REMOVAL OF LEAD (II) IONS FROM WASTEWATER USING EGGPLANT PEELS

by

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A Thesis Presented to the Faculty of Chemical Engineering
American University of Sharjah
College of Engineering
in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science in
Chemical Engineering

Sharjah, United Arab Emirates

January 2013

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Acknowledgement

I express gratefulness to Allah Almighty, the originator of universe, the greatest, the most benevolent and the most merciful, who gave me strength and courage in difficult and hard circumstances to complete this master thesis.

I am obliged to my parents who have always supported me for my betterment. It was my training under their watchful eye that I gained so much motivation and ability to tackle challenges ahead. Apart from my efforts, the success of any project depends largely on the cooperation of many others. I take this opportunity to pay my gratitude to all those who made this thesis successful. I am grateful to my thesis advisor Dr. Taleb Hassan Ibrahim for his encouragement, guidance, remarkable suggestions, keen interest, and constructive criticism and worthy friendly discussions which made it possible for me to complete this thesis. The blessing, help and guidance given by him time to time shall carry me a long way in the journey of life on which I am about to embark. Without his sincere guidance and exemplary consultation, I would not have been able to complete this laborious task successfully.

I am really thankful for the cooperation and assistance provided by Dr. Hassan A. Arafat, PhD, Water and Environmental Engineering program, Masdar Institute of Science and Technology, Abu Dhabi, UAE regarding measurement of surface areas.

I want to thank Mr. Thomas Job for helping in carrying out important measurements and other analysis at chemistry department. I am really thankful to Mr. Riccardo for helping me out in the preparation of desired equipment over and over again.

Dedication

Dedicated to Allah Almighty, Prophet Muhammad (PBUH), parents, sincere brother and sisters, teachers and, extremely cooperative adviser

Abstract

In this study, three methods have been tested for the production of eggplant peel activated charcoal (EPPAC) from eggplant peel charcoal (EPPC). A new method has also been devised which does not include continuous involvement of inert gas stream from any external source. Activation parameters used for the production of activated charcoal such as activation temperature, activation time have been optimized. Based upon the maximum removal efficiency of 70% for lead (II) from wastewater, EPPAC-2 (prepared by physical mixing of grinded KOH and EPPC) has been considered most efficient as compared to EPPAC-1 (prepared by the physical mixing of KOH lentils and EPPC) and EPPAC-3 (impregnation). The surface area of EPPAC-2 is 739m^2/g. Surface characterization of EPPAC-2 involves the determination of physical and chemical properties such as surface structure, pH, surface area, and surface functional groups. Adsorption of lead (II) ions has been confirmed by energy dispersive X-ray spectrometry (EDS) analysis on lead (II) loaded EPPAC-2. Adsorption experiments have also been conducted for the removal of lead (II) ions from wastewater by using EPPAC-2 as adsorbent. Optimum pH, adsorbent dose and equilibrium time are 5.1, 0.32g and 24h respectively. Adsorption kinetics of lead (II) has been best described by pseudo-second-order kinetic model. The adsorption equilibrium data has been fitted by using different models such as Langmuir, Freundlich, Duninin-Radushkevich, Temkin, Toth and Langmuir-Freundlich isotherm models. Langmuir adsorption model suits best for the equilibrium data. Maximum adsorption capacity of 140.84 mg/g has been given by Langmuir isotherm model. This study demonstrates that EPPAC-2 can be used as a low cost adsorbent for the removal of lead (II) ions in water treatment.

Keywords: Eggplant peel activated charcoal; Adsorption; Isotherm; Low cost adsorbent; Wastewater treatment; Heavy metals

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CHAPTER 1
INTRODUCTION

1.1. Background

Heavy metals are the elements having atomic masses between 63.5 and 200.6, and a specific gravity greater than 5.0 [1, 2]. Heavy metals such as lead, cadmium, chromium, copper, zinc, mercury, selenium and silver are toxic and have detrimental health effects on human health [3].

Among all the possible pollutants that are responsible for the contamination of surface and ground water, heavy metals are most important. They pose risks not only to humans but also to plants and animals because of their extremely toxic effects and have been the main reason behind large number of afflictions [4].

The aqueous waste streams generated from different industries such as metal plating industries, manufacturing industries and other agricultural source producing industries (fertilizers and fungicides) generally contain high level of heavy metal contamination. These contaminated aqueous waste streams with heavy metals generated from the industries are the main source of polluting ground water and other resources of water. Heavy metals tend to accumulate in the living organisms since they are not readily biodegradable and cause various diseases and disorders [5-13].

The discharge of wastewaters containing heavy metals to the environment have been increased pacifically in developing countries prompt growth of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc. [2]. Through food chain these heavy metals reach human body.

Some of heavy metals such as zinc, copper are good for the human health but in certain concentrations. Zinc is responsible for governing various physiological functions of the living tissues. Different biochemical processes in the living organisms are also controlled by Zinc. However, excessive zinc can cause health problems such as stomach cramps, skin irritations, vomiting, nausea and anemia [14]. It also causes short term illness called “metal fume fever” and restlessness [15].

Similarly, too much intake of copper results in its accumulation in the liver. Excess copper causes gastrointestinal problems, kidney damage, and anemia. Lung cancer is

related to long term inhalation exposure of copper containing sprays [16-21]. Long term exposure also causes nose, mouth and eyes irritation, headache, dizziness and diarrhea [15]. According to World Health Organization the maximum acceptable concentration of Cu (II) in drinking water is 1.5 mg/L [22].

When the concentration of Nickel is greater than its critical concentration it causes serious damage to lungs and kidneys, gastrointestinal problems, pulmonary fibrosis and skin dermatitis [23]. It is a human carcinogen. The acceptable limit of Ni is 20.0 mg/L [24, 25].

Mercury is a neurotoxin that can cause damage to the central nervous system. High concentrations of mercury result in health problems related to pulmonary and kidney functions, chest pain and dyspnoea [26].

Due to the contamination of toxic heavy metals in aquatic streams various past catastrophic events have occurred on the surface of globe such as Minimata disaster in Japan due to methyl mercury contamination and “Itai-Itai” due to the contamination of cadmium in Jintsu river of Japan [27, 28]. Cadmium also causes lung fibrosis, dyspmea and weight loss.

Long term exposure of drinking water contaminated with arsenic causes skin, lung, bladder, and kidney cancer. It also causes pigmentation changes, skin thickening (hyperkeratosis) neurological disorders, muscular weakness, loss of appetite, and nausea. High levels of arsenic causes vomiting, esophageal, abdominal pain, and rice water diarrhea. According to the World Health Organization (WHO), the permissible limit for arsenic in drinking water is 10 ppb [29].

Chromium exists in +III and +VI oxidation states which are poisonous to living organisms [30]. In low concentration, Cr(III) is beneficial for the living organisms but it is highly toxic in high concentrations [31]. Cr(VI) is 500 times toxic than Cr(III) [32]. Cr(VI) causes severe and serious health problems such as lung tumors and cancer. It also poses problems such as kidney, liver and gastric damages [33].

Lead causes damage to central nervous system. Lead can also damage vital organs such as kidney, liver. It has unhealthy effect on the reproductive system, basic cellular and brain functions. Various diseases such as anemia, insomnia, headache, and dizziness, and irritability, weakness of muscles, hallucination and renal damages [34]

are also caused by high lead concentrations. According to EU (European Union), USEPA (United Stated Environmental Protection Agency) and WHO (World Health Organization), the maximum acceptable values of lead in drinking water and surface water used for drinking are 10 mg/L and 50 mg/L, respectively [35]. However, recently as per instructions mentioned in an EPA (Environmental Protection Agency) document, a zero lead value has been recommended as national primary drinking water standard [36]. In India, the permissible limit of lead in drinking water is 0.01mg/L [37].

Many countries have drinking water contaminated with heavy metal lead. For example, in Bangladesh, drinking water is contaminated with lead [38]. Accumulation of the lead in humans causes abnormal calcium metabolism [39] and immune disorders [40]. Fetuses and babies are particularly vulnerable to lead-induced intelligence impairment [41].

So, it is extremely important to eliminate these heavy metals from wastewater in order to protect living organisms and environment. Therefore, it is necessary to develop new; environmental friendly process for the treatment of wastewater and industrial effluents [42].

