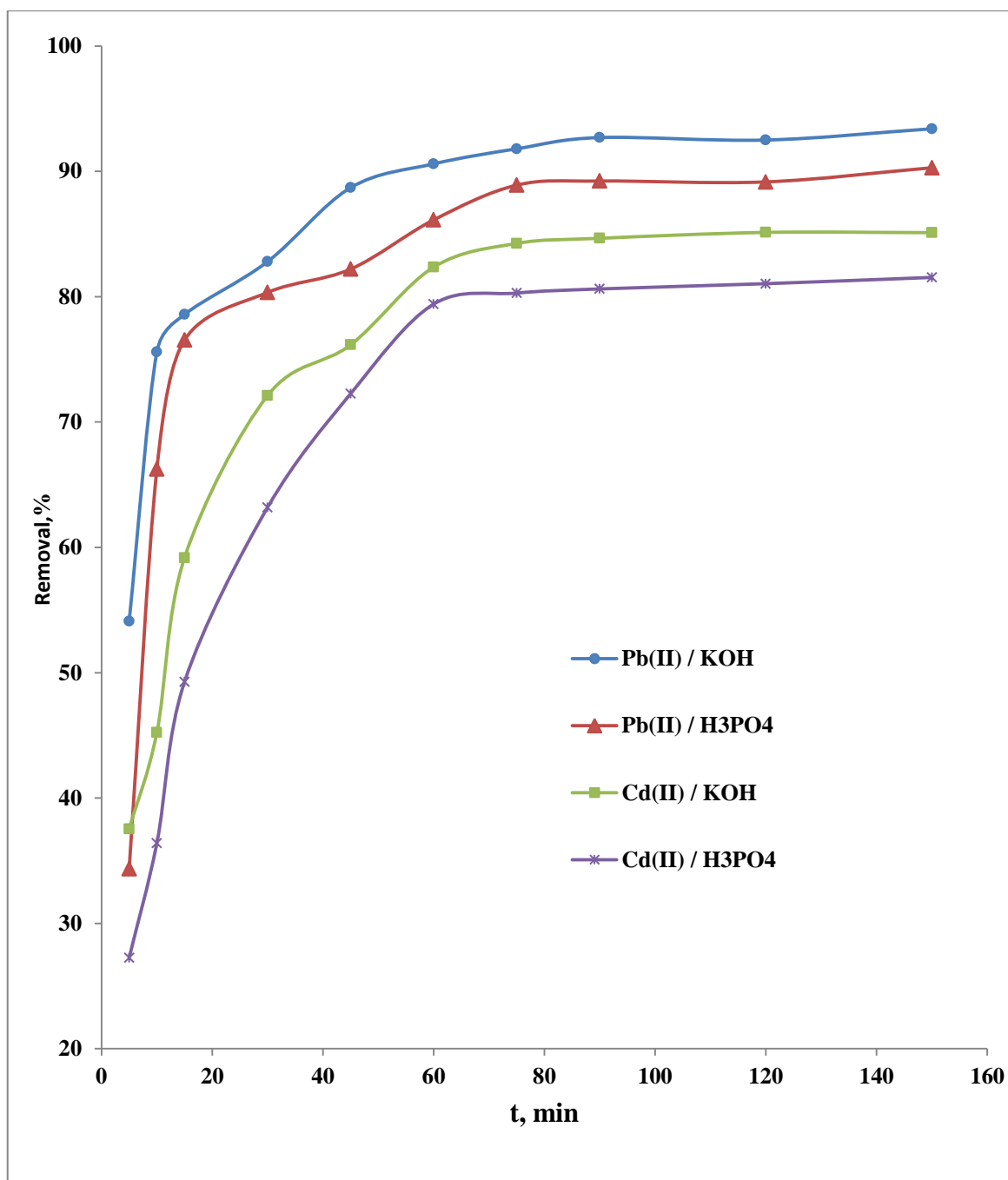


Figure (4.9) Effect of Contact Time on Pb(II) and Cd(II) removal by AC (KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite, (C₀=75 mg/L, pH = {5& 6 and 6& 8}, Dose = 0.25g, T = 25C⁰ ± 0.50)

