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DEPARTMENT OF CHEMISTRY

A THESIS ON

DETERMINATION OF LEVELS OF Pb AND Cr IN WATER SAMPLE AND ITS REMOVAL BY ADSORPTION ONTO ACTIVATED CARBON PREPARED FROM PINEAPPLEPEEL

October, 2014

JIMMA, ETHIOPIA

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A RESEARCH THESIS SUBMITTED TO SCHOOL OF GRADUATE STUDIES JIMMA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTERS OF SCIENCE IN CHEMISTRY

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APPROVED BY EXAMINERS

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October, 2014

Jimma, Ethiopia

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Abbreviations and Acronyms

AAS: - Atomic Absorption spectroscopy

UV-Vis: - Ultra Violet Visible Spectrophotometer

PPAC: - Pineapple peel activated carbon

ASTM:-American Society for Testing and Materials

FT-IR: - Fourier transforms infrared

MPL: - Maximum permissible level

USEPA: - United States Environmental Protection Agency

WHO: - World Health Organization

ABSTRACT

Heavy metal contamination of water could occur anywhere at resources, course of distribution or consumption place. Precise knowledge on amount and type of water pollutants especially heavy metal are essential to protect the environment, and public health. This research aimed to evaluate concentration of heavy metal (Lead and Chromium) in drinking water of Jimma city and study means of removing the metals from the water. Accordingly, water samples were collected from five different sites which comprise raw and treated water, and the study showed that concentration of Pb {in Kochi [0.0196 ppm], Agaro ber [0.0195 ppm]}, and Cr (VI) {in Merkato [0.055 ppm]} drinking water of Jimma was higher than WHO standard limits among all samples. To this end, ways of mitigating heavy metal pollution should be investigated. Adsorption was found to be as one of the most widely used means. Varieties of precursor materials have been used for the preparation of activated carbons. In this study, activated carbon prepared from pine apple peel waste by KOH activation was investigated as adsorbent for the removal of Pb (II) and Cr (VI). Batch method was employed in this study to investigate the efficiency of the adsorbent. The optimum value for parameters influence adsorption:(adsorbent dose [0.25 g], [Pb (II)] and [Cr (VI)]: 0.02 & 0.05 mg/l, pH: 5 and 3 for Pb (II) and Cr (VI) respectively, contact time: 100 min and 70 min for both Pb (II) and Cr (VI), respectively and temperature 25°C) were obtained. To understand the adsorption isotherm, the Langmuir and Freundlich adsorption isotherm models were investigated. The results were found best fit to Freundlich adsorption isotherm which states that heterogeneity of the adsorbent surface. Kinetic studies of the data showed that the adsorption follows the pseudo-second-order kinetic model. Thermodynamic parameters for Pb (II) and Cr(VI) adsorption, enthalpy change (H) {-0.149 and -0.081}, entropy change (S){0.183 and 0.012}, and Gibbs free energy change (G){-3.138 and -3.554 at 293 K, -3.191 and -3.615 at 298 k, -3.245 and -3.675 at 303 k}, respectively have also been calculated. The results of these parameters showed that adsorption was feasible, spontaneous in nature, and exothermic.

Keywords: chromium; lead; drinking water; Adsorption; Adsorbent; adsorption isotherms; kinetic studies; Adsorption thermodynamic.

1. Introduction

Water is one of the most essential substance needed to sustain human life, animals, plants and other living beings and is vital resources to all known forms of life, development and environment; but is susceptible to pollution by various forms of natural factors. It is a finite and vulnerable resource which has quantitative limitations and qualitative vulnerability.

Water pollution by heavy metals is considered a serious environmental problem due to their toxicity, long persistence, and bioaccumulation and bio magnifications in food chain [1]. In fact, heavy metals are toxic to aquatic flora, animals and human beings even at relatively low concentrations[2]. However some of the metals like Cu, Fe, Mn and Ni are essential as micronutrients for plants and microorganism while other metals like Pb, Cd and Cr are proved detrimental beyond a certain limits [3-4].

The analysis of the natural water for physical, chemical properties including trace element contents are very important for public health studies. These studies are also a main part of pollution studies in the environment [5-11].

Also, investigations of the quality of drinking water samples have been continuously performed by researchers around the world. The determinations in drinking water have been performed using classical analytical techniques including titrimetry, gravimetry and modern instrumental techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (ICP-MS), UV-Vis spectrophotometry, and etc. Because of the high quality assurance and easiness in usage, atomic absorption spectrometry is the main instrument for the determinations of the trace heavy metal ions in drinking waters [12-14].

To this end, study socially acceptable and economically feasible methods of removing the pollutant is essential for safety assessments of the environment and human health. Adsorption of heavy metals on activated carbon is the most used treatment method to reach water pollution regulations and environmental standards. A great variety of lignocellulosic precursors and activating agents has been used for the preparation of activated carbons for heavy metal removal. Of various adsorbents activated carbon is particularly useful because of its high adsorption capacities, cost effectiveness and preparation from locally available materials.

1.1. STATEMENT OF THE PROBLEM

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. So, they are of great concern because of their extreme toxicity, even at trace concentration.

Industrial development, modern civilization, poor planning and rapid population growth that utilize large range of chemicals have led to the introduction of uncontrolled and unknown contaminants into water bodies particularly, in developing countries. Heavy metals have been discharged into the environment as industrial wastes as mining, textile; petro-chemical, tannery and plating among others and contaminate natural waters [21]. So it become important to detect the level of these metals in water treatment plant and from different points of municipal water distribution system so as to determine the concentrations of the metals in water parallel to the maximum permissible limits of water quality standards.

Now a days to mitigate these toxic metals, researchers' devised different conventional and advanced methods such as chemical precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, membrane separation, electrochemical treatment and evaporation [22] . However, these methods face drawbacks as cost incompatibility, sludge production, and removal inefficiency. Thus, the searches for low-cost adsorbents that have high metal binding capacities are needed. Activated carbon is undoubtedly considered as universal adsorbent for the removal of diverse kinds of pollutants from aqueous solutions and waste water. Thus, the study was aimed to investigate the level of Pb and Cr relative to the maximum permissible limit and also the removal of these metals by adsorption onto activated carbon.

During this study, the following questions were answered.
➢ Are the concentrations of Pb and Cr in water sample of Jimma town found above the permissible limit?
➢ Is activated carbon prepared from locally available pineapple peel will remove Pb and Cr?
➢ What type of adsorption mechanism is responsible?
➢ What reason will be responsible for the difference in giving response with different adsorbents?

1.2. OBJECTIVES OF THE STUDY

1.2.1. GENERAL OBJECTIVE

To investigate the concentration level of Pb and Cr as well as kinetics and thermodynamics studies of these metal ions removal by adsorption onto activated carbon prepared from pine apple peel.

1.2.2. SPECIFIC OBJECTIVES

➢ To determine the concentration level of Pb and Cr in water samples collected from the treatment plant and different points in Jimma town.

➢ To prepare activated carbon from pineapple peel by chemical activation.

➢ Determining the effects of pH, contact time, adsorbent dosage, initial metal ion concentration and temperature on the adsorption efficiency of activated carbon.

➢ Identify the adsorption mechanisms of Pb and Cr ions onto activated carbon in terms of thermodynamics, kinetics and isotherms.

1.3. SIGNIFICANCE OF THE STUDY

Investigations of the quality of drinking water samples and study on means of removing pollutants from water have been continuously performed by researchers around the world by various methods to have water with purification needed. However, Adsorption is found to be one of the most widely used methods. Even though commercial activated carbons have long been known as adsorbents for remediation of metal ions, they are often known by cost incompatibility. In this study, locally available adsorbent was investigated to evaluate its efficiency and suitability as the effort to find inexpensive and environmentally friendly adsorbent.

2. REVIEW OF RELATED LITERATURE
2.1. HEAVY METALS AND ITS ENVIRONMENTAL IMPACTS

Heavy metals are toxic pollutants released into the surface and ground water as a result of different activities such as industries, mining and agriculture [23]. They can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater. The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. The problem of removing pollutants from water and wastewater has grown with rapid industrialization. (i.e., the rapid pace of industrialization has led to severe problem of water pollution). The discharge of toxic metals into water courses is a serious pollution problem, which may affect the quality of water supply. Increasing concentrations of these metals in the water constitute severe health hazard mainly due to their non-degradability and toxicity. Awareness encouragement of pollutant toxicity has forced industries and municipal authorities to treat wastewater before discarding to the natural water bodies [24].

Among the heavy metals Pb and Cr are the most common pollutants possibly enter to the ecosystem through soil, air and water. The contamination of water by heavy metals has increased over the last few decades due to Industrial processes such as petroleum refinery process and the development of new technology in refining of petroleum [25]. Toxic metals have adverse effect on the health of human, when they penetrated through the human organ and tissue as well as the entire systems.

Chromium (VI) penetrates cell membranes and causes genotoxic effect and cancer [26]. Due to its widespread used in industrial applications such as chromium plating, dye manufacturing and preservation of wood and leather materials, chromium concentrations in environmental samples have to be monitored on a routine basis. Dissolved hexavalent chromium can be determined as chromate (CrO_4^{2-}) by ion chromatography in drinking water, groundwater, and industrial wastewater effluents [27, 28].

Lead in refinery waste water with the quantity of 0.1mg/l can cause chronic poisoning if the water is used continuously [29]. Lead (Pb) can be a problem in districts with extensive networks of Pb pipe work for water conveyance [30]. This can particularly happen in relatively old housing

districts. The Pb concentration can be reduced by conditioning the water in order to reduce the metal solubility from the plumbing.

Many wastewater treatment plants receive discharges not only from residential area but also from industry. Sludge generated at these plants contains heavy metals at relatively high concentrations, which may vary considerably with time and mostly depend on industrial activities [31].

The application of chemical extraction as a part of the treatment is a feasible option, especially when it is applied as a pre-treatment aiming at heavy metals removal. Once they are soluble, heavy metals can be precipitated again and further be removed by a physical separation, e.g. flotation [32]. Various wastewater treatment technologies are used including chemical treatment, ultra-filtration, reverse osmosis, electrolysis, solvent extraction, ion exchange chromatography and etc., but these methods have some short comings and require large time [33].

Several investigations on the use of clays and zeolites (natural and synthetic) for heavy metal removal have been reported. Pilot tests using kaolinite with sand media filtration removed Zinc (Zn), Copper (Cu) and Lead (Pb) with efficiencies of about 50, 90 and 90%, respectively [34].

In order to decrease the content of heavy metals in the environment, it is necessary to treat waste water before its discharge. Many methods are suggested for the removal of toxic metals from water sources as well as from aqueous solution. The most useful and economic method is adsorption. Removal of such toxic heavy metal is done by naturally occurring adsorbent like tea leaves, cotton capsule shell, bajarahull, moong shell, Bidi leaves, saw dust, paddy husk [35].