1.2. Technologies for treatment of waste water containing heavy metals

Different techniques have been used for the removal of heavy metals from wastewater. Chemical, physical, biological and electrochemical techniques are the most common for the removal of toxic metals from wastewater. Chemical techniques for the wastewater treatment include chemical precipitation, ion exchange, and adsorption. In biological treatment, micro-organisms are used for removal of heavy metals in the wastewater. Examples of physical processes are membrane filtration, flotation, coagulation and flocculation. Conventional methods include reverse osmosis, electrochemical treatment, evaporative recovery, ion exchange, chemical precipitation, membrane filtration, chemical oxidation reduction, electro dialysis, ultrafiltration and solvent extraction [43-54]. The applicability and use of all these common techniques is limited by their less efficiency, critical operating parameters and production of secondary sludge [24, 55-57]. The most efficient methods for the

heavy metal removal are ion exchange and adsorption. In these methods, various types of adsorbents are used with simple, easy convenient procedures for having high removal efficiency [58, 59]. However, ion exchange is expensive and the use of this technique is limited because of its selectivity for specified metal ions in comparison with other metal ions. In adsorption, a certain adsorbent is used for the removal of heavy metal from wastewater and it is considered to be the most effective process because of its high efficiency [60]. Adsorption also produces high quality effluent. Adsorbents can also be regenerated by using suitable adsorption processes.

1.3. Adsorption

Adsorption is binding process which involves the adhesion of one substance (atoms, ions, molecules) on the surface of the other substance. The substance that is adsorbed is called adsorbate (metal or organic compound) and the medium on which adsorption of the adsorbate takes place is called adsorbent. The adsorption process consists of following steps:

a) Bulk solution transport
b) Film diffusion transport
c) Pore transport
d) Adsorption

Adsorption of the adsorbate occurs on the surface of the adsorbent at specific sites called adsorption sites. Adsorption can occur on the outer surface of adsorbent or with in macro-pores, meso-pores and micro-pores surface. Meso-pore and macro-pore surface area is small as compared to the micro-pore surface area thus the adsorption capability of the meso-pore and macro-pore surface area is considered negligible as compared to the adsorption capacity of micro-pore surface area [61].

1.4. Adsorption Isotherms

The amount of adsorbate that is adsorbed per amount of adsorbent is determined as a function of concentration at constant temperature. The resulting function is called adsorption isotherm. Adsorption experiments are carried out to develop adsorption isotherms in which the amount of the adsorbent is changed while the initial concentration and volume of the adsorbate are kept constant. Most

commonly used adsorption isotherms are Langmuir adsorption isotherm and Freundlich adsorption isotherm [61].

1.4.1. Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm is given as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (1)$$

where the independent variable C_e is the equilibrium concentration (mg/L), q_e is the amount of the substance adsorbed at equilibrium per amount of the adsorbent (mg/g), q_m is the saturation monolayer adsorption capacity (mg/g), and b is the equilibrium adsorption constant (l/mg).

The assumptions in the Langmuir isotherm are (i) maximum adsorption of the adsorbate occurs at homogeneous saturated monolayer sites on the adsorbent surface, (ii) the energy of the adsorption is constant [62]. Equilibrium in the adsorption process occurs when all the adsorption sites of the adsorbent gets saturated with adsorbate (atoms, molecules, ions) or when the rate of the adsorption of the adsorbate molecules becomes equal to the rate of desorption of the adsorbate molecules from the surface of the adsorbent.

1.4.2. Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm is an empirical relation and is given as:

$$q_e = k_f C_e^{1/n} \quad (2)$$

where the independent variable C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium per amount of the adsorbent (mg/g) and k_f (mg/g) and n are the Freundlich constants related to the adsorption capacity and adsorption intensity [61].

1.4.3. Dubinin-Radushkevich Adsorption Isotherm

Dubinin-Radushkevich isotherm is very good in the prediction of the equilibrium data for organic compounds in gas phase condition in the porous solids. However it is not commonly applied to liquid phase adsorption [63]. Mathematically it is expressed as:

$$q_e = q_D \exp(-B_D(RTln(1 + \frac{1}{C_e}))^2) \quad (3)$$

where q_e is the equilibrium adsorption capacity mg/g, B_D is the free energy of adsorption per mole of adsorbate, C_e is the equilibrium concentration mg/L.

1.4.4. Temkin Adsorption Isotherm

Temkin model have been used in many studies for the prediction of adsorption of heavy metals from aqueous solutions but in these studies it has been concluded that this model is not suitable for prediction of their experimental data [64-66]. Although this isotherm is suitable for the prediction of gas phase equilibria but it is not suitable for prediction of liquid phase adsorption especially in case of heavy metal adsorption. This is because liquid phase adsorption is much more complex than gas phase adsorption. In gas phase adsorption the adsorbed molecules are arranged in a tightly packed structure but in liquid phase adsorption due to the presence of the solvent molecules and formation of aggregates from the adsorbed molecules, it becomes much more complex [67]. Mathematically it is expressed as:

$$q_e = Blogk_t + BlogC_e \quad (4)$$

where B and k_t are the Temkin isotherm constants. $B = RT/b$, R is the universal gas constant, T is the absolute temperature in Kelvin and $\frac{1}{b}$ represents the adsorption potential of the adsorbent.

1.4.5. Toth Adsorption Isotherm

Toth adsorption isotherm has three parameters and it is based on the potential theory. It is quite helpful in predicting the adsorption behavior pacifically on heterogeneous surfaces. It is represented as followed

$$q_e = \frac{K_T C_e}{(a_T + C_e^t)^{1/t}} \quad (5)$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium per amount of the adsorbent (mg/g), K_t is the maximum adsorption capacity at equilibrium (mg/g), a_T is the adsorption equilibrium constant and t is the constant known as dissociation parameter and it gives information about the heterogeneity of the surface [63].

1.4.6. Langmuir Freundlich Isotherm

Langmuir-Freundlich isotherm model is also a three parameter empirical model. It is a combination of Langmuir adsorption isotherm and Freundlich adsorption isotherm. Generally it fits a wide range of equilibrium data especially when Langmuir and Freundlich sorption isotherms do not fit the data for this purpose it is very famous [68]. The Langmuir-Freundlich isotherm is defined as followed

$$q_e = \frac{Kq_{LF}C_e^{1/n_{LF}}}{1+KC_e^{1/n_{LF}}} \tag{6}$$

where C_e the equilibrium concentration (mg/L) is, q_e is the amount adsorbed at equilibrium per amount of the adsorbent (mg/g), q_{LF} is the maximum adorption capacity at equilibrium (mg/g), and n_{LF} is the model constant known as heterogeneity parameter.

This isotherm reduces to Freundlich isotherm at low concentration of the adsorbate where at high adsorbate concentration it gives the monolayer adsorption capacity and it follows Langmuir isotherm [63].

1.5. Parameter determination of adsorption Isotherms

Linear plots were used for the determination of parameters of Langmuir, Temkin, D-R and Freundlich. In order to determine the parameters of Toth and Langmuir-Freundlich isotherms, non-linear regression is used (SOLVER in MS EXCEL). Actually iterative method is used and the accuracy of the method can be determined in terms of the error calculated in the method. There are two types of error relative error and absolute error. Absolute error is defined as [69]

$$Absolute\ Error = Approximate\ Value - Exact\ Value \tag{7}$$

And relative error is defined as

$$Relative\ Error = \frac{Absolute\ Error}{Exact\ Value} \tag{8}$$

Convergence criteria can be defined in terms of absolute error or relative error. If ε is the convergence tolerance, for the absolute error convergence criteria following choices are possible

$$|(\Delta Q_i)_{max}| \leq \varepsilon \tag{9}$$

$$\sum_{i=1}^{n}|\Delta Q_i| \leq \varepsilon \quad (10)$$

OR

$$\left[\sum_{i=1}^{n}(\Delta Q_i)^2\right]^{1/2} \leq \varepsilon \quad (11)$$

For the relative error criteria following choices are possible

$$\left|\frac{(\Delta Q_i)_{max}}{Q_i}\right| = \varepsilon \quad (12)$$

$$\sum_{i=1}^{n}\left|\frac{\Delta Q_i}{Q_i}\right| \leq \varepsilon \quad (13)$$

OR

$$\left[\sum_{i=1}^{n}\left(\frac{\Delta Q_i}{Q_i}\right)^2\right]^{1/2} \leq \varepsilon \quad (14)$$

The sum of the squares of the residuals is

$$S_t = \sum_{i=1}^{n}(y_i - \bar{y})^2 \quad (15)$$

$$S_r = \sum_{i=1}^{n} e_i^2 = \sum_{i=1}^{n}\left(y_i - \hat{y}_{i,model}\right)^2 \quad (16)$$

The goodness of fit is characterized by the correlation coefficient

$$R^2 = \frac{S_t - S_r}{S_t} \quad (17)$$

1.6. Adsorbents

In the recent years, special attention has been focused on the use of the natural adsorbents as an alternative to replace the conventional adsorbents, based upon both the environmental and economic point of view [70, 71]. A wide variety of materials such as fly ash [72], pine barks [73], saw dust [74] and animal bone [75] are being used as a low cost alternatives to expensive adsorbents. Summary of the adsorbents used in the removal of lead are mentioned in Table 1.