4.4.4 Effect of initial concentration

The initial concentration of Pb(II) and Cd(II) in their solutions is an important parameter since their concentrations change over a broad range in effluent applications. The batch adsorption experiments were carried out with different initial concentrations (C_i) of each metal ion. The variation of removal percentage for the different initial concentrations using the prepared AC(KSCB) activated carbon with KOH/ H₃PO₄ Combined with Natural Zeolite was shown in [Table(4.4) and Figure(4.4)]. The figure shows an excellent performance of AC(KSCB) activated carbon with KOH/ H₃PO₄ Combined with Natural Zeolite at equilibrium state and the optimum metal ion initial concentrations, (75.0 mg/L) under the experimental conditions. It is also evidently observed that the removal percentage of Pb(II) when using KOH and H₃PO₄ as activators were sufficiently high, (76.01%, 68.16% respectively) while for Cd(II) was higher, (80.08%, 91.17% respectively) and no significant further increase as the concentration increases. The influence of this behavior could be summarized according to the following Sequence:

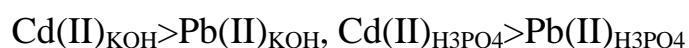
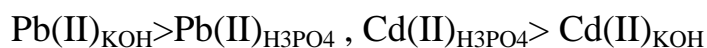


Table (4.4) Effect of Initial concentration on Pb(II) and Cd(II) removal by AC (KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite, pH={5&6 and 6& 8}Dose=0.25g, Contact Time=60 min., T=25± 0.50C⁰).

Activator	Initial Conc., C ₀ (mg/L)	Pb(II)			Cd (II)		
		C _e (mg/L)	q _e (mg/L)	R%	C _e (mg/L)	q _e (mg/L)	R%
KOH	10	1.959	8.041	80.410	1.780	8.220	82.200
	25	4.768	20.232	80.928	4.059	20.941	83.764
	50	7.812	42.188	84.376	8.620	41.380	82.76
	75	17.992	57.008	76.011	14.940	60.060	80.08
	125	32.632	92.368	73.894	27.380	97.620	78.096
	150	47.27	102.73	68.487	38.310	111.690	74.46
H ₃ PO ₄	10	3.580	6.420	64.200	1.087	8.9130	89.13
	25	8.640	16.360	65.440	3.090	21.910	87.64
	50	12.810	37.190	74.380	3.940	46.060	92.12
	75	23.880	51.120	68.160	6.620	68.380	91.173
	125	39.110	85.890	68.712	9.890	115.110	92.088
	150	46.670	103.330	68.887	12.350	137.650	91.767