2.2. ACTIVATED CARBON

Activated carbon (AC) is solid, porous and tasteless black carbonaceous materials which have been subjected to reaction with gases during or after carbonization in order to increase porosity [36]. AC is distinguished from elemental carbon by the removal of all non-carbon impurities and the oxidation of the carbon surface.

It has been found that the activated carbon's properties depend greatly on the composition of their raw materials [37]. The materials selected now a days to be potential precursors of activated

carbons must be materials with high carbon contents and low inorganic compound levels in order to obtain a better yield during the carbonization processes [38].

The most common raw materials are nut shells, fruit pits, wood, peanut husk, lignite, peat, bone and paper mill waste(lignin), are used for manufacturing of activated carbon. Activated carbon produced from hard material is preferable for adsorption because charcoal obtained from soft material, such as pinewood, is very unstable and readily crumbles. It has been reported that the best grades of AC are obtained from the coconut shell and apricot pits [39].

In recent years, the researchers have developed many biomass adsorbents to remove the heavy metals from both aqueous solution and polluted water. The removal rate of metal ions depended on the types of biomaterials. The bio sorptions by various biosorbents such as wheat bran, potato peel waste, and rice bran have been reported. Wheat bran had 87.8% removal in 1 hr. at pH 2 [41].Adsorption capacity of potato peel waste (8.012 mg/g) is also reported [42]. The rice bran as an adsorbent is used to remove the metal ions from aqueous solutions and the sorption capacity was strongly dependent on the nature and the initial metal ions concentration, pH and rice bran showed 0.069 mg/g Freundlich adsorption capacity [43].

Generally, activated carbons are commonly prepared by a physical activation or chemical activation process. Physical activation consists of two steps: a carbonaceous material is carbonized under the oxygen-free atmosphere (carbonization process) and then activated with an activating gas such as CO_2 and H_2O (activation process).

In chemical activation, both carbonization and activation processes occur simultaneously at a lower temperature and a shorter time than that in physical activation. Therefore it saves time and energy. Moreover chemical activation is reported to give activated carbon with higher specific surface area and much better developed porosity than physical activation [40].

Activating agents play a critical role in surface area and porosity development. The high adsorptive capacities of activated carbons are highly related to porous characteristics such as surface area, pore volume, and pore size distribution. The porous structure of AC formed during the carbonization process and was developed further during activation, when the spaces between the elementary crystallites are cleared of tar and other carbonaceous material. The structure of

pores and pore size distribution largely depends on the nature of the raw material and activation process route. The activation process removes disorganized carbon by exposing the crystallites to the action of activating agent which leads to the development of porous structure. This is why AC has higher adsorption efficiency comparable to the raw material from which it's made from.

In spite of the availability of vast literature on various activation methods meant for improving the performance of carbon materials, detailed knowledge of the process of activation is still poor.

KOH is the most effective activating agent in producing activated carbon materials. The researchers could offer a convincing description of the process of activation of carbon precursor by KOH. Based on the thermodynamic considerations, the reaction between KOH and carbon precursor can result in the formation of functional groups such as –OK using oxygen of the alkali salt.

$$K_2O + C \quad \rightarrow \quad C\text{-}O\text{-}K + K$$
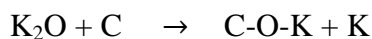
The presence of such potassium and oxygen bond in the char leads to the oxidation of cross linking carbon atoms in the adjacent lamella during the process of activation. Surface functional groups are created at the edges of the lamella. As a result of removal of cross linking between adjacent lamella and also the formation of new functional groups on individual lamella, the lamellas of the crystallite are disturbed from their normal (completely flat) form into a slightly wrinkled or folded or puckered form. Also the potassium metal produced in the process of activation, *in-situ*, intercalates in to the lamella of the crystallite. After the activation process, when the carbon material is washed with water, the potassium salts present in the carbon particles are removed by leaching. At the same time, the lamella cannot return to their original state (nonporous state) creating interlayer voids. Thus the lamella remains apart causing porosity and yielding high surface area carbon [90]. In addition to the development of porosity and improvement in specific surface area, another prominent advantage with KOH activation is the creation of -OH surface functional groups on the carbon surface. The (-OK) groups formed on the carbon surface upon KOH activation gets transformed to (-OH) groups on washing with water by ion exchange reaction. Thus, in addition to creation of voids by the removal of K, upon washing with water, polar functional groups like –OH are created in large numbers making the carbon surface hydrophilic.

In general the chemical reaction between KOH and carbon material can be written as follows:

$$4 \, KOH + C \quad \rightarrow \quad K_2CO_3 + K_2O + 2 \, H_2 \qquad\qquad (1)$$

KOH reacts with disordered or amorphous carbon at high temperatures to form K_2CO_3 as well as the decomposition product K_2O along with the evolution of hydrogen.

Considering the decomposition of KOH into K_2O as well as the reducing ability of carbon, additional reactions do take place during the process of activation as shown:

$$2 \, KOH \quad \rightarrow \quad K_2O + H_2O \qquad\qquad (2)$$

$$C + H_2O \, (steam) \quad \rightarrow \, H_2 + CO \qquad\qquad (3)$$

$$CO + H_2O \quad \rightarrow \quad H_2 + CO_2 \qquad\qquad (4)$$

$$K_2O + CO_2 \rightarrow \quad K_2CO_3 \qquad\qquad (5)$$

$$K_2O + H_2 \rightarrow \, 2 \, K + H_2O \qquad\qquad (6)$$

$$K_2O + C \quad \rightarrow \quad 2 \, K + CO \qquad\qquad (7)$$

$$K_2CO_3 + 2 \, C \quad \rightarrow \quad 2 \, K + 3 \, CO \qquad\qquad (8)$$

The steam generated in (step 2) causes removal of amorphous carbon as CO as shown in (step 3) leading to formation of pores. Additional carbon is also consumed for reducing K^+ to K as shown in steps (7) and (8). All these carbon losses contribute to the creation of porous network in the carbon material. It is interesting to note that KOH activation has the benefit of activating the carbon material or the carbon precursor with steam (step 3) as well as activation with K_2CO_3 (step 8).

The effectiveness of KOH activation relative to either physical activation methods or activation by other chemical agents can be attributed to the ability of K to form intercalation compounds with carbon easily. In addition, the K_2O formed during the process of KOH activation, *in-situ* can easily infiltrate into the pores. K_2O is reduced to K by carbon resulting in carbon gasification with a subsequent emission of CO_2 leading to the formation of pores.

3. MATERIALS AND METHOD

3.1. Materials

3.1.1. Chemicals

Analytical reagent grade chemicals were used. Potassium hydroxide solution, KOH (25% W/V, sigma Aldrich), hydrochloric acid aqueous solution, HCl (5% V/V, 37%, Riedel-de Ha n, Germany), distilled water, Lead nitrate, Pb $(NO_3)_2$ (Riedel-de Ha n, Germany),Potassium dichromate, $K_2Cr_2O_7$(99.5%, FINKEM, England), Nitric acid, HNO_3 (Riedel-de Ha n, Germany), glacial acetic acid,CH_3COOH (99.99%, Riedel-de Ha n, Germany), sodium acetate,CH_3COONa (98%Riedel-de Ha n, Germany),ammonia,NH_3 (23-25%, Mumbai, India), and ammonium chloride, NH_4Cl(99.5%,Riedel-de Ha n, Germany).

3.1.2. APPARATUS

The apparatus used for this study were: plastic bottles, volumetric flask, Measuring cylinder, Crucible, Mortar and pestle, and Sieve (Model DSCO 1674 JPG, 150 µm, UK).

3.1.3. INSTRUMENTS

Atomic Absorption spectroscopy (AAS) (Model analytic jena nov AA 300, Germany), Electrical furnace (Model Naber therm[R], Germany), pH meter (HANNA instruments, pH 211), Electronic balance (Model AFP-110L, ADAM, China),Thermostatic water bath(Model Grant GLS 400, England),Oven (Model GENLAB WIDNES, England),UV-ViS Spectro photometry (Model DR 5000, Hach USA), Scanning Electron Micrograph (SEM) (JSM 6510 LV; Jeol, Japan).

3.2. METHODS

3.2.1. Analysis of water sample for identifying concentration level of Cr (VI) and Pb (II)

3.2.2. Cleaning of Sample Containers

Sample containers should be scrupulously clean so as not to introduce contaminants that could interfere with quantification of the target analyte(s). This is of particular importance when determining trace or ultra-trace analyte concentration levels. Accordingly, the following cleaning sequence has been performed to be adequate to minimize contamination in the sample bottle.

At the beginning, plastic bottles containers were washed with detergent and tap water followed by 1:1 HNO_3 and distilled water and finally rinsed with diluted HCl.

3.2.3. Collection of water Sample

The study was conducted in Jimma town, southwestern Ethiopia. For the purpose of this study, the town was divided into four quadrants. Figure 1, illustrates the location of Jimma town in Ethiopia and the sampling sites.
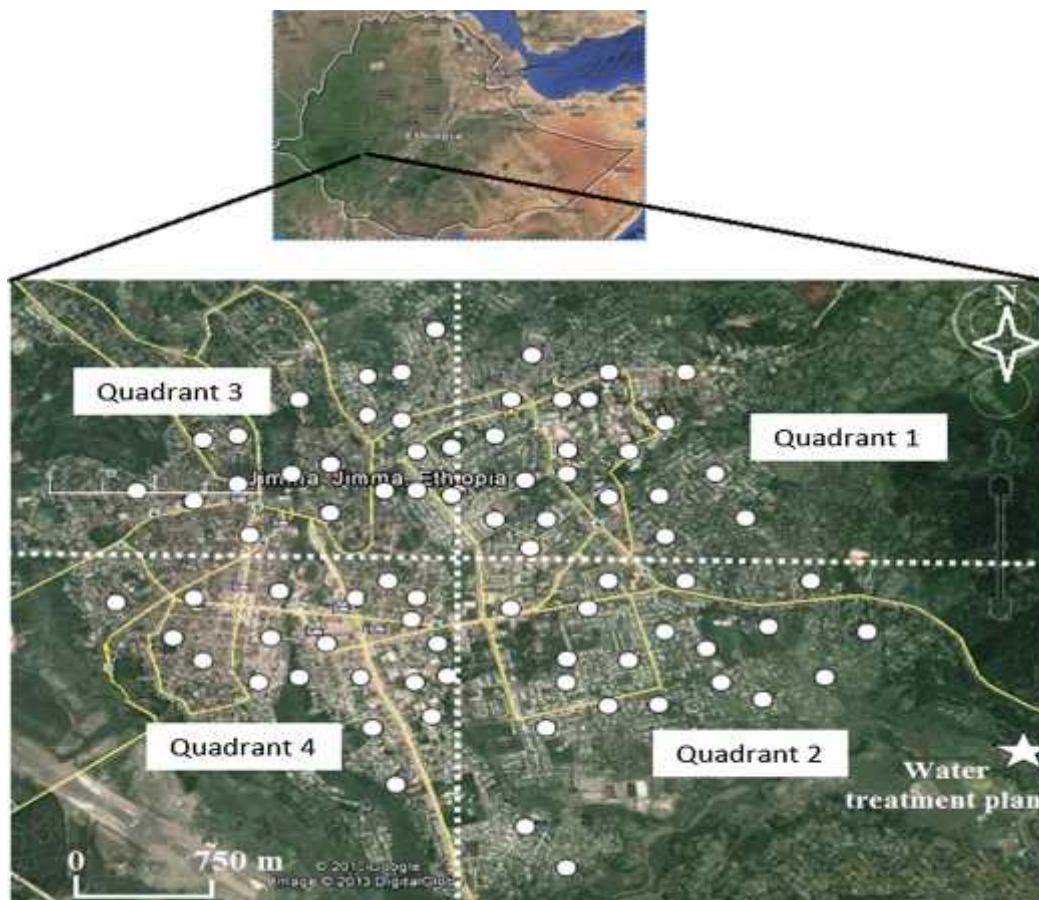
Figure 1: Location of Jimma town in Ethiopia and the sampling sites (at the different quadrants which is divided in white dash line).