Table 1: Summary of adsorbents for lead removal

Adsorbents	**References**
Algae, marine, dead biomass	[76]
Aliginate beads	[77]
Apricot stone	[78]
Ash, brick kiln	[79]
Azolla filiculoides	[80]
Bacteria, sulfate reducing	[81]
Bed sediments	[82]
Biomass of spirulina maxima	[83]
Biomass, filamentous fungi	[84]
Biomass, mucor rouxil dead	[85]
Biomass, mucor rouxil alive	[85]
Biomass, pinus sylvestris cone	[86]
Biosurfactant	[87]
Commercial carbonate hydroxyapatite	[88]
Ceramics	[89]
Cereal chaff	[90]
Charcoal, natural	[91]
Chitin, natural	[92]
Chitin, phosphorylated	[92]
Chitin, xanthated	[92]
Chitins, surface modified	[92]
Coconut	[93]
Compost leaf	[94]
Duolite C-433	[95]
Ferrihydrite	[96]
Fish scale, Atlantic cod	[97]
Green algae	[98]
Iron material recycled	[99]
Leaves, casurina glauca tree	[100]
Maize cobs	[101]

Palmyra palm fruit seed carbon	[102]
Red soil	[103]
Sago waste	[104]
Seaweed, brown	[105]
Slag, granular	[106]
Soil, fine loamy	[107]
Sugar beet pectin gels	[108]
Vegetable biomass	[109]
Silicate MCM-41, mesoporous	[110]

1.7. Activated carbon

Activated carbon is widely used adsorbent for the treatment of the waste water [111]. Due to extensive internal surface area, the adsorption capacity of the activated carbon is very high. Activated carbon is prepared by the carbonization and activation of the substances and raw materials that contain carbon [112].

1.8. Activation

Activation is used to develop the pore structure of the carbonaceous materials such as coal, charcoal and coke. Activation increased the adsorption capacity by enhancing the surface area of the carbon [111]**.** There are two types of activation processes: 1) physical activation and 2) chemical activation.

1.8.1. Physical Activation

Physical activation is carried out at high temperatures which involve the reaction between the carbon containing substance with steam, carbon dioxide, carbon monoxide, or oxygen. It increases the surface area of the carbon by removing the pore blocking substances.

1.8.2. Chemical Activation

Chemical activation uses dehydrating agents such as KOH, NaOH and H_2SO_4 which react with the surface of the carbon to enhance adsorption capacity**.** The chemical activation process increases the surface area by increasing the number of pores and increasing the dimensions of the pores.

1.9. Objectives

Main objectives of this study are to

a) Produce eggplant peel activated charcoal (EPPAC) from eggplant peels using three different methods.

b) Device a procedure for the production of activated charcoal (EPPAC) without the involvement of external continuous flowing inert stream.

c) Evaluate different activation parameters (activation time, activation temperature, activation ratio, impregnation ratio, time and temperature) for the three methods.

d) Select the method that produces efficient EPPAC based upon the maximum removal efficiency of lead (II) from wastewater.

e) Characterize the efficient EPPAC by performing SEM analysis for surface structure, surface area and pH measurements, SEM/EDS elemental analysis, ash content and surface functional groups analysis.

f) Investigate the effectiveness of the optimized EPPAC for the removal of lead (II) from wastewater using adsorption studies.

g) Determine the optimum adsorption parameters for the removal of lead (II) such as initial pH, contact time, adsorbent dose etc.

h) Apply the available adsorption models (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Toth, and Langmuir-Freundlich) and select the best adsorption model that describes the removal of lead (II) from wastewater.

CHAPTER 2
EXPERIMENTAL PROCEDURE

2.1. Materials

Eggplants were bought from local market in Sharjah, UAE. All the chemicals used were analytical grade reagents. All the glassware was cleaned with 20% nitric acid and washed thoroughly with double distilled water and drying was carried out in vacuum oven. Nitric acid (0.1M) and sodium hydroxide (0.1M) were used for pH adjustments. The chemical reagents such as nitric acid (MERCK), sodium hydroxide pellets (Riedel-de Haën), lead nitrate pellets (HIMEDIA) were used. Nitrogen gas (99.9% purity) was also used.

2.2. Instrumentation

The following instruments have been used in the current study

a) Water Still Aquatron A4000D for double distilled water.
b) WiseVen WOV-30 vacuum oven at -60cmHg.
c) Vecstar furnace at temperatures ranging from 500 ^{o}C to 800 ^{o}C.
d) Wise shake flask shaker at 120 RPM.
e) AA240FS fast sequential atomic absorption spectrometer.
f) SEM (TESCAN VEGA.3-LMU) for determining surface structure.
g) NOVA quanta-chrome instrument version 11.02 for measuring surface areas.

2.2. Preparation of Eggplant peel charcoal (EPPC)

Eggplant peels are solid waste that is readily available throughout different parts of the world. Initially eggplant peels were dried in the sunlight for 24h and then washed thoroughly 2-3 times with double distilled water to remove the dust and undesired particles. Then they were dried by using Fluid Bed Dryer (Sherwood Scientific). Then they were put in steel container and purged with nitrogen gas for 120 seconds and then burnt in the furnace at 700^{o}C for 1h in the absence of oxygen. The process block diagram is shown in the figure 1. EPPC powder of 500μm or less was obtained using mesh screen. The percentage yield of EPPC was 30.78%.

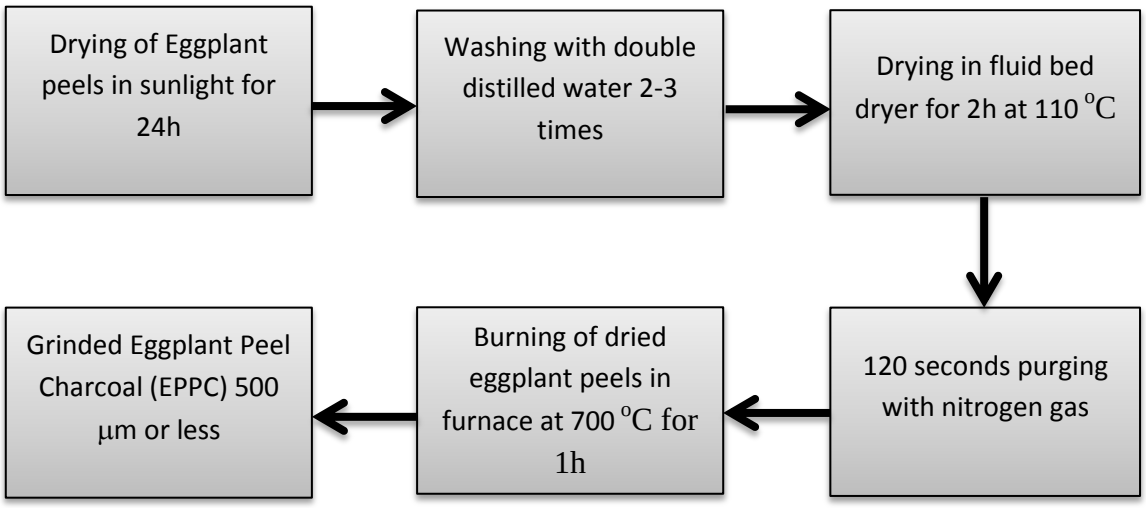

Figure 1: Process block diagram for EPPC production from Eggplant peels.