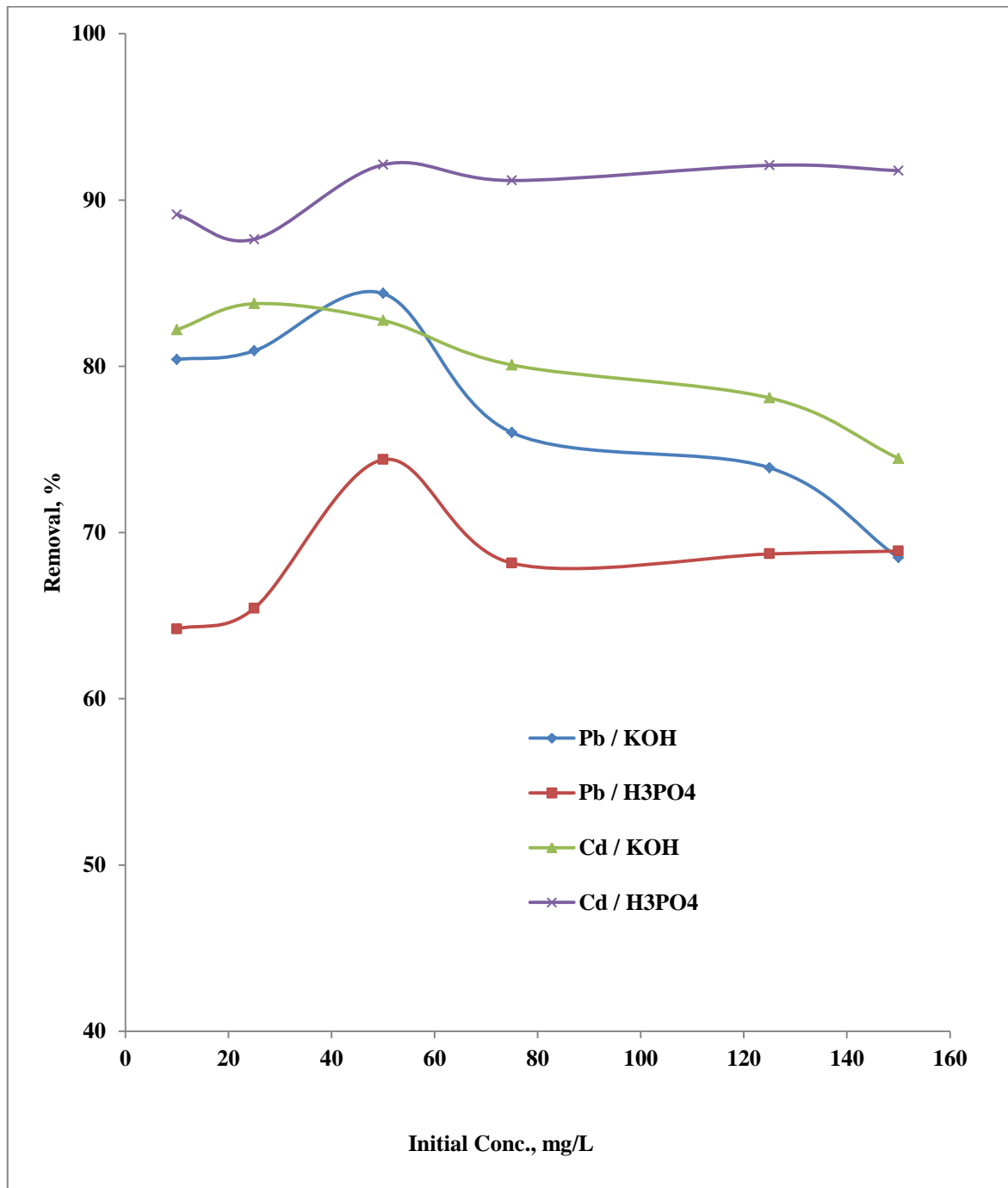


Figure (4.10) Effect of Initial concentration on Pb(II) and Cd(II) removal by AC(KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite, pH={5&6 and 6&8}, Dose=0.25g/ml, Contact Time=60 min., T=25±0.50C⁰)

4.5 Adsorption Properties

The successful representation of the dynamic adsorptive separation of solute from solution by an adsorbent depends upon a good description of the equilibrium between the two phases. Adsorption equilibrium is established when the amount of solute being adsorbed onto the adsorbent is equal to the amount being desorbed [101]. The equilibrium adsorption isotherms were depicted by plotting solid phase concentration (q_e) against liquid phase concentration (C_e) of solute. Adsorption isotherm explains the interaction between adsorbate and adsorbent and is critical for design of adsorption process. The Langmuir and Freundlich, isotherms are the most frequently used models to describe the experimental data of adsorption. In the present work these Langmuir and Freundlich adsorption isotherms were applied to investigate the adsorption process of Pb(II) and Cd(II) metal ions adsorption on prepared AC (KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite, at different conditions of process parameters.

4.5.1 Langmuir Isotherm

The Langmuir isotherm is applicable to homogeneous sorption where the sorption of each sorbet molecule on to the surface has equal sorption activation energy and is represented as follows [91].

$$C_e / q_e = 1/q_m K_L + C_e / q_m \quad (4.1)$$

Where q_m (mg/g) is the maximum adsorption capacity of the adsorbent, K_L (L/mg) is the affinity parameter or Langmuir isotherm constants. Dividing equation (4.1) by C_e one can obtain:

$$1/q_e = 1/q_m + 1/q_m K_L C_e \quad (4.2)$$

The adsorption data were analyzed according to the linear form of equation (4.2). The plots of $1/q_e$ versus $1/C_e$ are linear which indicate that the adsorption data fitted reasonably to the Langmuir isotherm Figures (4.2.1.a) and (4.2.1.b). The constants were evaluated from the slope ($1/q_m K_L$) and intercept ($1/q_m$).

According to R^2 values, (0.9902 and 0.9895 for Pb(II) & (0.9953 and 0.9856 for Cd(II) removal when using KOH and H_3PO_4 activators respectively, the Langmuir equation well fitted the experimental adsorption data for Pb(II) and Cd(II) removal using AC(KSCB) Activated Carbon with KOH/ H_3PO_4 Combined with Natural Zeolite, thereby representing a monolayer adsorption in each.