Untreated (raw) and treated water samples were collected from different five sites (Boye, Kochi, Ajip, Merkato, and Agaro bar) from each two samples were collected and a total of 20 samples for both Cr (VI) and Pb (II) analysis. The water samples were treated at the time of collection by 2% NaOH / 3% Na_2CO_3 solution and HNO_3 for both Cr (VI) and Pb (II) analysis respectively, and then preserved at a temperature of 4°C.

3.2.5. Digestion of water samples for determining concentration level of Cr (VI) [NIOSH Method]

50 ml of a well-mixed solution was transferred to a 50 ml beaker, and 5.0 mL filter extraction solution, 2% NaOH / 3% Na_2CO_3 was added to it. The beaker was Covered with a watch glass and heated at 95 ^oC on a hotplate with occasional swirled for 30 to 45 min.

The solution was cooled and filtered and then transferred quantitatively with distilled water rinses to a 25 mL volumetric flask.1.90 mL 6N sulfuric acid was added to the solution in the volumetric flask and swirled to mix. To the same solution, 0.5 ml diphenylcarbazide solution was added, and the solution was diluted to the mark with distilled water and mixed thoroughly. About one-half of the contents of the flask were poured out, and the flask was stoppered and shaked vigorously several times.

An aliquot of the solution remaining in the flask was transferred to a 5 cm cuvette and analyzed using spectrophotometer at wave length of 540 nm.

3.2.6. Digestion of water samples for determining concentration level of Pb (II) [USEPA]

The entire samples were acidified at the time of collection with conc.HNO_3, 5 ml/l.Then100.0 ml of well-mixed acidified samples were measured into a 125 ml beaker and to the same samples 5 mL of conc. HCl was added.

The samples were heated on a hot plate in a well-ventilated hood until the volume has been reduced to 20 ml. The samples were cooled and filtered through a suitable filter into 100 mL volumetric flasks and were adjusted to volume.

Finally, the concentrations of the samples were determined using Atomic absorption spectrometer at wave length of 283.3 nm.

### 3.2.7. PREPARATION OF ACTIVATED CARBON ADSORBENT

3.2.8. SAMPLE COLLECTION

The Pine apple peel (*Ananas cosmosus)* which is the precursor material for activated carbon adsorbent was collected from Café of Jimma town.

3.2.9. PREPARATION PROCEDURE

The collected pine apple peel (*Ananas cosmosus)* was washed several times with tap water and then air dried for two weeks in the laboratory. The dried sample was again washed with distilled water and air dried for three (3) days followed by oven dried for 24 hr at 65°C for proper drying. The well dried sample was grinded and then sieved.

The dried, grinded and sieved biomass was soaked in 25% (w/v) of KOH solution. The mixture was stand for 3hr for agitation. Then, oven dried for 12hr at 105°C.

The dried sample was carbonized at a temperature of 800°C for 2hour, and the carbonized sample was cooled. The cooled activated carbon product was treated with 5%HCl solution followed by washing with distilled water until the pH of the washing solution became neutral. Then, the carbonization product which is now called '*activated carbon of the raw sample* 'was kept in air tight plastic container. The above explanations are shown as the following flow chart:

(a)   (b)   (c)   (d)
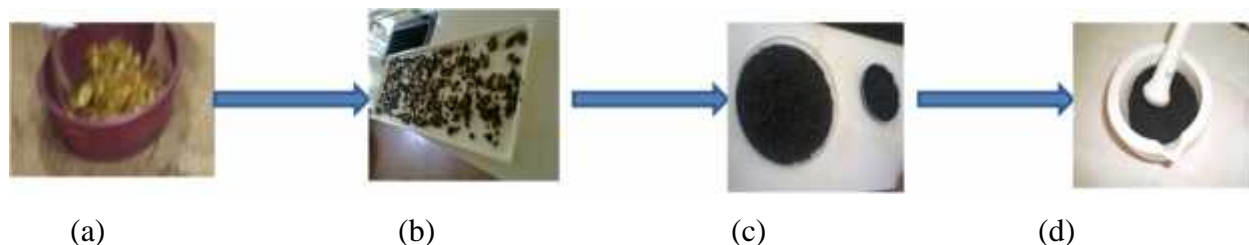
Figure 2: Shows pine apple peel while (a) washed, (b) dried, (c) after activated, (d) grinded.

3.2.3. Preparation of stock solution

The stock solution of both Cr (VI) and Pb (II) with a concentration of 1000mg/l were prepared from $K_2Cr_2O_7$ and Pb $(NO_3)_2$ respectively.

This was done by dissolving 2.827g and 1.599g of $K_2Cr_2O_7$ and Pb $(NO_3)_2$ in 1000ml distilled water respectively. From this stock solution, both chromium (VI) and Lead (II) solutions with a concentration of 10 mg/l were prepared by dilution with distilled water. Therefore, dilution of 10ml of stock solution whose Cr (VI) and Pb (II) concentrations are 1000 mg/l to 1000ml with distilled water would give Cr (VI) and Pb (II) concentration appropriately equal to 10mg/l respectively.

3.3. Adsorption study

The study of the adsorption of heavy metals Pb (II) and Cr (VI) on to activated carbon have been performed by taking contact time, initial metal ion concentration, adsorbent dosage, temperature and pH as parameters influence adsorption.

3.3.1. Effects of pH

This is an important parameter on which the adsorption of Pb (II) and Cr (VI) is strongly depended. It was carried out by varying a pH between (1-11) and by contacting 0.25 g of AC with 25 ml of 10 ppm both $K_2Cr_2O_7$ and Pb $(NO_3)_2$ solution.

The mixture was shaken in thermostatic water bath shaker at 200 rpm and a temperature of 25 ^{o}C for 180 min. Then it was cooled and filtered through what man 42 filter paper. The filtrate was isolated and analyzed using UV-Vis and AAS.

3.3.2. Effects of contact time

This was done by varying time interval in the range between 10-180 min with variations of 30 minute. In this case, 0.25g of AC was contacted with 25ml of 0.02 to 20 ppm both $K_2Cr_2O_7$ and Pb $(NO_3)_2$ solutions and the mixture was shaken in the water bath shaker at 200rpm and temperature of 25°C until their respective final time.

It was cooled and filtered with filter paper (what man 42). The filtrate was separated and analyzed by using UV-Vis and AAS so as to know the optimum time at which maximum adsorption is appeared.

3.3.3. Effect of adsorbent dosage

The adsorption of Pb (II) and Cr (VI) by Pineapple peel activated carbon (PPAC) at different adsorbent doses (0.1–0.35g) and at the lead and chromium concentration of 2.5 mg/L is investigated. This was done by weighing 0.1, 0.15, 0.2, 0.25, 0.3 & 0.35 g of PPAC into each boiling tube and 25 mL of 2.5 mg/L of Pb (II) and Cr (VI) ion solutions at optimal pH and contact time. The tubes were left in a thermo stated water bath and shaken at 200 rpm on 25 °C. The activated carbon was removed from the solution and the concentration of residual metal ion in each solution was determined using UV-Vis and AAS.

3.3.4. Effect of temperature on adsorption

The batch adsorption process was studied at different temperatures (20–45°C) in order to investigate the effect of temperature on the adsorption process. This was done by contacting 0.25 g of activated carbon with 25 mL of 0.02 and 0.05 mg/L of Pb (II) and Cr (VI) ion solutions at the optimal pH and contact time.

3.4. Statistical analysis

Triplicate measurements were considered during the determination of Pb (II) and Cr (VI) ions and the obtained results were analyzed by averaging the values. The curve fittings of the data obtained were performed using microcal origin 6.0 software.

4. RESULT AND DISCUSSION

4.1. Lead and Chromium contents of drinking water

Water Pollution is common and is an area of high alert. Therefore water needs to be preserved. For this reason, study has been conducted to detect concentration level of Pb and Cr (VI). In this study, ten water samples were collected for each metal ion from different five sites in Jimma town. The samples collected were classified into three different categories which consist of raw water, treated water ;(which are before and after distributed for residents).

The results were determined as mean±SD of three replicates in each test. Figure 3 and 4, revealed that sites Merkato, kochi and Agaro ber in Jimma city had chromium and Lead contents above Maximum Contaminant Level (MCL):0.05 milligrams per liter (mg/l) Chromium and 0.01 mg/l Lead content which is recommended by EPA and WHO[44](US/EPA, 2013; WHO, 2007).

The concentration, C (mg/l), of Cr (VI) and Pb (II) in the water sample were calculated using the following formula:

$$C = \frac{W-B}{V}, \text{mg/l} \tag{9}$$

Where; W (μg) is the mass of Cr (VI) or Pb (II) in each sample

B (μg) is the mass of Cr (VI) or Pb (II) in the average blank

V (L) is the water volume sampled

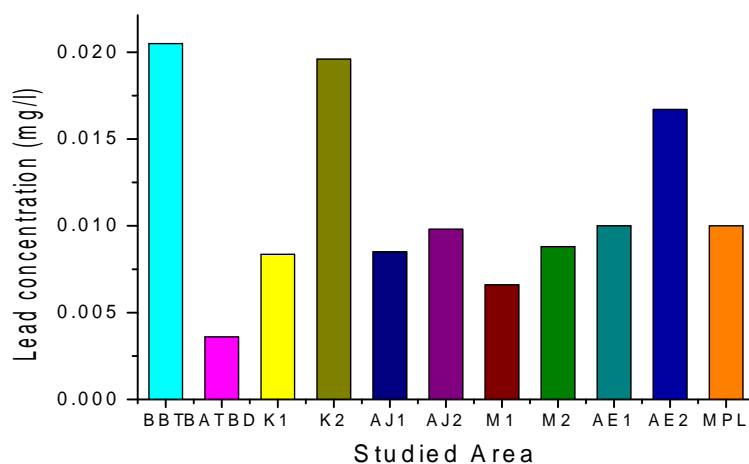The mean level of Lead and Chromium contents (mg L^{-1}) ±SD in Jimma drinking water samples of studied sites are shown as table below:

Table 1. The mean level of heavy metal contents (mg L^{-1}) ±SD, in different sites.