2.3. Preparation of Eggplant peel activated charcoal (EPPAC) using chemical activation

The eggplant peel charcoal (EPPC) was chemically activated by using potassium hydroxide KOH. Although different activating agents can be used for the activation such as $ZnCl_2$, H_3PO_4, K_2CO_3, steam and CO_2, but KOH is preferred because the rate of reaction between the activating agent (steam and CO_2) and charcoal is low so a high temperature greater than 800^oC is required for the activation [113]. Also KOH requires less energy, so comparatively low temperature is required for activation and as far as environmental impact is concerned, it is less harmful in comparison with $ZnCl_2$ and H_3PO_4 [114].

The eggplant peel activated charcoal (EPPAC) was obtained by using KOH as chemical activator by following three methods [115]:

a) EPPAC-1: Physical mixing of KOH lentils and EPPC
b) EPPAC-2: Physical mixing of grinded KOH and EPPC
c) EPPAC-3: Impregnation

In first two methods after the mixing, the mixture based upon activation ratios (w/w) of EPPC to KOH ranging from 1:0.5 to 1:4 was put in steel container. Container was purged with nitrogen gas for 120 seconds. Then the container was heated in furnace at activation temperatures ranging from 500^oC to 800^oC for different activation times from 1h to 3h. In the third method (impregnation), KOH lentils and EPPC of different weight ratios from 1:1 to 1:5 were mixed in 10 ml double distilled water, stirred and

heated at impregnation temperatures ranging from 25^{o}C to 160^{o}C for impregnation times between 1h to 3h. After then the obtained slurry was dried in the vacuum oven at -60cmHg for 24h. Then the dried product was put in container and purged with nitrogen gas for 120 seconds. The container was placed in furnace at activation temperatures ranging from 500^{o}C to 800^{o}C for different activation times ranging from 1h to 3h. In these three methods, container was cooled slowly to room temperature after heating it in the furnace.

For all the three methods mentioned, optimum activation parameters (activation temperature, activation time, activation ratio, impregnation temperature, and impregnation ratio and impregnation time) were selected based upon the maximum removal efficiency of lead (II) from wastewater.

After cooling EPPAC-1, EPPAC-2 and EPPAC-3 were washed with double distilled water to remove water soluble contents and then with 5M HNO_3 to remove ash and rest of the activating agent. This was followed by washing with double distilled water till the pH of the residual solution reached 6-7 to ensure the removal of any remained chemicals from the final activated charcoal. Then the drying was carried out in vacuum oven at -60cmHg for 24h. The percentage yields of EPPAC-1, EPPAC-2 and EPPAC-3 were 67.5%, 64.9% and 63.3% respectively. The process block diagram is shown in figure 2.

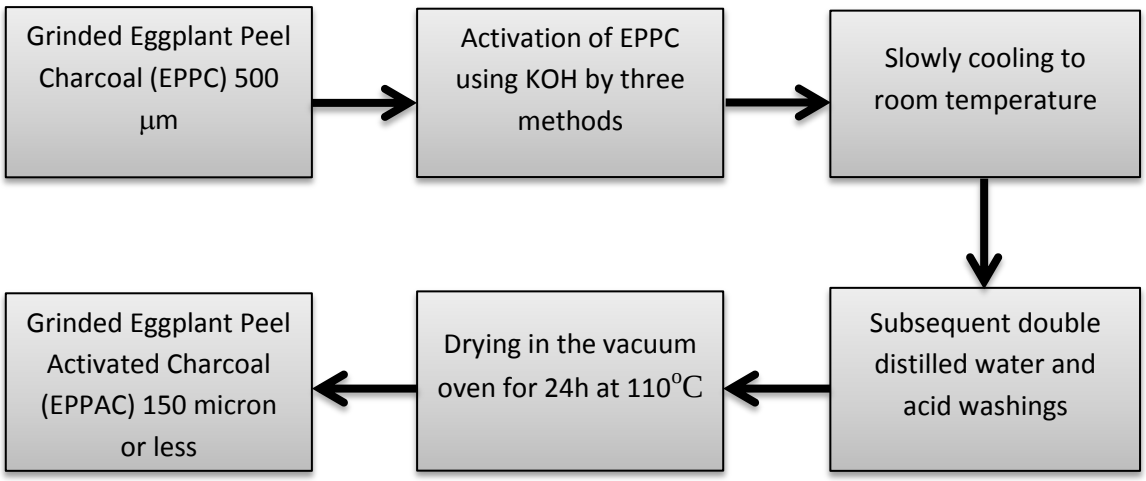

Figure 2: Process block diagram for EPPAC production from EPPC.

The details of three different methods are given in Table 2.

Table 2: Details of three methods for production of eggplant peel activated charcoal.

Method	**Sample ID**	**Activating agent**	**Post treatment**	**Percentage Yield**
Physical mixing	EPPAC-1	KOH	5M HNO_3	67.5%
Grinding and physical mixing	EPPAC-2	KOH	5M HNO_3	64.9%
Impregnation	EPPAC-3	KOH	5M HNO_3	63.3%

CHAPTER 3
RESULTS AND DISCUSSION

3.1. Effect of activation parameters on the removal efficiency of EPPAC-1

Effects of the activation parameters (activation time, activation temperature and activation ratio) on the removal efficiency of EPPAC-1 were investigated. All the runs were performed at the same adsorption conditions; initial concentration of lead (II): 300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25 ± 2^0C.

3.1.1. Effect of the activation temperature

In order to observe the effect of activation temperature on the removal efficiency of EPPAC-1, the activation temperature was changed from 500^0C to 800^0C while all other activation parameters such as activation time and activation ratio were kept constant at 2h and 1:1 (EPPC to KOH ratio) respectively. Figure 3 shows the relationship between the removal efficiency of EPPAC-1 and activation temperature.

As the activation temperature is increased from 500^0C to 700^0C, removal efficiency also increases from 46.8% to 57.7%. However at 800^0C, the removal efficiency is decreased to 54.8%. Initially as the temperature is increased, rate of reaction between activating agent KOH and EPPC is also increased which results in the enhancement of the removal efficiency. Figure 3 shows that at 700^0C, maximum removal efficiency of 57.7% is obtained and this is optimum activation temperature. The increase in the removal efficiency is due formation of porous structure which results in the attainment of high surface area. Also, at lower temperature, the rate of reaction between EPPC and KOH will be slow and thus the removal efficiency is less as compared to removal efficiency obtained at 700^0C [114, 116].

3.1.2. Effect of the activation time

Effect of the activation time on the removal efficiency of EPPAC-1 is demonstrated in figure 4. All other activation parameters such as activation temperature and EPPC to KOH activation ratio were kept constant at 700^0C and 1:1 respectively.

As the activation time is increased from 1h to 2h, the removal efficiency of EPPAC-1 also increases from 54.7% to 57.7%. Also, as the activation time is increased from 2h

to 3h, decrease in the removal efficiency is observed from 57.7% to 47.1%. So activation time affects the removal efficiency of EPPAC-1. The optimum activation time is 2h at the activation temperature of 700^0C and activation ratio of 1:1. The decrease in the removal efficiency of EPPAC-1 for lead (II) removal is due to decrease in the surface area. Shorter activation time is not enough for the formation of pores responsible for the high surface area due to which removal efficiency is low. Similarly too longer activation time causes the destruction of porous structure necessary for the high surface area which also results in the reduction of removal efficiency [114, 116, 117].