To investigate in details the Langmuir isotherm, a dimensionless parameter. Namely, separation factor R_L , [92]. And is defined by equation (4.3):

$$R_L = 1 / (1 + K_L C_O) \quad (4.3)$$

Where C_O is the initial metal ion concentration. The R_L values for the prepared adsorbent, AC (KSCB) with KOH/ H_3PO_4 Combined with Natural Zeolite, were between 0.005 and 0.012 which were in the range of:

$0 < R_L < 1$; hence the prepared adsorbent sample show satisfactory adsorption of the two metal ions under the specified conditions[93]. In addition, R_L was closed to zero at high C_O values, thereby suggesting that the prepared adsorbent sample undergo irreversible metal ion adsorption process at high initial metal ion concentration.

The maximum adsorption capacity of the prepared adsorbent sample was compared with those of various conventional adsorbent (Table 2). Although the adsorption conditions differed among them, the prepared adsorbent sample had a level of adsorption capacity similar to that of conventional adsorbents, thereby suggesting that the prepared adsorbent sample can be used for the adsorption of an ionic dyes. The adsorption data were well fitted to the Langmuir equation with reasonably high regression coefficient. The constants obtained are summarized in Table (4.1).

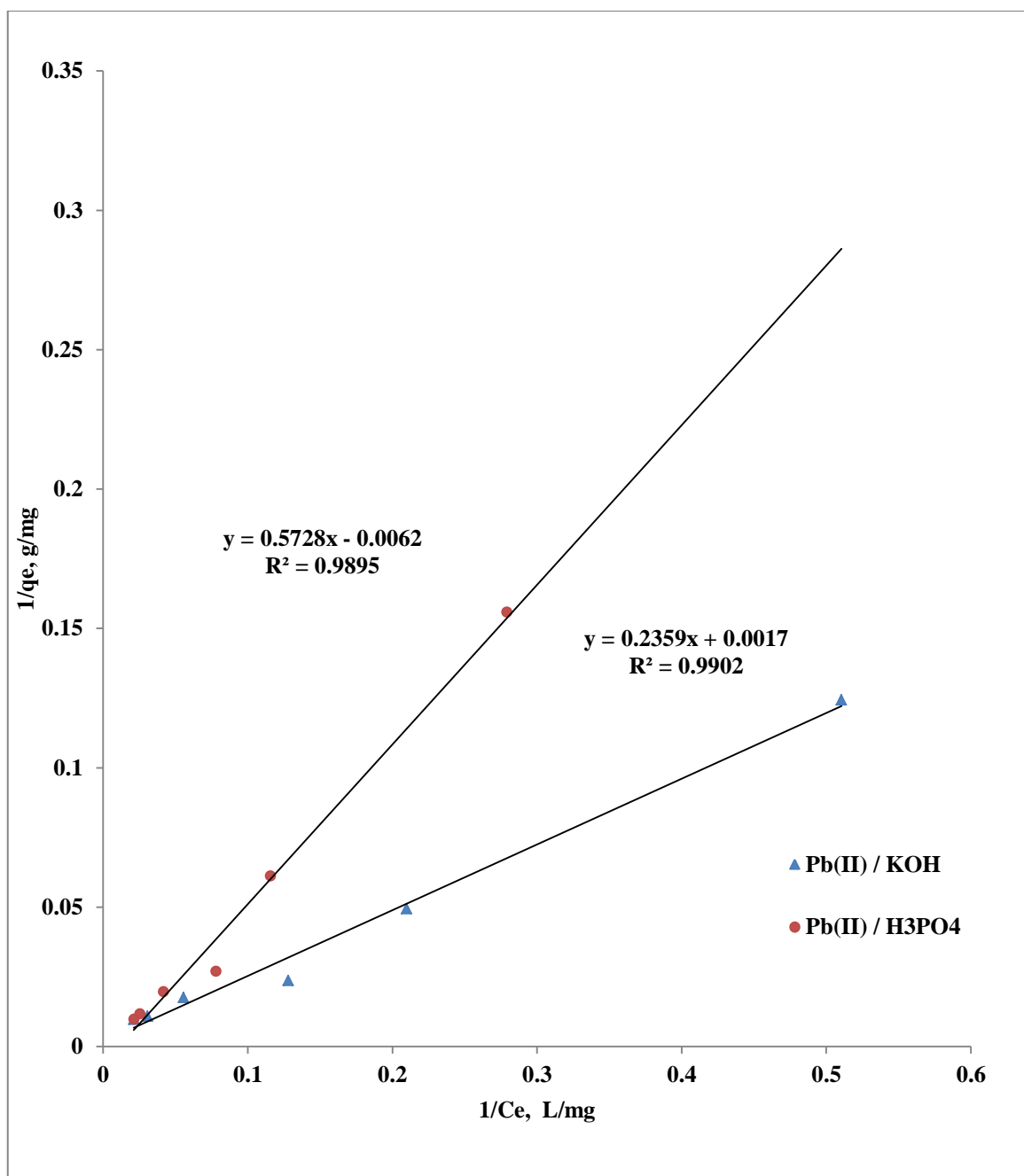


Figure (4.11. a) Langmuir isotherms of AC (KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite for Pb(II) removal at 25C⁰ ± 0.50