S.No	Sample type	Pb (mg L^{-1}) ±SD, n=3	Maximum permissible limit, 0.01(mg L^{-1})	Cr (VI) (mg L^{-1}) ±SD, n=3	Maximum Permissible limit, 0.05 (mg L^{-1})
1	**Untreated Water (BBT)**	0.0205 ± 0.0005	above	0.104± 0.0123	above
2	**Treated water(BATBD)**	0.0036 ±0.0013	below	0.01 ± 0.0024	below
	Distributed Water				
3	**K$_1$**	0.00836 ± 0.0011	below	0.012 ± 0.0031	below
4	**K$_2$**	0.0196 ± 0.0002	above	0.031 ± 0.0036	below
5	**AJ$_1$**	0.00425 ± 0.0012	below	0.026 ± 0.0035	below
6	**AJ$_2$**	0.0049 ± 0.0022	below	0.018 ± 0.0032	below
7	**M$_1$**	0.0066 ± 0.0028	below	0.011 ± 0.0055	below
8	**M$_2$**	0.0088 ±0.0011	below	0.055 ± 0.0113	above
9	**AE$_1$**	0.01 ± 0.0030	equal	0.024 ± 0.0003	below
10	**AE$_2$**	0.0195 ± 0.0011	above	0.035 ± 0.0015	below

Where; n = no of replicate measurements &SD = standard deviation of the measurements.

The mean level of Lead (mg/l) and Chromium (VI) (mg/l) contents in water samples under study are shown together with maximum permissible limit value as below Figure 3 and 4:

Figure 3: The Mean content of Lead (mg/L) in drinking water samples in studied sites of Jimma.
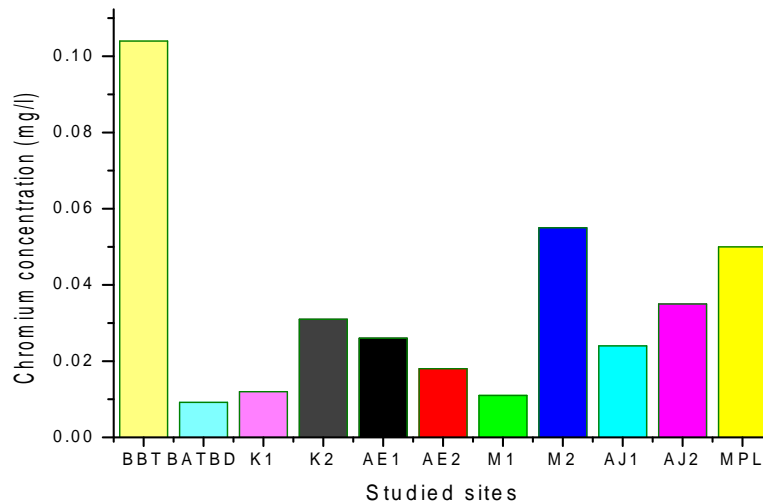
Figure 4: The Mean content of Chromium (mg/L) in drinking water samples in studied sites of Jimma.

As shown from the figure 3 and 4, lead and chromium concentration in raw water are found higher than in treated water. This may be due to the fact that heavy metal contamination of surface water is found at a higher level than the underground water. This could be probably as a result of agricultural runoff, city street runoff, construction sites, residential lawns and concluding accumulation of pollutants which can easily reach the water source by erosion.

On the other hand, among treated water studied, three sites (Kochi, Agaro exit, and Merkato) out of five studied sites in present study is polluted and Lead and Chromium concentrations are found higher than WHO guidelines [0.01 ppm for lead and 0.05 ppm for chromium] and EPA standards and probably have public health problem by their consumption, and constantly determination of heavy metals should be measured by responsible organizations.

In this study, the lead content in different area in city were compared with each other by statistical calculations and the results showed there's a significance different between lead contents in different geographical location of city. Significant variation in the concentrations of Lead and Chromium in tap water is probably the results of old water distribution pipe lines and the presence of heavy automobile traffic, garages and gasoline stations in the area which can easily contaminate surrounding soil and water.

The mean Lead concentration from tap water samples was 0.011 ± 0.0015 mg/L. From all the water samples, samples from Kochi(2) (i.e., near dippo) and Agaro bar(2) have lead concentration greater than the WHO(2007) recommended value of 10 $\mu g/L$. Water samples

collected relatively far from the treatment plant has higher lead concentration than the closest sites. There is significant correlation between the lead concentrations of tap water and distance of the sampling points from the treatment plant. This could suggest that the longer the distance from the water treatment plant the higher lead concentration in tap water of Jimma town. This may be due to the fact that the water flowing through the pipe to a longer distance has higher contact time with the piping materials than the closer sites. The longer water remains standing in the plumbing systems, the more lead it can absorb from any lead sources accessible to it [45-46].

As seen from figure 4, hexavalent Chromium concentration in Merkato (2) water; [0.055 mg/l] was found higher than MCL. Cr (VI) at the consumer's tap may arise from a variety of sources. Source waters may have naturally occurring or anthropogenic ally elevated levels of Cr (VI).

Chromium may be added to water via leaching from distribution system materials or through reactions with main distribution system or premise plumbing. Chromium is contained in materials typically used in water plant and distribution system infrastructure such as cast iron, cement, and stainless steel, and this chromium could be released to the water through leaching or corrosion of these materials [48-56].

4.2. Calibration and quality control

Working standards whose concentrations range from {0.01 – 0.32 $\mu g/ml$} were prepared from 10 $\mu g/ml$ calibration stock solution of K_2CrO_4. These working standards were analyzed together with blanks and samples. The result is shown as below by plotting absorbance reading vs. concentration of working standards.
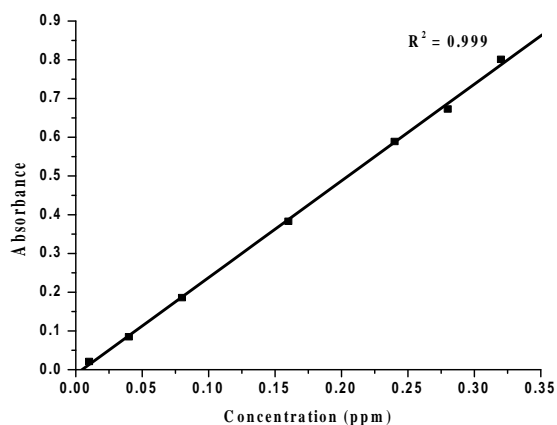
Figure 5: A calibration graph of absorbance vs concentration (ppm) of K_2CrO_4 solution of working standards.
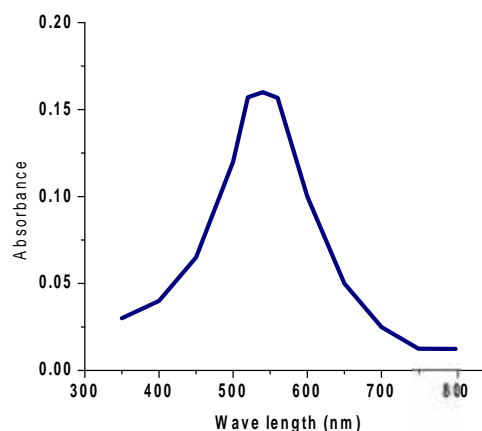
Figure 6: UV-Vis spectra of 0.05 $\mu g/ml$ of K_2CrO_4 at varies wavelength.
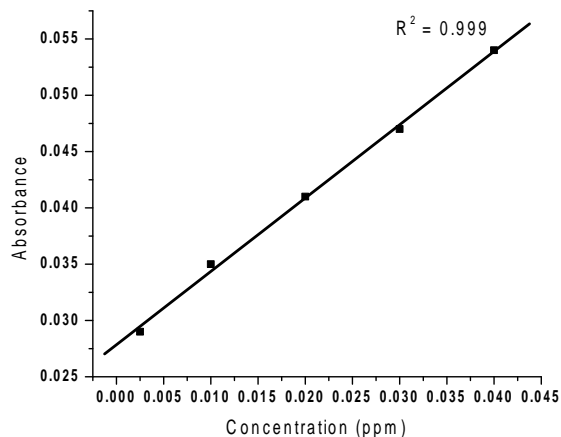
Figure 7: A Calibration gragh of Pb $(NO_3)_2$ solution of working standards

4.3. Method Validation

A stock solution containing dilute nitric acid and 2.5 $\mu g/L$ lead was prepared. Seven aliquots of the sample were analyzed. The results (in $\mu g/L$) are summarized in Table 2 below.

The number of observations is equal to the number of replicates, seven, with six degrees of freedom. The Student's t-value for 7 replicates and 6 degrees of freedom is 3.143.

Table 2: Seven aliquots of the sample analyzed for method validation of Lead analysis.

Sample#	Results ($\mu g/D$)	%Recovery
sample 1	2.4	96
sample 2	2.2	88
sample 3	2.1	84
sample 4	2	80
sample 5	2.2	88
sample 6	2.3	92
sample 7	2.3	92
Mean	**2.2**	**88**
SD	**0.13**	

The MDL is calculated and rounded:

MDL= (s) (t-value) = 0.13 x 3.143 = 0.41 $\mu g/L$

The LOQ is also calculated:

LOQ = 10(s) = 10 x 0.13 = 1.3 $\mu g/L$

4.4. **Proximate analysis of PPAC product**

Activated carbons are widely used as adsorbents due to its high adsorption capacity, high surface area, and micro porous structure. Some important proximate analysis of PPAC product is given in Table 3.Moisture content of the carbon has no effect on its adsorptive power; it dilutes the carbon and necessitates the use of additional weight carbon during treatment process. Any porous material will have the tendency to absorb moisture. The moisture content of PPAC obtained is normal and comparable with the values reported elsewhere [57].The PPAC sample was determined using standard test method for moisture in AC [58].The lower ash content is attributed to lower inorganic content and higher fixed carbon content. Higher value of fixed carbon content shows that the adsorbent is having more efficiency and stability. The sample was determined using standard test method for ash content of AC [59].Fixed carbon is a calculated value and it is the resultant of summation of percentage moisture, ash, and volatile matter subtracted from 100.

Fixed carbon (%) = 100 – (moisture, % + ash, % + volatile matter, %)   (10)

The proximate analysis of AC product was obtained and shown as follows:

Table 3: Proximate analysis of PPAC.