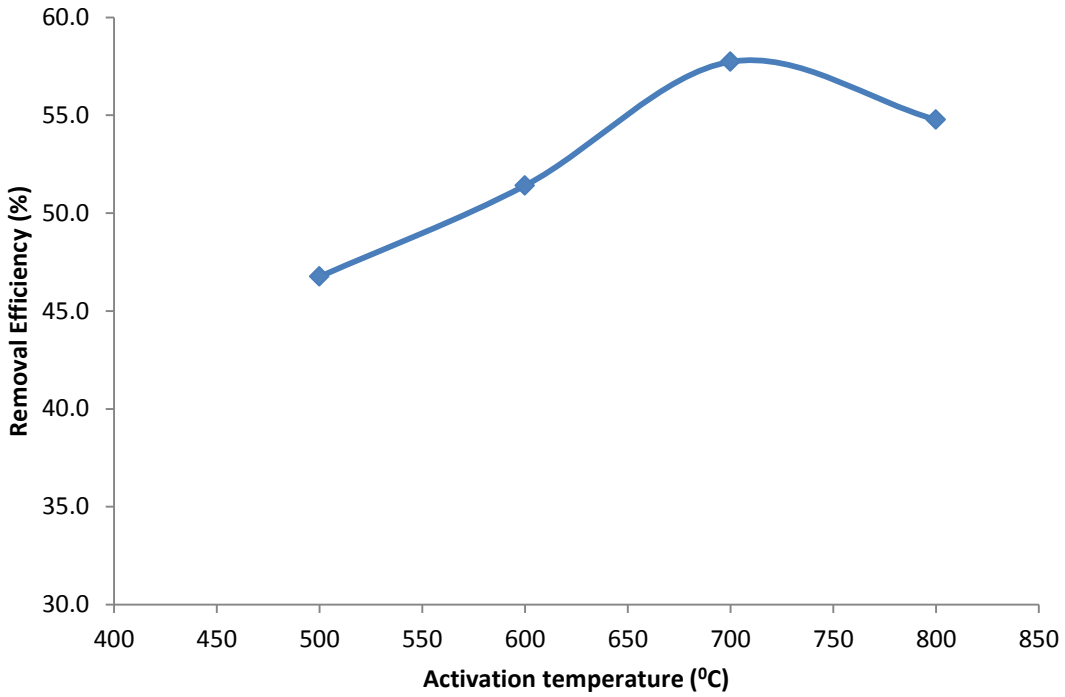

Figure 3: Effect of activation temperature on EPPAC-1 for removal efficiency of lead (II) at initial concentration of lead (II): 300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25 ± 2^0C.

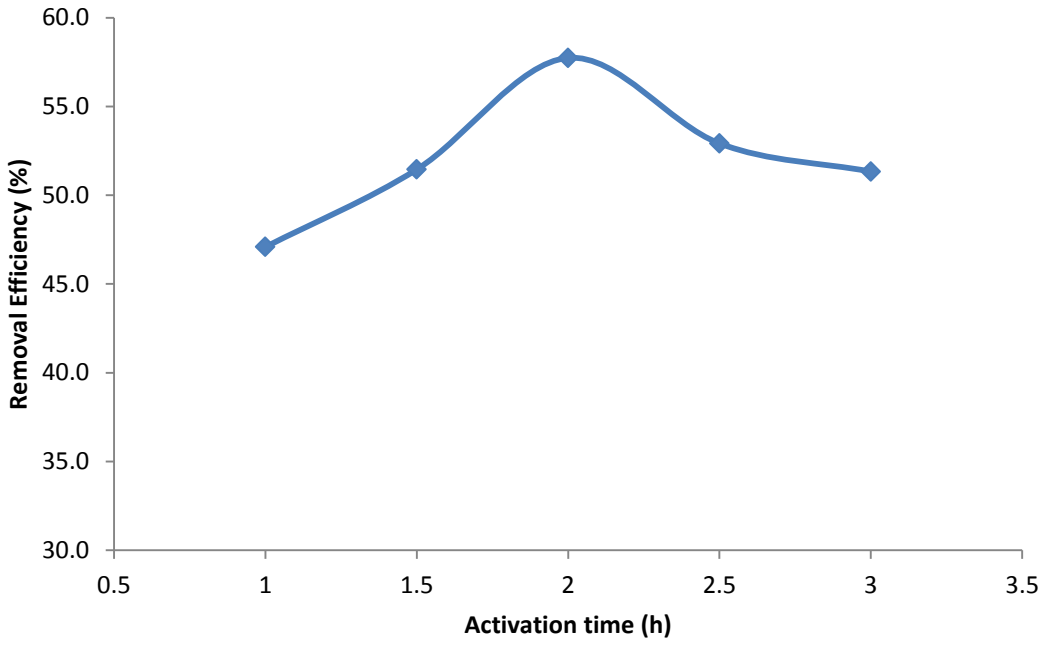

Figure 4: Effect of activation time on EPPAC-1 for removal efficiency of lead (II) at initial concentration of lead (II): 300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25±2 ^{0}C.

3.1.3. Effect of the EPPC to KOH activation ratio

The effect of EPPC to KOH activation ratio for EPPAC-1 is presented in figure 5. Activation time and activation temperature were kept constant at 2h and 700^{0}C respectively.

In figure 5 it is shown that as the EPPC to KOH activation ratio is increased from 1:0.5 to 1:1 the removal efficiency of EPPAC-1 increases from 54.7% to 57.7% but when the EPPC to KOH activation ratio is increased further up to 1:4 from 1:1 gradual decrease in the removal efficiency of EPPAC-1 occurs from 57.7% to 38.9%. Thus it is evident that EPPC to KOH activation ratio significantly affects the removal efficiency of EPPAC-1. The optimum EPPC to KOH activation ratio is 1:1 at the activation temperature of 700^{0}C and activation time of 2h. Actually as the amount of KOH is increased i.e. as the activation ratio is increased from 1:0.5 to 1:1, an increase in the removal efficiency is detected which is due to the fact that greater amount of KOH causes the rate of reaction between EPPC and KOH to increase, due to which the phenomenon of the pore formation also increases.

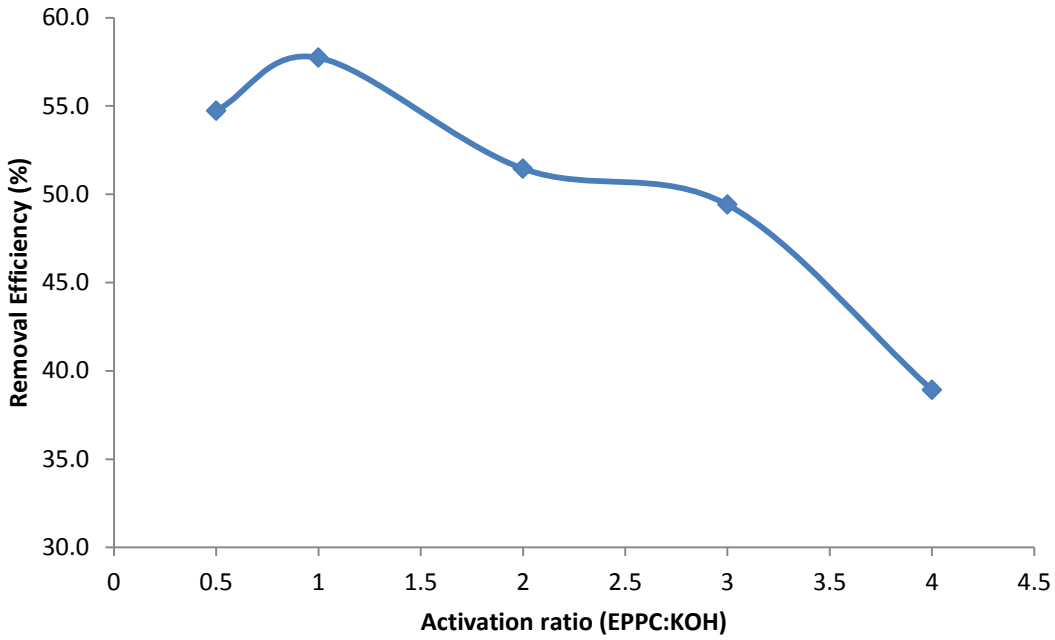

Figure 5: Effect of EPPC to KOH activation ratio on EPPAC-1 for removal efficiency of lead (II) at initial concentration of lead (II): 300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25±2 ^{0}C.

But as the activation ratio is increased from 1:1 to 1:4 i.e. as the amount of KOH is further increased, it results in the decrease of removal efficiency which indicates that increase in the amount of KOH after certain limit has adverse effect on removal efficiency by destroying the porous structure [114].

Thus all the three activation parameters: activation temperature, activation time and EPPC to KOH activation ratio have notable effect on the removal efficiency of EPPAC-1 for lead (II) removal. Figure 6 demonstrates that EPPC to KOH ratio is most dominant factor which results in the huge variation of removal efficiency of about 18.8% as compared to other two activation parameters which give the variation of removal efficiency equivalent to 11.0% and 10.7% [116].