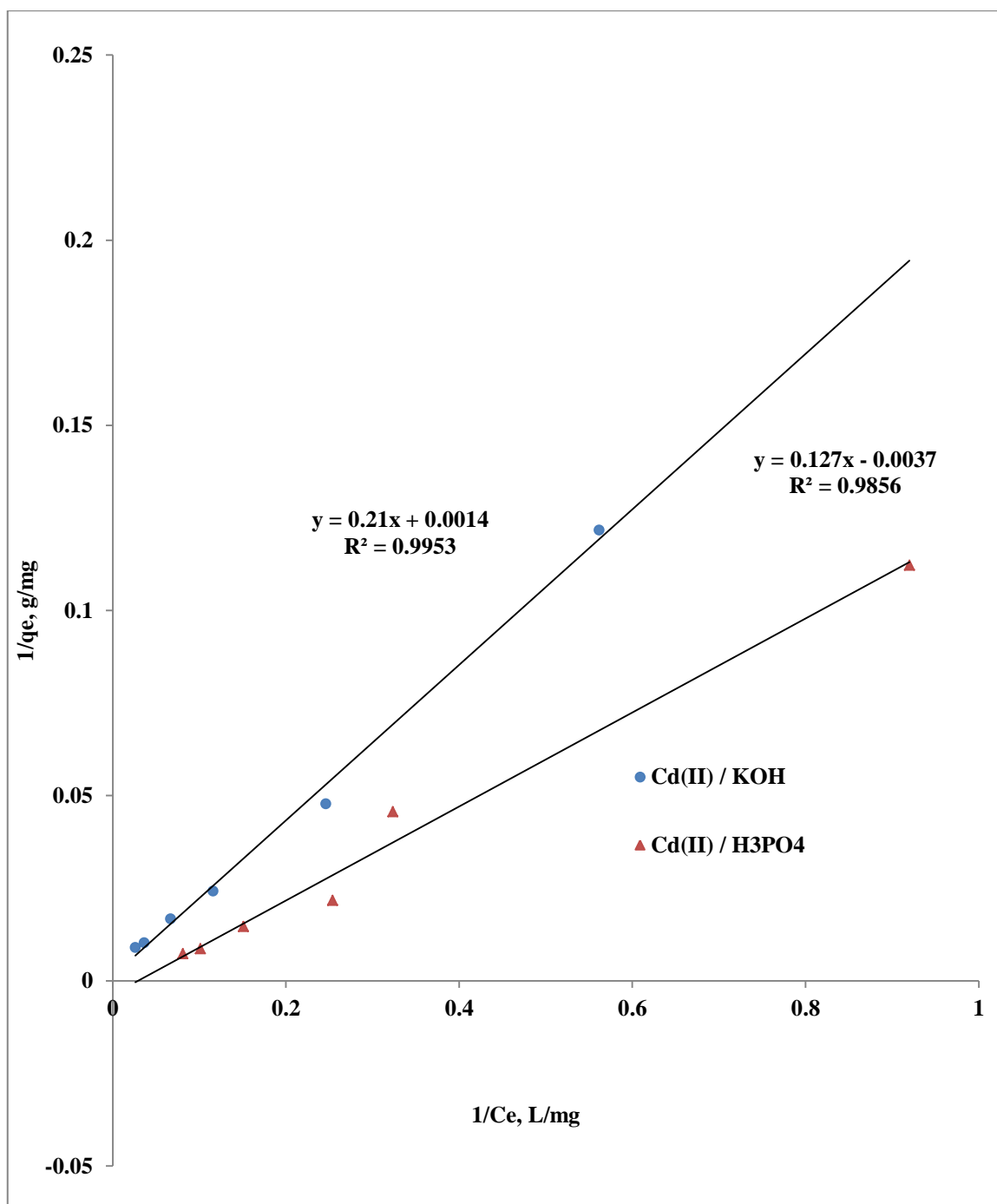


Figure (4.11.b) Langmuir isotherms of AC (KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite for Cd(II) removal $25\text{C}^0 \pm 0.50$