Parameter	% Yield
Moisture content (%)	10.8
Ash content (%)	21.8
Volatile matter (%)	3.9
Fixed carbon (%)	63.5
pH	7.44

4.5 SEM and EDX analysis of activated carbon adsorbent

Scanning electron micrograph (SEM) and energy dispersive spectrum of X-ray (EDAX) were carried out for the biosorbents before and after equilibration using Scanning Electron Microscope, JSM 6510LV, JEOL, Japan. The SEM enables the direct observation of the surface microstructures of different adsorbents [90].

SEM micrographs of the activated carbon were presented in figure 8. From the figure, well-developed porous surface was observed at higher magnification. The pores observed from SEM images are considered as channels to the micro porous network. From the figure, it can be observed that the adsorbent has rough texture with heterogeneous surface and a variety of randomly distributed pore size.

The SEM photograghs showed that the progressive changes occurred in the surface of native adsorbent (Figure 8a) after its surface was loaded by lead and chromium ions (Figure 8b & 8c). The SEM of exhausted adsorbents clearly indicates the presence of layer over the surface of metal – loaded adsorbents which are absent in the native adsorbent [91]. The lead and chromium ions cover the surrounding adsorbent particles and fill the voids (Figure 8b and 8c).

EDX measurements were recorded for qualitative analysis of the element constitution of the adsorbents and the spectra of the native adsorbent and lead and chromium ions loaded adsorbent are illustrated in Figure 8a, 8b and 8c below. From the EDX spectra, lead and chromium ions were sorbed onto the adsorbent. The EDX analysis provided direct evidence for the adsorption of lead and chromium onto the adsorbent [90].
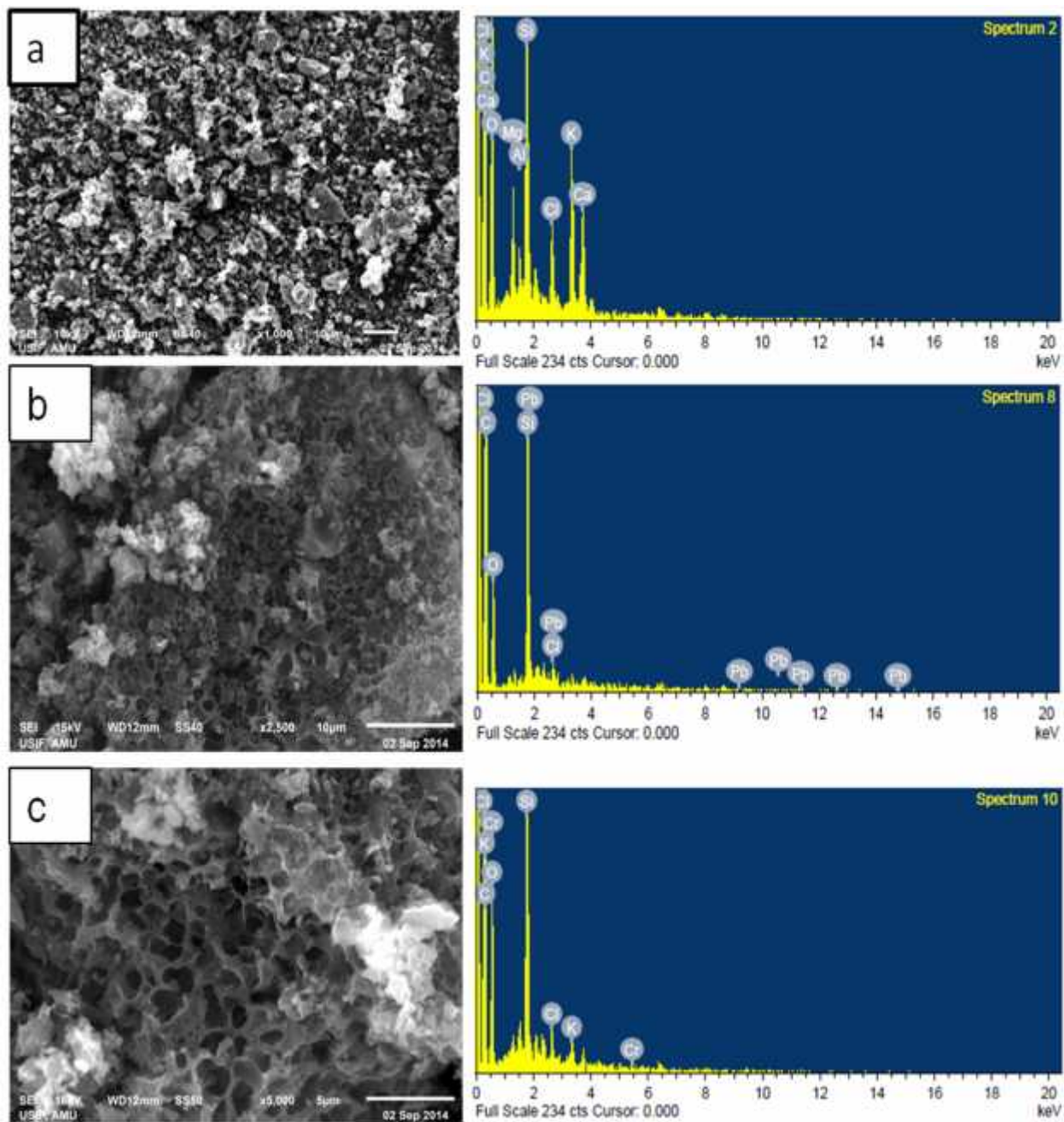
**Figure** 8: SEM of native adsorbent (a), lead loaded adsorbent (b), and chromium loaded adsorbent (c) along with their respective EDX spectra.

4.6. Sorbent characterization

The activated carbon product was characterized for its functional groups using Fourier Transform Infrared Spectrophotometer (FT-IR) analysis. The type and net charge of functional groups bonded to the carbon surface is important in understanding the mechanism of adsorption of ionic adsorbate on activated carbons. FT-IR spectrum is an essential tool to identify the surface functional groups which can contribute significantly to enhance adsorption efficiency of the activated carbon by surface complexation. The functional groups, on the surface of activated carbon analyzed by FT-IR demonstrated the existence of carboxyl, hydroxyl, and amine groups which were mostly negatively charged.

The FT-IR spectroscopic characteristics of the origin and metal laden activated carbon are shown in Table 4. This demonstrates that after the adsorption the shifting occurs both to higher and lower wave numbers. This shifting indicated that there were binding processes, taking place on the surface of activated carbon.

The peak at 3411 cm^{-1} is associated to O-H stretching vibration mode. The peak at 2920 cm^{-1} may be aliphatic methyl asymmetric C-H stretching. The peak observed around 1568 cm^{-1} is because of C=C stretching band. The peak at 1038 cm^{-1} is associated to carboxylic group, and alcoholic C-O stretching. FT-IR transmission spectra in the range of 500–4000 cm^{-1} for the original activated carbon, the activated carbon laden with Cr (VI), and Pb (II) are shown in Fig.9a, 9b, and 9c, respectively.
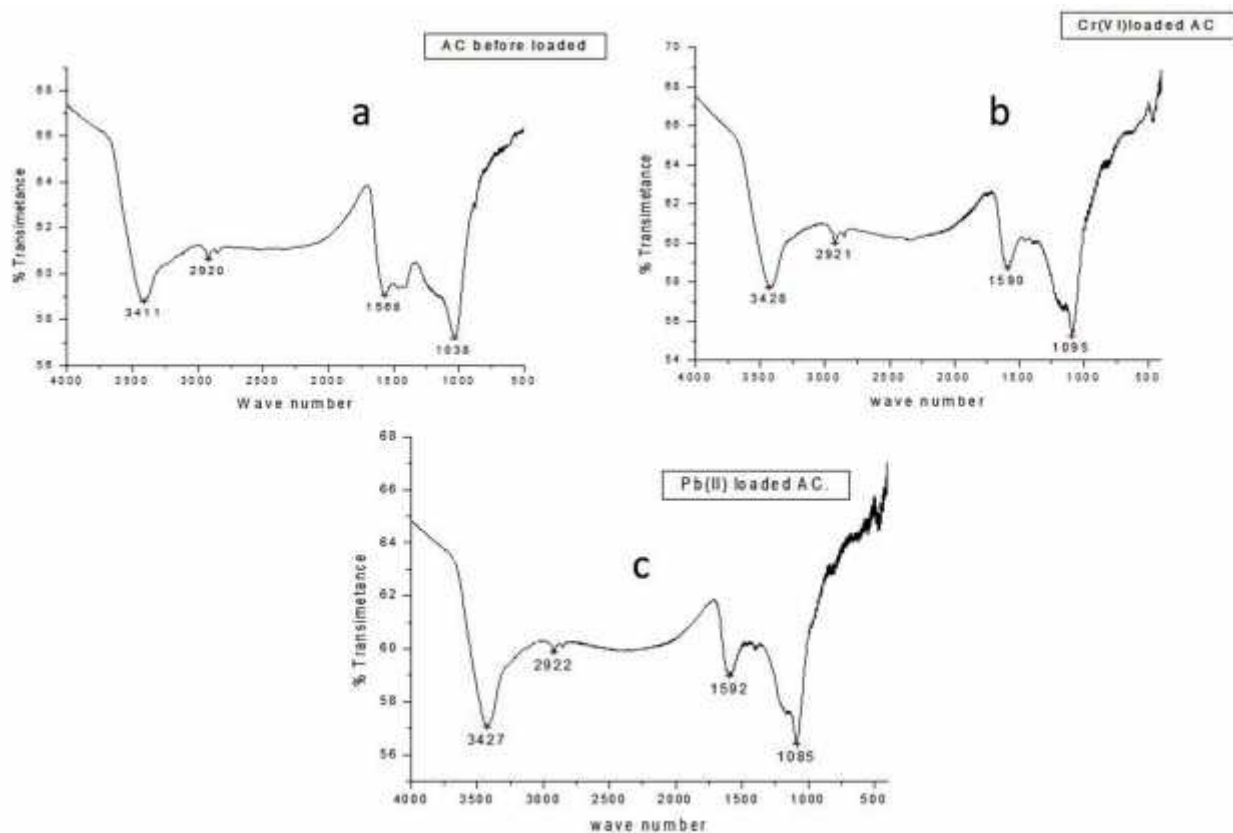
Figure 9: FT-IR transmission spectra of (a) unloaded activated carbon, (b) Cr (VI) laden and (c) Pb (II) laden

Table 4: FT-IR results from metal laden activated carbon

S.No	Absorption bands (cm^{-1})					
	Before adsorption	**Cr(VI) laden AC**	**Difference**	**Pb(II) laden AC**	**Difference**	**Assignment**
1	3411	3428	17	3427	16	Bonded –OH groups
2	2920	2921	1	2922	2	Aliphatic C–H group
3	1568	1590	22	1592	24	Secondary amine group
4	1038	1095	57	1085	47	Carboxylic group, alcoholic C-O stretching