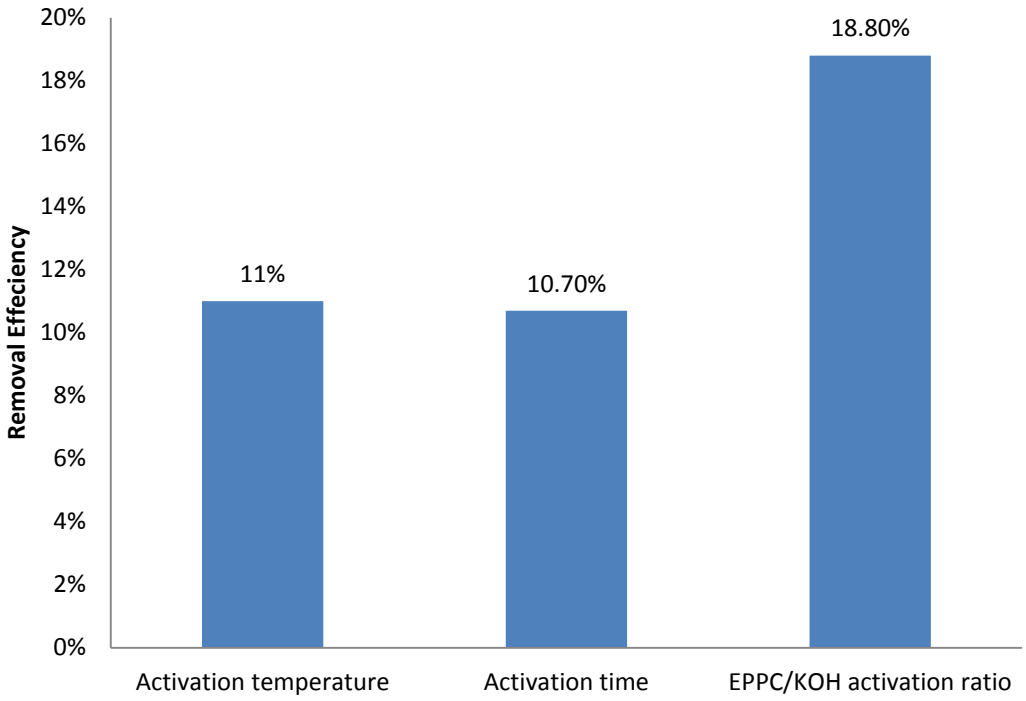

Figure 6: Effect of the three factors (activation temperature, activation time, EPPC to KOH activation ratio) on the removal efficiency of EPPAC-1.

3.2. Effect of activation parameters on the removal efficiency of EPPAC-2

In order to investigate the effect of the activation parameters (activation time, activation temperature, activation ratio) on the removal efficiency of EPPAC-2 different runs were carried out by varying the activation conditions at the same adsorption conditions; initial concentration of lead (II): 300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25 ± 2^{0}C.

3.2.1. Effect of the activation time

Effect of the activation time on the removal efficiency of EPPAC-2 is shown in figure 7. For studying the effect of activation time on the removal efficiency of EPPAC-2, all other activation parameters such as activation temperature and EPPC to KOH activation ratio were kept constant at 700^{0}C and 1:1 respectively.

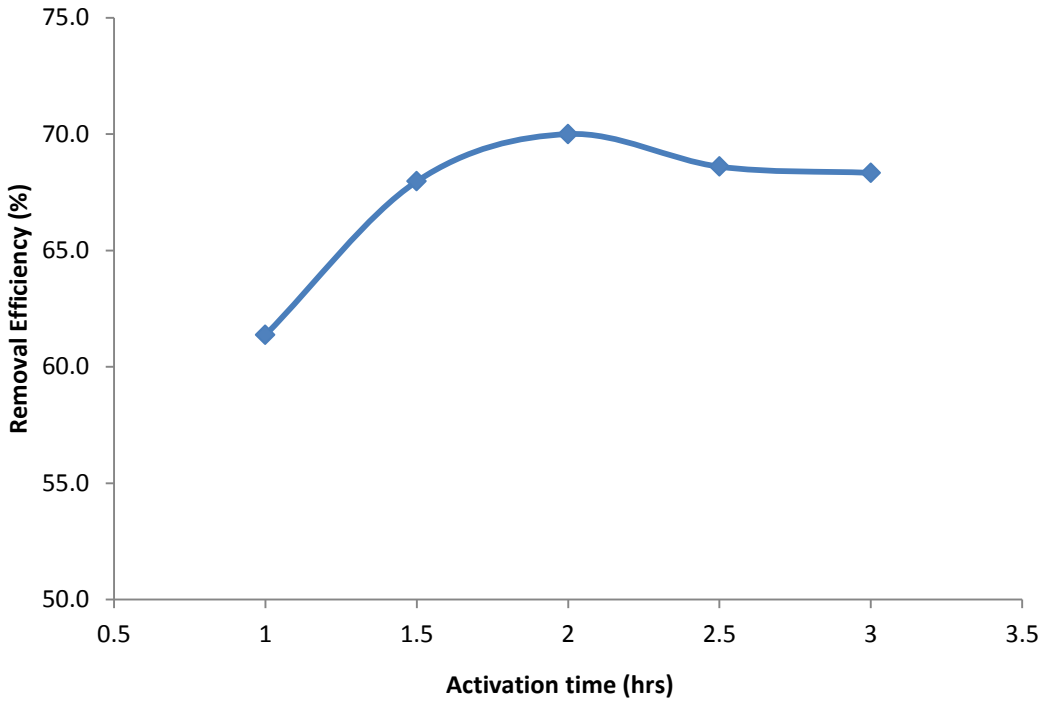

Figure 7: Effect of activation time on EPPAC-2 for removal efficiency of lead (II) at initial concentration of lead (II): 300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25 ± 2^0C.

According to figure 7, as the activation time is increased from 1h to 2h, the removal efficiency of EPPAC-2 rapidly increases to 70%. But when the activation time is increased from 2h to 3h, a little decrease in the removal efficiency is observed from 70% to 68.3%. The optimum activation time is 2h at the activation temperature of 700^0C and activation ratio of 1:1. If the activation time is too long or too short, in both cases the removal efficiency of EPPAC-2 for lead (II) removal decreases. But the decrease in the removal efficiency is significant at low activation time. Shorter activation time is not enough for the generation of pores responsible for the high removal efficiency [114, 116, 117].

3.2.2. Effect of the activation temperature

In order to observe the effect of activation temperature on the removal efficiency of EPPAC-2, the activation temperature was changed from 500^0C to 800^0C while all other activation parameters such as activation time and activation ratio were kept constant at 2h and 1:1 (EPPC to KOH ratio) respectively. Figure 8 shows the variation of removal efficiency with the activation temperature.

As the activation temperature is increased from 500^0C to 700^0C, removal efficiency increases sharply from 49.9% to 70% but as the temperature is further increased to 800^0C, the removal efficiency decreases to 65.6%. Thus it is clear that the removal efficiency of EPPAC-2 depends upon the activation temperature. Actually as the temperature is increased, rate of reaction between activating agent KOH and EPPC also increases which is responsible for the increase in the removal efficiency. Figure 8 shows that at the optimum activation temperature is 700^0C with the maximum removal efficiency of 70%. At high temperature, the rate of reaction is high which produces effective surface area for high removal efficiency. Also, at lower temperature, the rate of reaction between EPPC and KOH is slow due to which insufficient pore formation occur for generating high surface area and thus removal efficiency is less as compared to removal efficiency obtained at 700^0C [114, 116].

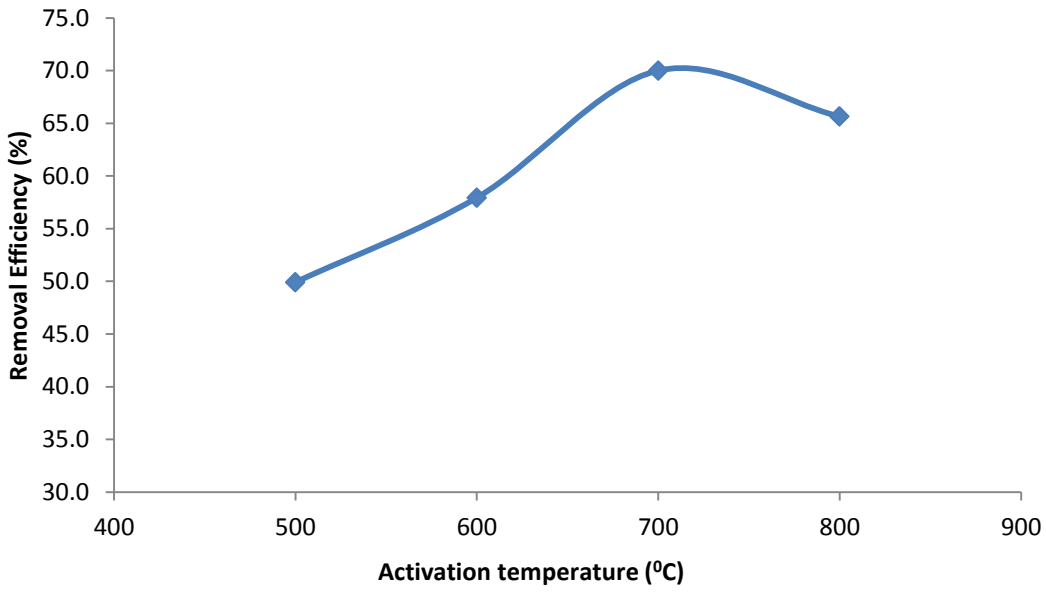

Figure 8: Effect of activation temperature on EPPAC-2 for removal efficiency of lead (II) at initial concentration of lead (II): 300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25 ± 2^0C.