4.5.2 Freundlich Isotherm

Freundlich isotherm is derived to a model of the multilayer adsorption and for the adsorption on heterogeneous surfaces, the linearized of Freundlich equation is given by:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (4.3)$$

Where K_F and n are Freundlich constants, q_e is the extent of Pb(II) and Cd(II), adsorbed per unit mass of adsorbent (mg/g) and C_e is the equilibrium concentration of Pb(II) and Cd(II) (mg/L). A plot of $\ln q_e$ against $\ln C_e$ would give the values of n and K_f (L/mg) and n (dimensionless) from the slope and its intercept respectively. The slope of $1/n$ ranging between 0 and 1 is the measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero, while K_F represents the quantity of adsorbate on the adsorbent. The values of Freundlich constants with the correlation coefficients are shown in Table (4.1).

As a result from these isotherms one can show that, the equilibrium adsorption amount of AC(KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite for Pb(II) and Cd(II) with different initial concentrations of the two metal ions solutions. According to the fitting curves and correlation coefficients (R^2), Langmuir model was more suitable to describe the adsorption of Pb(II) and Cd(II) onto the prepared adsorbent sample, indicating that the surface of AC(KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite was homogeneous and the adsorption was monolayer, where its adsorption capacity (q_m) for Pb(II) and Cd(II) were 588.24 and 714.29 mg/g when using KOH activator, while it was 161.29 and 270.27 mg/g when using H₃PO₄, according to the linear fitting of Langmuir model. Figures (4.2.1.a-b).