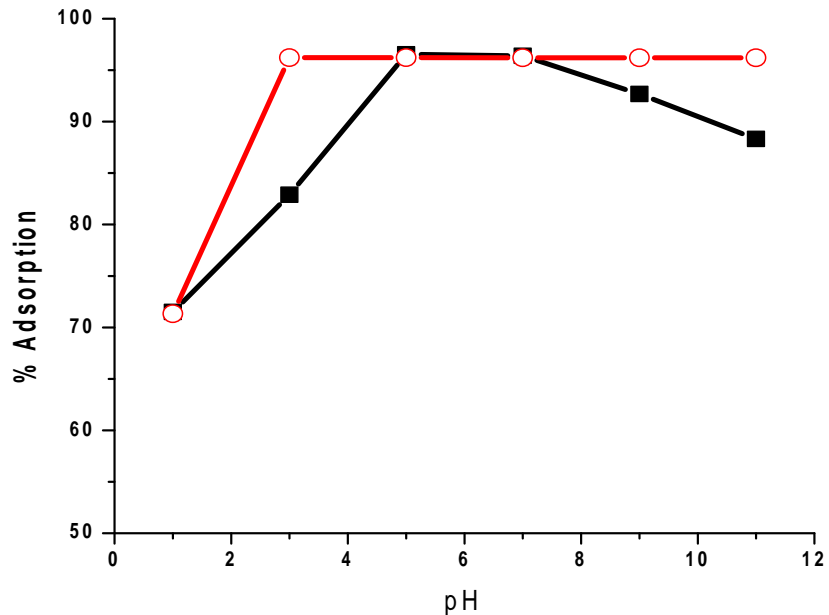## 4.7. Effect of pH on adsorption of Pb (II) and Cr (VI) on AC adsorbent

The pH value of the solution is an important controlling parameter in the adsorption process, and the initial pH value of the solution has more influence than the final pH, which affects both the adsorbent surface metal binding sites and the metal chemistry in water [60].

The adsorption experiment was carried out showing the effect of pH ranging from 1.0-11.0 by contacting 0.25 g of AC with 25 ml of 10 ppm Pb $(NO_3)_2$ and $K_2Cr_2O_7$ solution. The mixture was shaken in thermostatic water bath shaker at 200 rpm and temperature (25 ^{o}C) for 180 min. Figure 10 shows the effect of pH on adsorption percentage of lead and chromium by PPAC.

In the case of Pb (II) the maximum adsorption was obtained at pH 5.0. Removal of Pb^{2+} onto the activated carbon is pH dependent as shown in Figure 10. At pH < 2.5, H^+ ions compete with Pb (II) ions for the surface of the adsorbent which would hinder Pb (II) ions from reaching the binding sites of the sorbet caused by the repulsive forces. At pH > 6.0, the Pb (II) gets precipitated due to hydroxide anions forming a lead hydroxide precipitate. For this reason the maximum pH value was selected to be 5.0.

The highest efficiency [96.46%] was observed at pH of 5.0. In this study percent adsorption decreased as pH of the solution increases after equilibrium was achieved.

For Cr (VI) the observed result suggest that at lower pH [pH = 3] percentage adsorption was higher (96.22%) and after equilibrium was reached the adsorption decreases and remains the same with increasing pH up to 11, (Figure 10). This is because of the fact that Cr (VI) removal by activated carbon is enhanced in the acidic range of pH. Similar results have been reported [61, 62]. The favorable effect of low pH can be attributed to the neutralization of negative charges on the surface of the adsorption by excess hydrogen ions, thereby facilitating the diffusion of hydrogen chromate ions ($HCrO_4^-$) or CrO_4^{2-} ions and their subsequent adsorption. $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$ are the predominant species and ionic form of Cr (VI) at low pH [63, 64]. This ionic form was found to be preferentially adsorbed on the surface of carbon. Effect of pH on adsorption of Cr (VI) and Pb (II) onto activated carbon adsorbent is shown below:

Figure 10: Effect of pH on adsorption of Cr (VI) (circle), and Pb (II) (square)

4.8. Effect of contact time

The influence of contact time for the adsorption of Pb (II) and Cr (VI) on the activated carbon was investigated by successively increasing the contact time from 10 to 180 minutes in 30 minute intervals (Figure 11).

As shown in Figure 11(a) & (b), the equilibrium time is dependent on the adsorbate concentration. At 10-100 and 10 - 70 min for Pb (II) and Cr (VI) respectively, percent adsorption was found slightly increased. At lower adsorbate concentration (0.02 mg/L) percentage of adsorption was found to be high at 98.36% and gradually becomes constant. From above observation in the early stages it is exposed that the rate of uptake was fast but progressively decreased and become constant when equilibrium reached, similar results has also been reported [65].

This fast uptake rate could be due to the large number of vacant spaces available on the adsorbent surface at the early stage. Above 100 min and 70 min a relatively slower adsorption was observed until it appeared to reach constant state after 100 and 70 minutes of shaking time. Further increase in contact time did not show any increase in adsorption. The relatively slower

adsorption above 100 and 70 min until equilibrium can be explained in such a way that at about 100 and 70 min of shaking time, most of the adsorption sites on the surface of the adsorbent are occupied by adsorbate ions and repulsion between adsorbed ions and those approaching to occupy the remaining vacant surface sites from the bulk solution increases. As a result, the rate at which both Pb (II) and Cr (VI) ions get adsorbed will decrease [66].
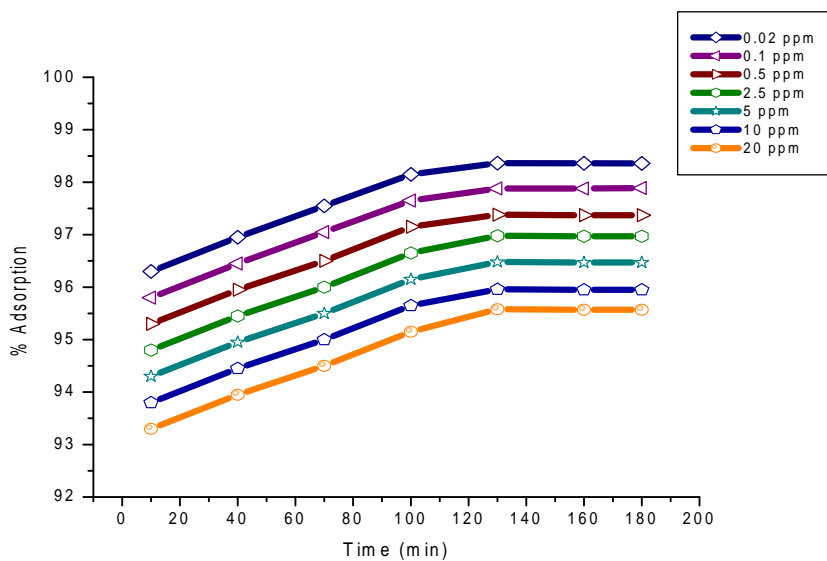
Figure 11(a): Effect of contact time on Pb (II) adsorption at different time interval from 10-180 min.
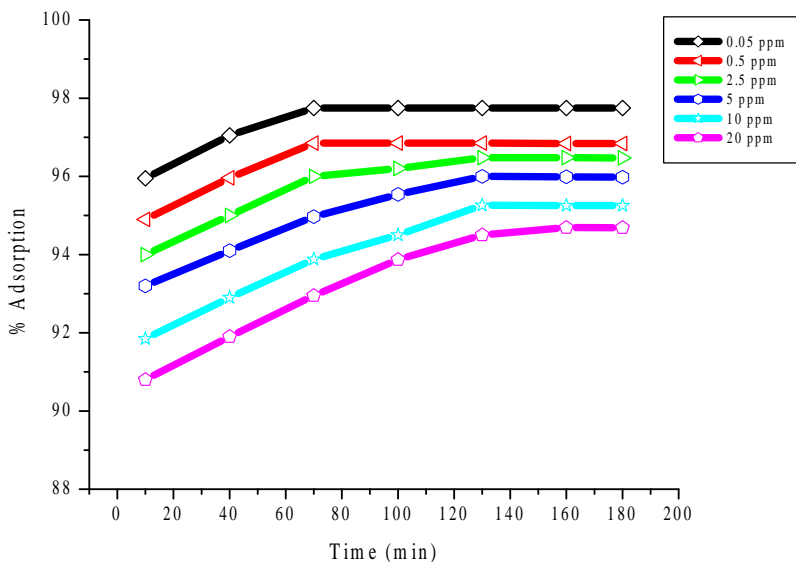
Figure 11(b): Effect of contact time on Cr (VI) adsorption at different time interval from 10-180 min.

4.9. Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption of Pb (II) and Cr (VI) ions was investigated (Figure12). As shown in Figure12, the percentage removal increases from 97.34% to 98.375%and 97.44% to 98.26% with increasing dosage from 0.1 to 0.25 g for both Pb (II) and Cr (VI), respectively. Beyond 0.25 g, the percentage was not increased significantly and reached the maximum of 98.375% and 98.26% for both Pb (II) and Cr (VI) at dosage of 0.25 g respectively. This phenomenon can be due to the greater availability of active sites or surface area making easier penetration of the Pb (II) and Cr (VI) ions to the adsorption sites of activated carbon, and increasing beyond dosage of 0.25 g had no much effect after equilibrium is reached. These results are in agreement with other work reported in the literature [67].The effect of adsorbent dose on the adsorption of Pb (II) and Cr (VI) is shown in Figure 12 below:
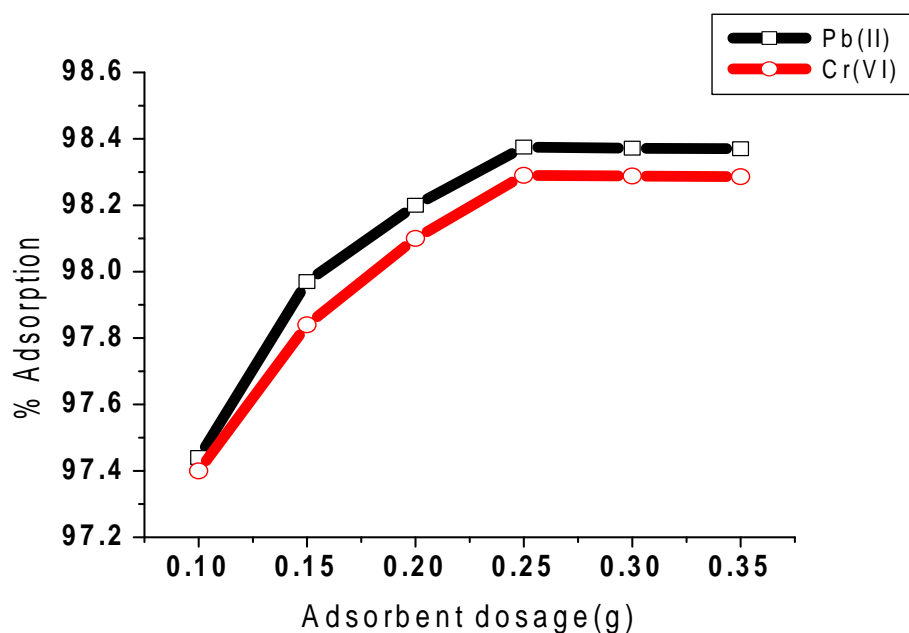
Figure 12: Effect of Adsorbent dosage on adsorption of Pb (II) (rectangle) and Cr (VI) (circle).