3.2.3. Effect of the EPPC to KOH activation ratio

The effect of EPPC to KOH activation ratio on the removal efficiency of EPPAC-2 for lead (II)) removal is shown in figure 9. All other activation parameters such as activation time and activation temperature were kept constant at 2h and 700^0C respectively.

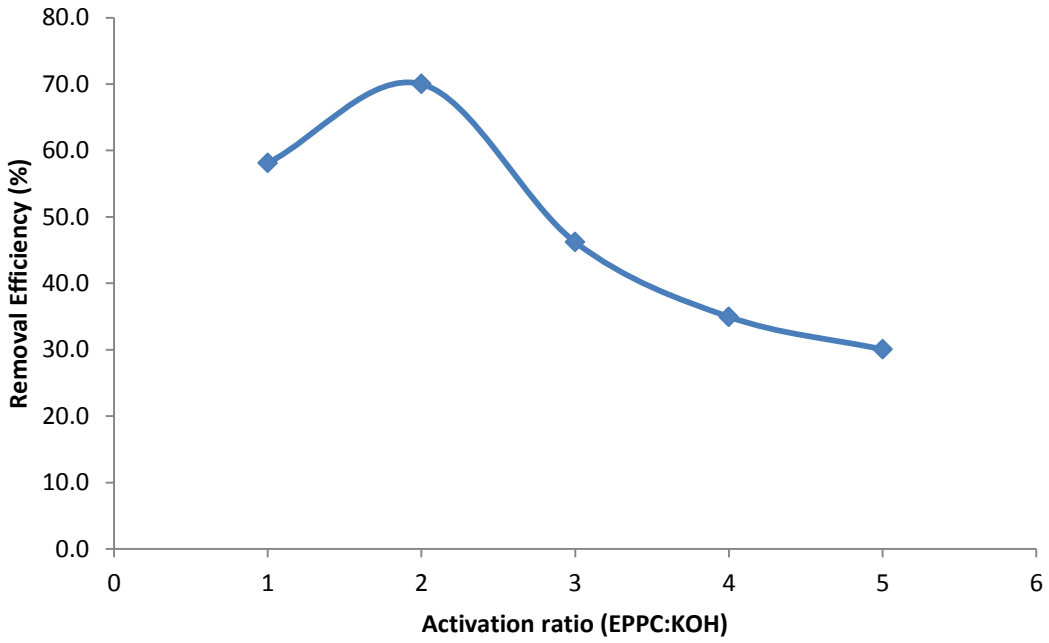

Figure 9: Effect of EPPC to KOH activation ratio on EPPAC-2 for removal efficiency of lead (II) at initial concentration of lead (II): 300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25±2 ^{0}C.

According to figure 9, as the EPPC to KOH activation ratio is increased from 1:0.5 to 1:1, the removal efficiency of EPPAC-2 increases from 58.1% to 70% but when the EPPC to KOH activation ratio is increased to 1:4 from 1:1, sharp decrease in the removal efficiency of EPPAC-2 occurs from 70% to 30%. Thus the removal efficiency of EPPAC-2 is very significantly affected by the change in EPPC to KOH activation ratio. The optimum EPPC to KOH activation ratio is 1:1 at the activation temperature of 700^{0}C and activation time of 2h. Actually as the amount of KOH is increased the rate of reaction between EPPC and KOH also increases. This accelerates the phenomenon of pore formation which increases the removal efficiency. But as the activation ratio is increased from 1:1 to 1:4 i.e. as the amount of KOH is further increased, it results in the decrease of removal efficiency which indicates that increase in the amount of KOH after certain limit has suppressing effect on removal efficiency by destroying the pore structure [114].

Figure 10 shows the variation in removal efficiency of EPPAC-2 for lead (II) removal caused by three activation factors: activation time, activation temperature and EPPC to KOH activation ratio. As it is obvious from the figure 10 that most significant impact on the removal efficiency of EPPAC-2 is caused by the change in EPPC to

KOH activation ratio. The variation for EPPC to KOH is 40% which is very high as compared to variation in removal efficiency caused by activation time (8.6%) and activation temperature (20.1%).

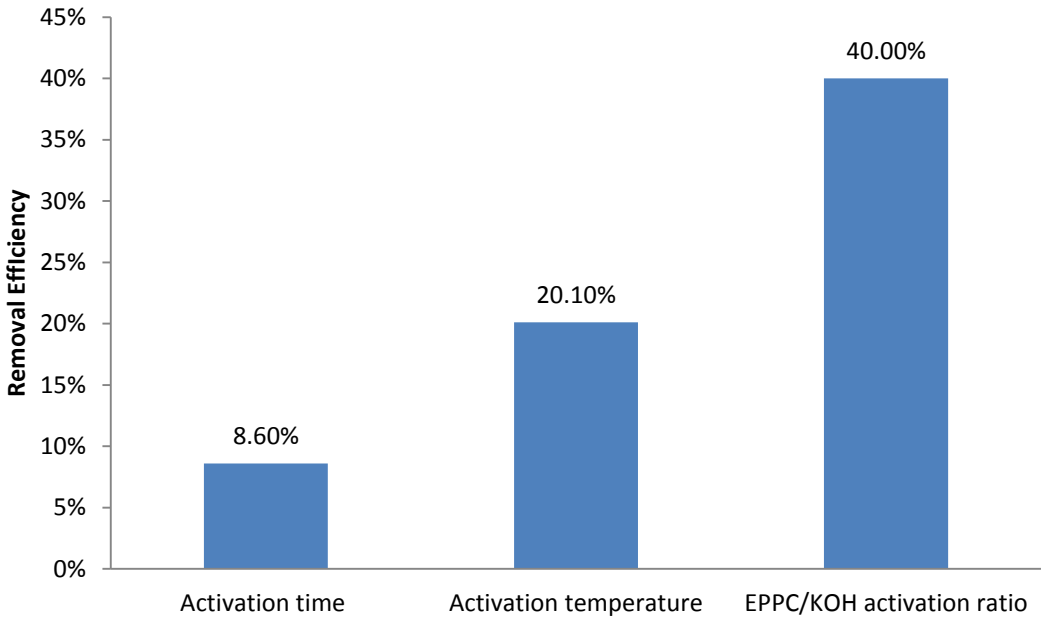

Figure 10: Effect of the three factors (activation temperature, activation time, EPPC to KOH activation ratio) on the removal efficiency of EPPAC-2.

3.3. Effect of activation parameters on the removal efficiency of EPPAC-3

In order to determine the effect of activation parameters such as impregnation temperature, impregnation time, impregnation ratio, activation temperature and activation time, adsorption studies at the same conditions were carried out. All the runs were performed at mentioned adsorption conditions: 300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25 ± 2^0C.

3.3.1. Effect of the impregnation temperature

The effect of impregnation temperature is shown in figure 11. Other activation parameters such as impregnation time, activation temperature, activation time and impregnation ratio were kept constant at 1.5h, 500^0C, 1h and 1:1 (1g EPPC: 1g KOH) in 10 mL double distilled water respectively.

As the impregnation temperature is increased from 25^0C to 120^0C, the removal efficiency also increases from 20.5% to 24.7% but then with further increase in the impregnation temperature to 160^0C, there is no appreciable change in the removal efficiency (see figure 11). In fact impregnation temperature doesn't have significant

effect on the removal efficiency. The optimum impregnation temperature is 120^0C at the impregnation ratio of 1:1, impregnation time 1.5h, activation temperature 500^0C and activation time of 1h.