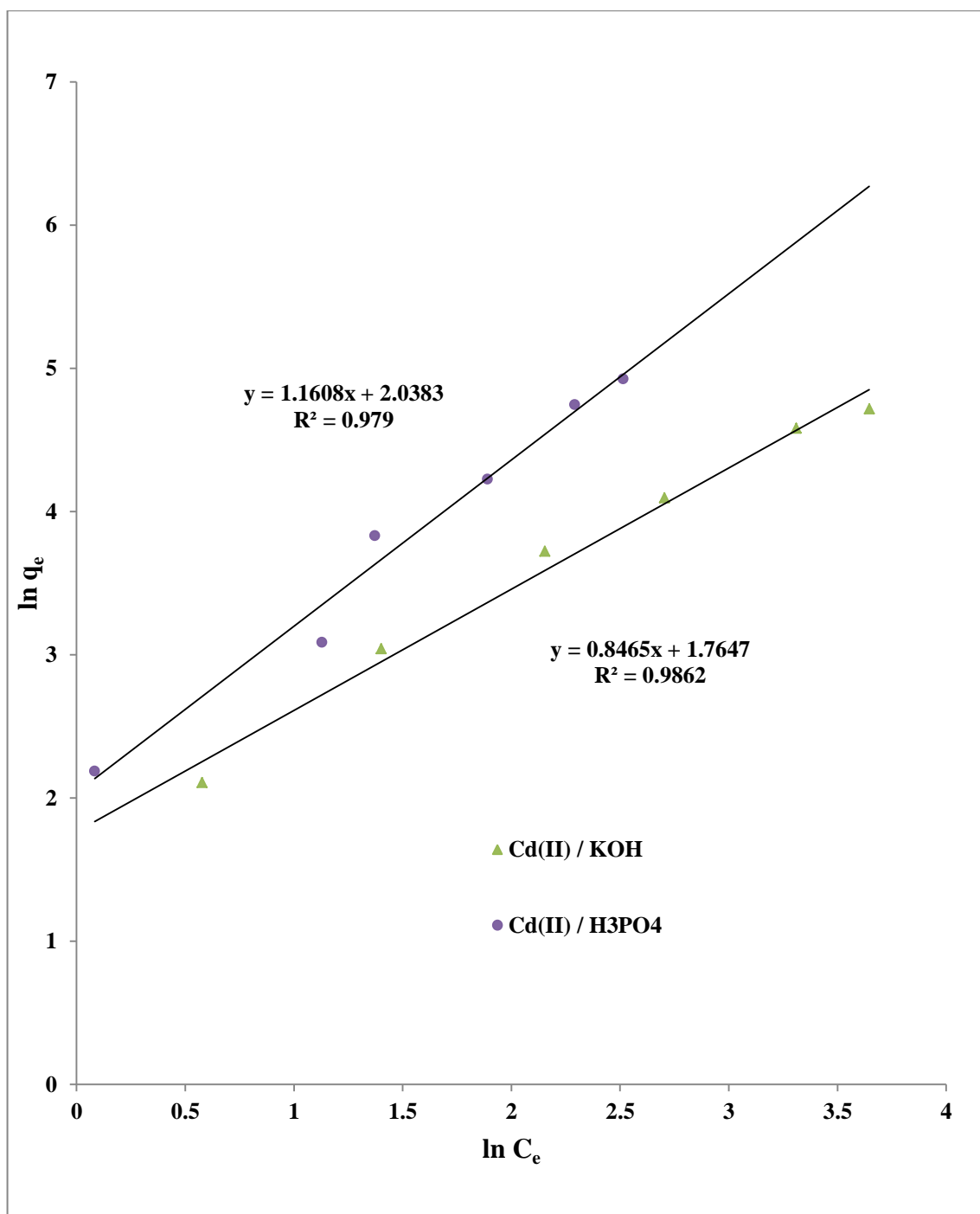


Figure (4.12.a) Freundlich isotherms of AC (KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite for Cd(II) removal at 25C⁰ ± 0.50