5. Effect of temperature

Temperature is an important parameter in the adsorption process of metal ions. Process temperature has a profound effect on heavy metal removal by using various adsorbents and the optimum temperature for better removal changes with the type of adsorbent and adsorbate. Percentages of Pb (II) and Cr (VI) adsorption were performed at different temperatures in the range of (20 ^{o}C - 45 ^{o}C). Adsorption of these ions on the adsorbent witnessed the increase in adsorption percentage from 20 ^{o}C to 25 ^{o}C and no significant change with further increase of temperature. It was observed that the percentage adsorption increases from 97.8 to 98.54% for Pb (II), and 97.37 to 98.364 for Cr (VI) ion with the rise in temperature from 20 to 45 ^{o}C. This observed increment may be due to the fact that increase in temperature is known to increase the diffusion rate of the adsorbate molecules across the external boundary layer and within the pores. Thus, the percentage adsorption of Cr (VI) and Pb (II) increases as the rate of diffusion of these ions in the external mass transport process increases with temperature [68].It would be expected that an increase solution temperature would result in the enlargement of pore size due to 'activated diffusion' causing the micro-pores to widen and deepen and create more surface for adsorption[69].The effect of temperature on the adsorption of Pb (II) and Cr (VI) is shown as in figure 13 below:
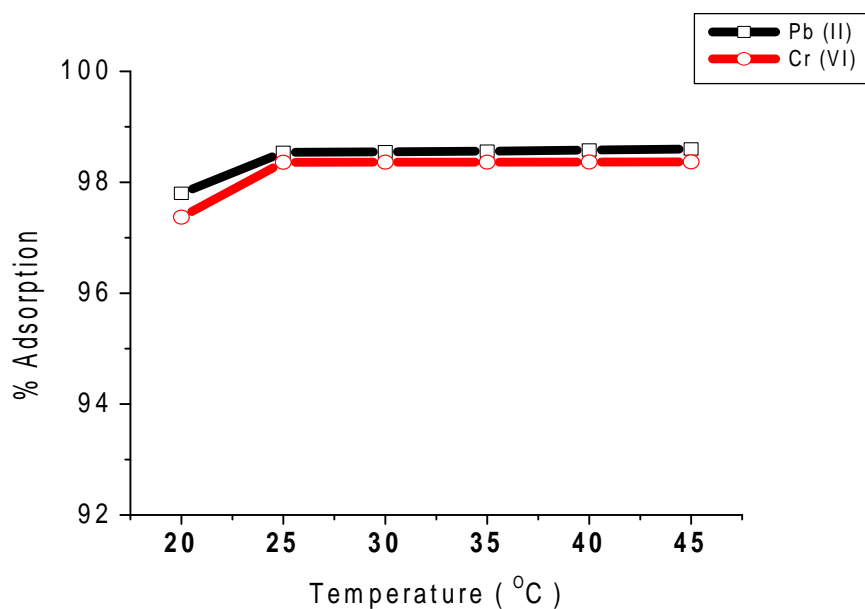
Figure 13: Effect of temperature on adsorption of Pb (II) (rectangle) and Cr (VI) (circle).

5.1. Adsorption isotherm study

Adsorption isotherm is a basic requirement for the design of an adsorption system. The adsorption capacity and also the performance of the adsorbents were usually predicted from equilibrium sorption isotherm [70]. Several models have been used to describe experimental data for adsorption isotherms.

The most commonly used isotherms for the application of activated carbon in water and wastewater treatment are the Freundlich and Langmuir isotherms. They were early adsorption models and are still frequently used. The relationship between adsorbent and adsorbate in the equilibrium and maximum bio sorption capacity of the biosorbents are studied using models of bio sorption, such as the Langmuir and Freundlich isotherms [71].

The two models differ from each other in their assumption concerning the existence of a finite adsorption capacity.

Langmuir adsorption Isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases [72]. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites.

The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface.

The linear form of the Langmuir isotherm is given as the following equation:

$$\frac{c_e}{q_e} = \frac{c_e}{q_n} + \frac{1}{q_n \, b_L} \tag{11}$$

Where; q_e(mg/g) is the equilibrium concentration of Pb (II) or Cr (VI) ion in the adsorbed phase and C_e (mg/l) is the equilibrium concentration of Pb (II) or Cr (VI) ion in the liquid phase. Langmuir constants, which are related to the maximum adsorption capacity (q_m) and energy of adsorption (b_L) can be calculated from the slope of the linear plot of C_e/q_e vs. C_e, a straight line with slope $1/q_{max}$ and intercept of $1/q_m b_L$ is obtained. The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L which is given as:

$$R_L = \frac{1}{1 + b_{LC_O}} \tag{12}$$

Where, C_o is the highest initial Pb (II) and Cr (VI) ion concentration (mg/l).
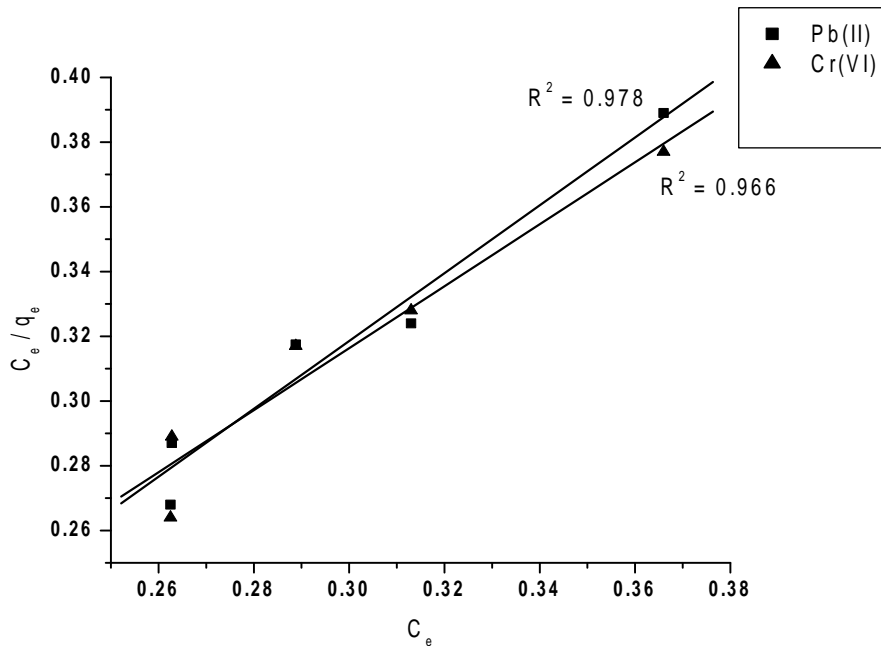
Figure 14: Langmuir plot of adsorption of Pb (II) (square) and Cr (VI) (triangle) onto PPAC

Freundlich adsorption isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface [73].The linear form of the Freundlich isotherm is given as the following equation:

$$logq_e = logk_f + \frac{1}{n}logC_e \tag{13}$$

The constant K_f is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process and the smaller $1/n$, the greater the expected heterogeneity[74]. If n lies between one and ten, this indicates a favorable sorption process [75]. From the data in table 5, that value of $1/n = 0.2$ and 0.28 while n=5 and n= 3.57 indicating that the sorption of Pb^{2+} and Cr (VI) onto PPAC is favorable and the R^2 value is 0.999 and 0.989 for both Pb(II) and Cr(VI) respectively.

The value of R_L found (0.0172 and 0.0174) is between 0 and 1, which indicates favorable adsorption [76]

Using the Freundlich isotherm, the value of n found 5 and 3.57 denotes spontaneous adsorption. Values of n in the range $1 < n < 10$ indicate favorable bio sorption [77]
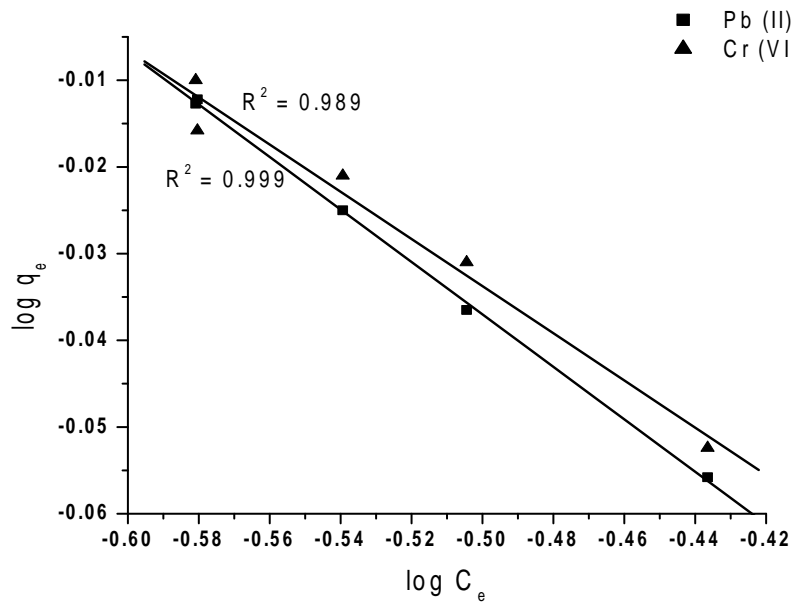
Figure 15: Freundlich plots of the adsorption of Pb (II) (square) and Cr (VI) (triangle)

Table 5: Results of isotherm models for the adsorption of Pb (II) and Cr (VI) onto PPAC at 298 K.