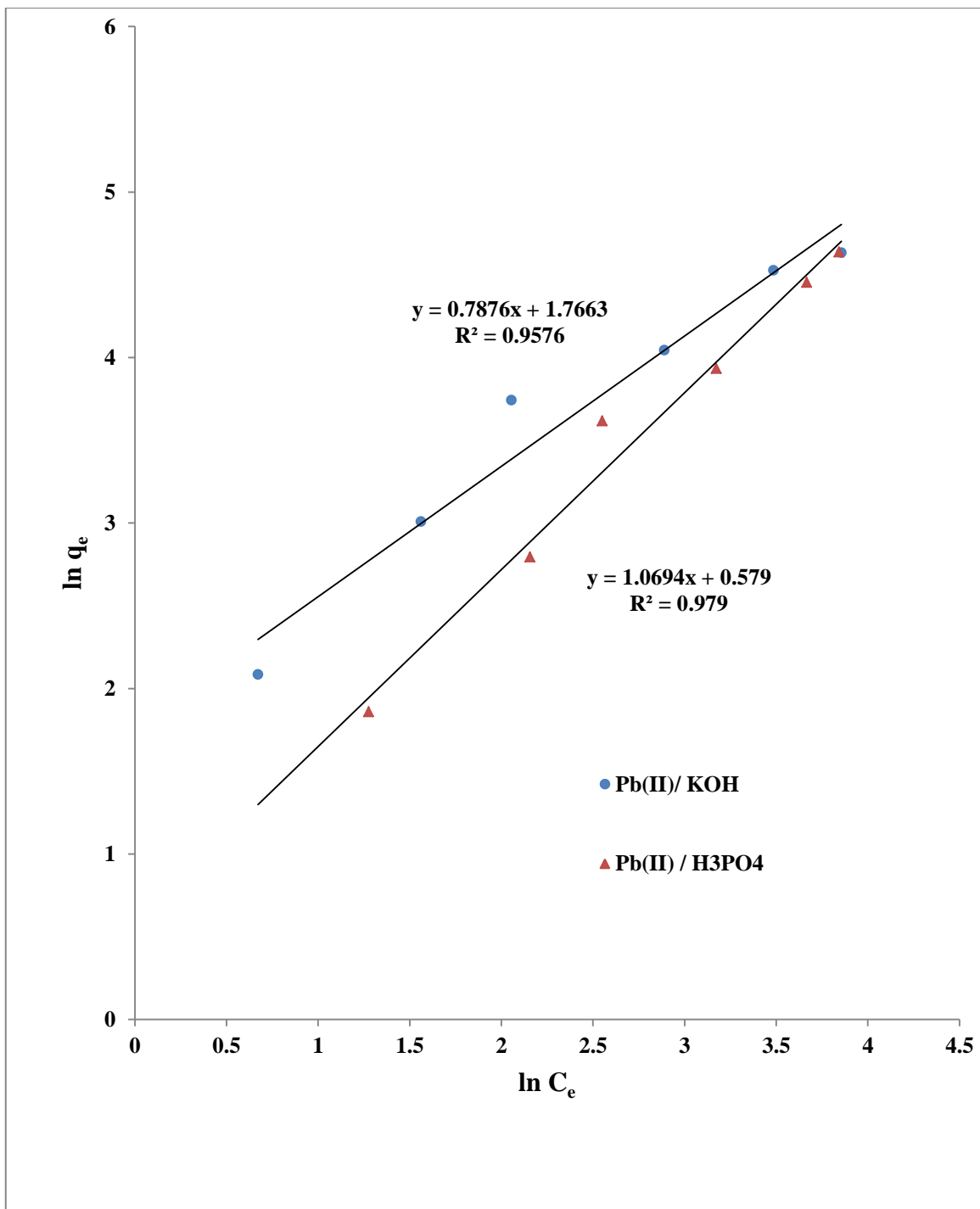


Figure (4.12.b) Freundlich isotherms of AC (KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite for Pb(II) removal at 25C⁰ ± 0.50

Table(4.5)Langmuir and Freundlich, isotherm constants for Pb(II) and Cd(II) removal by AC (KSCB) Activated Carbon with KOH/ H₃PO₄ Combined with Natural Zeolite at 25C⁰ ± 0.50.

Metal Ion	Langmuir					Freundlich		
	Activaitor used Combined with Natural Zeolite	q _m (mg/g)	K _L (L/mg)	R _L	R	K _f (mg/g)	n	R
Pb(II)	KOH	588.24	138.77	0.0053	0.9951	5.85	1.27	0.9786
	H ₃ PO ₄	161.29	92.39	0.0070	0.9947	1.87	0.94	0.9894
Cd(II)	KOH	714.29	150.00	0.0050	0.9977	5.84	1.18	0.9931
	H ₃ PO ₄	270.27	34.33	0.0117	0.9928	7.68	0.86	0.9894

Table (4.6) Comparison of heavy metal removal capacities (mg/g) by different adsorbents

Adsorbent	Pb(II)	Cd(II)	Sources
Unmodified rice husk and modified rice husk	- -	8.82 11.03	[19]
African white star apple shell	8.40	10.59	[35]
Sphagnum moss peat	12.30	-	[36]
Maple sawdust	3.19	-	[37]
Activated carbon Sigma C-3014	-	1.51	[38]
AC (KSCB)KOH combined with Natural Zeolite	588.44	714.29	This Study
AC (KSCB)H ₃ PO ₄ combined with Natural Zeolite	161.29	270.27	

Chapter Five

5. Conclusion and Recommendation

5.1 Conclusions

This study showed that an activated carbon can be prepared from raw widely available agricultural materials in Sudan. AC was derived from KSCB showed higher efficiency for removal of the Lead and Cadmium. The synthesized AC sample showed high adsorption capacities, so that AC sample can be used as good adsorbent materials. Also the synthesized materials showed that Sit has high porosity structure. These properties are considered as encouraging physical properties for these materials to be used as adsorbent material.

Based on the detail experimental investigation the conclusions derived are as Follows:

- Chemical activation of precursor by phosphoric acid and potassium hydroxide produced ACs of various surface characteristics.
- Maximum Pb(II) removal was observed at pH 5.0 - 6.0 when using KOH and H_3PO_4 , while it was showed a maximum removal for Cd(II) at pH 6.0 – 8.0 when using the same activators respectively.
- Lagmiur Model showd best obtained from the Langmuir plots were 714.29 $mg\ g^{-1}$ and 588.24 $mg\ g^{-1}$ respectively for Cd(II) and Pb(II) ions onto the AC (KSCB)KOH Combined with Natural Zeolite and 270.27 $mg\ g^{-1}$ and 161.29 $mg\ g^{-1}$ for their adsorption onto AC (KSCB) H_3PO_4 Combined with the same Natural Zeolite.

5.2 Recommendation

- Extensive investigation should be carried out to produce ACs with even better surface characteristics through different routes such as physical activation, two stage activation and microwave heating etc and can be compared with the results obtained with chemical activation.
- Lead and cadmium must be handled very carefully as they are dangerous and toxic elements.
- We appeal to provide a device Atomic absorption spectroscopy in the laboratories to reduce the cost for the student.
- We recommend a devices Scanning Electron Microscopy images (SEM), Energy Dispersive X-ray spectroscopy (EDX) and Fourier Transform Infrared Spectroscopy (FTIR).

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