Adsorption isotherms	Values	
	Pb(II)	Cr(VI)
Langmuir / constants		
q_m(mg/g)	0.952	0.935
b_L(L/mg)	2.850	2.822
R^2	0.978	0.966
R_L at 20 mg/L	0.017	0.017
Freundlich / constants		
K_f	1.030	1.029
$1/n$	0.200	0.280
R^2	0.999	0.989

5.2. Adsorption Kinetic studies

Adsorption kinetics is of great significance to evaluate the performance of a given adsorbent and gain insight into the underlying mechanisms. Kinetics analysis is required to get an insight of the rate of adsorption and the rate-limiting step of the transport mechanism, which are primarily used in the modeling, and design of the process. In order to evaluate the kinetic parameters, Pseudo first order and Pseudo second order models were implemented to analyze the experimental data. The pseudo first order equation [78] can be expressed as:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_1}{2.303}t \qquad (14)$$

Where, q_e and q_t represent the amount of adsorbed (mg/g) at equilibrium and at any time t, K_1 is the first order rate constant (min^{-1}). From the plots of log (q_e-q_t) versus t in Figure 10, k_1 can be calculated from the slope and theoretical q_e can be obtained from intercepts.

Pseudo second order equation can be given by [79].

$$\frac{t}{q_t} = \frac{1}{K_2\, q_e^2} + \frac{1}{q_e}t \qquad (15)$$

Where, K_2 is the rate constant of second order adsorption. The linear plots of t/q_t versus t determine 1/q_e as slope and 1/$K_2q_e^2$ as intercepts. The linear plots of pseudo second order model is shown in figure 11.

The experimental results for the adsorption of Pb (II) and Cr (VI) ions onto the adsorbent showed rapid initial adsorption rate followed by a slower rate. Initially, the adsorption sites are abundantly available and the metal ions interact easily with the sites and hence a higher rate of adsorption is observed. Moreover, the driving force for adsorption is higher initially and this leads to a higher adsorption rate. However, after the initial period, slow adsorption may be due to slower diffusion of adsorbate in to the interior of the adsorbents [80].The two adsorption kinetic models mentioned above have been used to understand the adsorption kinetics and the correlation coefficient, R^2, were calculated from these plots. The linearity of these plots indicates the applicability of the two orders [81]. These pseudo-first order and pseudo-second order models were calculated by using equations (14) and (15).

However, the correlation coefficient, R^2, values showed that the pseudo-second order model fits better to the experimental data than the pseudo-first order model (Figure 16 and 17 and Table 6). The pseudo second-order kinetic model has been successfully applied to several adsorption systems [82, 83].
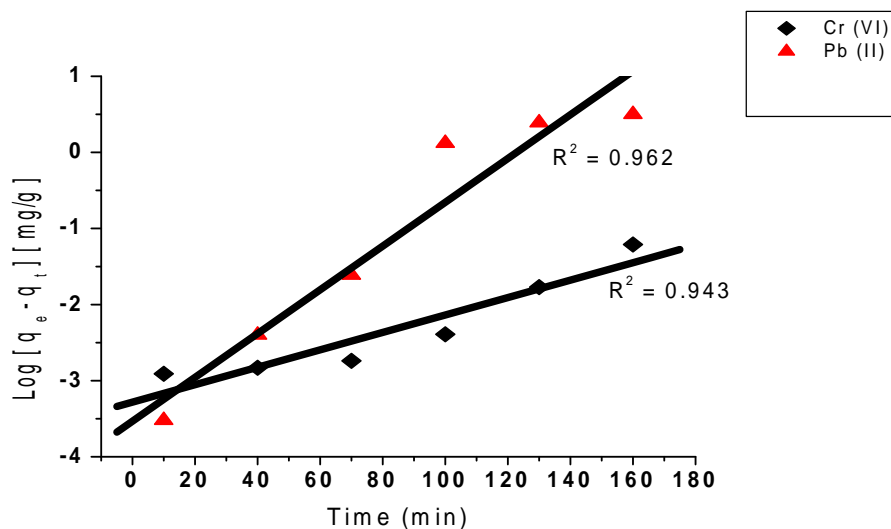
Figure 16: Pseudo-first-order kinetics plot for the adsorption of Pb (II) (triangle), and Cr (VI) (square) onto PPAC
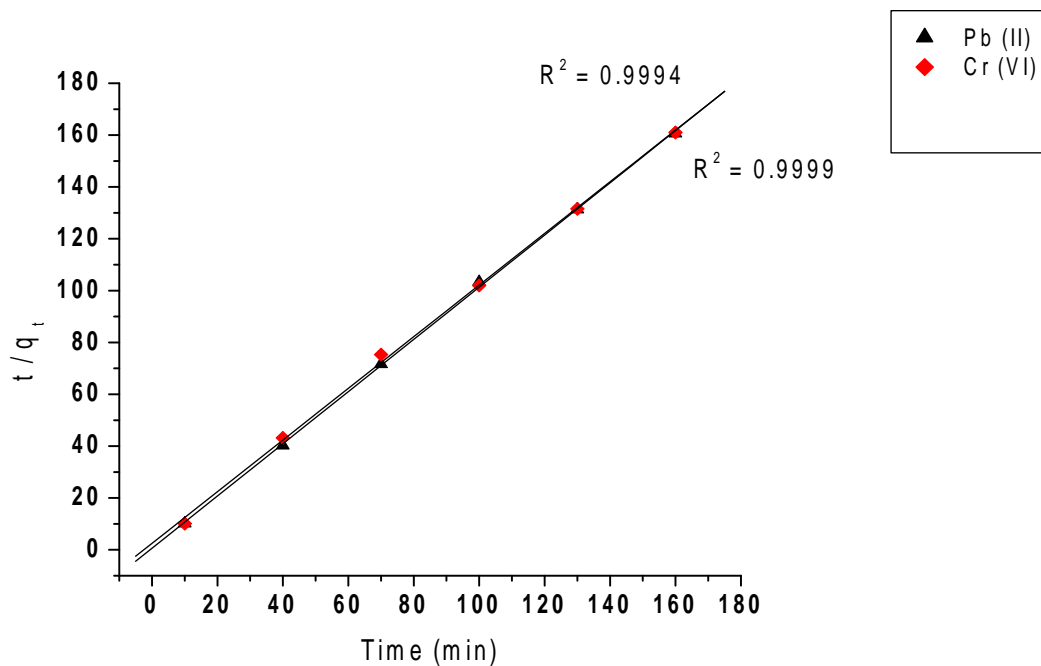
Figure 17: Pseudo-second-order kinetic plot for the adsorption of Pb (II) (triangle) and Cr (VI) (squares) onto PPAC

Table 6: Kinetics parameters for the adsorption of Pb (II) and Cr (VI) onto PPAC at 298 K

Kinetic parameters	Values	
Pseudo-first order / constants	**Pb(II)**	**Cr(VI)**
q_e (mg/g)	0.004	0.024
K_1(min^{-1})	0.007	0.146
R^2	0.962	0.943
Pseudo-second order / constants		
q_e (mg/g)	1.151	0.987
K_2 (g/mg.min)	0.017	0.025
R^2	0.999	0.999

5.3. Adsorption thermodynamic study

In order to fully understand the nature of adsorption the thermodynamic parameters such as the change in Gibbs free energy (ΔG), the change in entropy (S^O), and the change in enthalpy (H^O) could be calculated using the following equations:

$$\Delta G = -RT \ln K_C \tag{16}$$

Where R is the gas constant (8.314 J/ mol.K), T is the absolute temperature in Kelvin, and K_c (L/g) is the standard thermodynamic equilibrium constant defined by $\frac{q_e}{C_e}$. Similarly, the enthalpy change (ΔH^O) from 293 to 303 K was computed from the following equation:

$$\ln K_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{17}$$

ΔH^O(kJ.mol^{-1}) and ΔS^o (kJ.mol^{-1}.K^{-1}) were calculated from the slope and intercept of the linear plot of $\ln K_c$ versus $1/_T$. Standard enthalpy change (ΔH^O) is used to identify whether the adsorption process is exothermic or endothermic, but standard entropy change determines the dis order of the adsorption at solid-liquid interface[84] These thermodynamic parameters of the adsorption process were calculated using equations (16) and (17) above and the calculated values of these parameters are given in table 7.

Table 7: Thermodynamic parameters for the adsorption of Pb (II) and Cr (VI) ions onto PPAC at different temperatures

Heavy metals	H^o(kJ/mol)	S^o(kJ/mol.K)	ΔG^o(kJ/mol)		
			293 K	298 K	303 K
Pb (II)	-0.149	0.183	-3.138	-3.191	-3.245
Cr (VI)	-0.081	0.012	-3.554	-3.615	-3.675

The negative value of enthalpy change confirms the exothermic nature of the adsorption process and a given amount of heat is evolved during the binding of Pb (II) and Cr (VI) ions on the surface of adsorbent. The positive values of the standard entropy change, S represent the increased randomness at solid –liquid interfaces during the adsorption of metal ions onto adsorbent. Furthermore, the positive value of S also reflects that some structural changes occur in the adsorbate and adsorbent during the adsorption process [85- 87].

Negative values of G confirm the adsorption process is spontaneous, which becomes more negative with an increase in temperature. This indicates that a higher adsorption is actually occurred at higher temperatures [88]. At higher temperature, ions are readily desolvated and thereby their adsorption becomes more favorable [89].

6. CONCLUSION

In this study, locally available adsorbent pine apple peel (*Ananas cosmosus*) has been tested for its effectiveness in removing hexavalent chromium and divalent lead present in the water at low concentrations. Activated carbon was prepared from pineapple peel by chemical activation method. The batch study parameters: pH, adsorbent dose, initial concentration, contact time and temperature were investigated. The optimum value {pH = 5 and 3 for Pb and Cr, adsorbent dose = 0.25 g, initial concentration = 0.02 ppm and 0.05 ppm for Pb and Cr, contact time = 100 min and 70 min for Pb and Cr, Temperature = 25 ℃ } were obtained. The adsorption was found to be strongly influenced by pH, contact time and initial metal ion concentration. The adsorption kinetic data were modeled using the pseudo-first order and pseudo-second order kinetic equations. It was inferred that the Pseudo second order model gave better R^2 values confirming suitability of the model for describing the adsorption system. Both Freundlich and Langmuir models can be used to fit the data and estimate model parameters, but the overall data is slightly better fitted by Freundlich isotherm reflecting surface heterogeneity of PPAC. Different thermodynamic parameters (H = -0.149 and -0.081 for Pb and Cr, S = 0.183 and 0.012 for Pb and Cr, and ΔG = -3.138 and -3.554 at 293 k, -3.191 and -3.615 at 298 k, -3.245 and -3.675 at 303 k for Pb and Cr, respectively) have also been calculated and it has been found that the adsorption was favorable, spontaneous and exothermic in nature. The positive values of the entropy change suggest that the increased randomness at solid-liquid interfaces during the adsorption of metal ions onto adsorbent.

The result indicates the findings will be helpful up to a great extent for treating Pb (II) and Cr (VI) contaminated water. The method was simple, cost effective and environmental friendly. Heavy metals are toxic, and detrimental impacts become apparent when long-term consumption of contaminated water occurs. It is therefore suggested that regular monitoring of heavy metals in drinking water and also food items should be performed in order to prevent excessive buildup of these heavy metals in the human food chain.

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