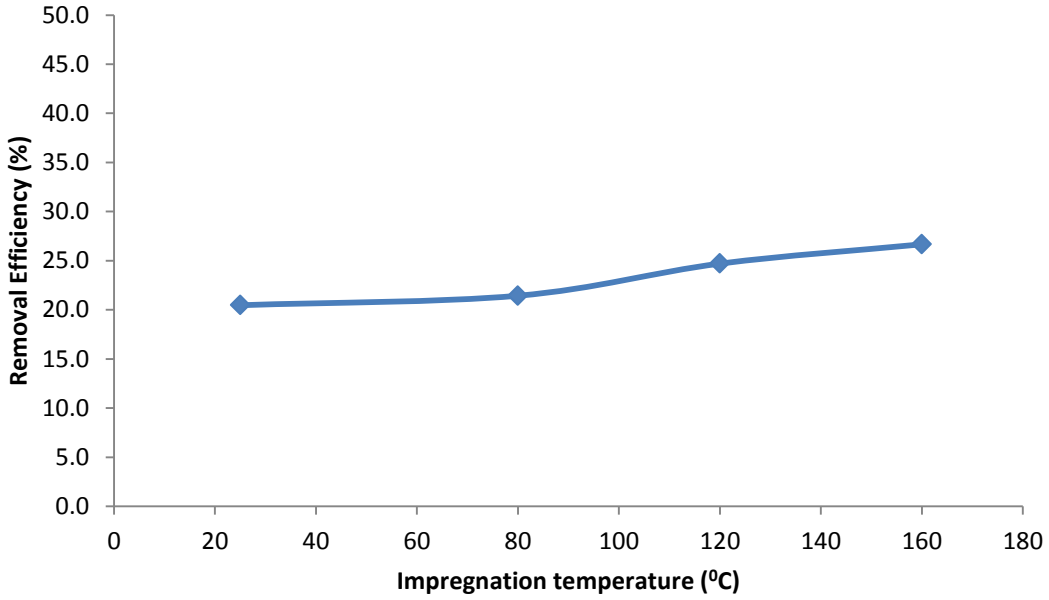

Figure 11: Effect of impregnation temperature on EPPAC-3 for removal efficiency of lead (II) at initial concentration of lead (II): 300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25 ± 2^0C.

3.3.2. Effect of the activation temperature

The effect of the variation of activation temperature on the removal efficiency of lead (II) by EPPC-3 is shown in figure 12. Runs were carried out at varying activation temperatures while all other activation parameters such as impregnation time, impregnation temperature, activation time and impregnation ratio were kept constant at 1.5h, 120^0C, 1h and 1:1 (1g EPPC: 1g KOH) in 10 mL double distilled water respectively.

Figure 12 shows that as the activation temperature is increased from 500^0C to 700^0C, the removal efficiency increases from 24.7% to 33.8%. With the further increase in the temperature to 800^0C the removal efficiency shows a decreasing trend and efficiency decreases to 31.51%. The optimum activation temperature is 700^0C. With the increase in the temperature, the development of pores increases due to which the adsorption capacity and removal efficiency also increases. Higher temperature may result in the suppressing of pore formation due to which the removal efficiency is low.

3.3.3. Effect of the impregnation ratio

In order to observe the effect of impregnation ratio on the removal efficiency of EPPAC-3, impregnation ratio was changed from 1:1 (1g EPPC: 1g KOH in 10 mL double distilled water) to 1:5 (1g EPPC: 5g KOH in 10 mL double distilled water), while all other parameters were kept constant: activation temperature 700^0C, impregnation temperature 120^0C, activation time 1h and impregnation time 1.5h.

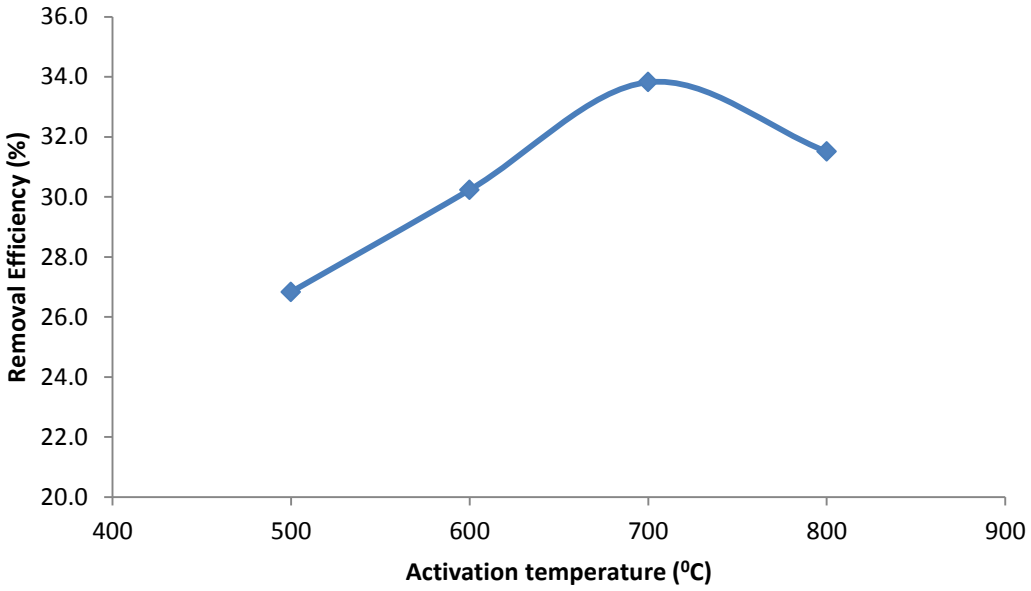

Figure 12: Effect of activation temperature on EPPAC-3 for removal efficiency of lead (II) at initial concentration of lead (II): 300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25±2 ^{0}C.

As the impregnation ratio is increased from 1:1 to 1:4, removal efficiency gradually increases from 33.8% to 60.1% (see figure 13). As the ratio is further increased there is no significant change in the removal efficiency. With the increase in the impregnation ratio from 1:1 to 1:5, the amount of KOH increases which is responsible for the increase in removal efficiency after drying and reactivation stages. Actually rate of reaction between EPPC and KOH increases with the increase in the amount of KOH, which further increases the pore formation process and consequently the removal efficiency, is increased.

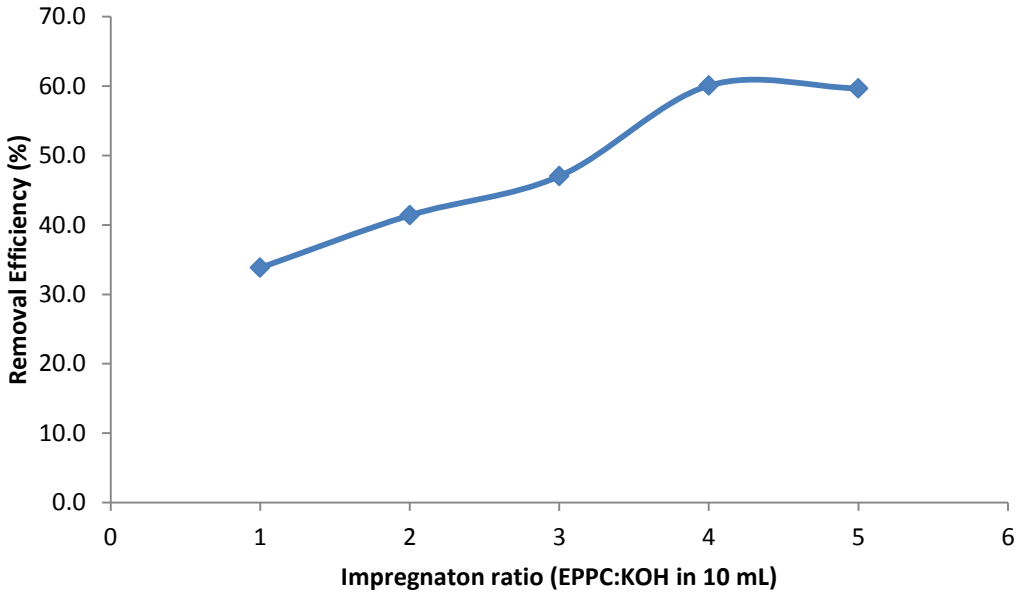

Figure 13: Effect of impregnation ratio on EPPAC-3 for removal efficiency of lead (II) at initial concentration of lead (II): 300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25±2^{0}C.

3.3.4. Effect of the impregnation time

The effect of the impregnation time is shown in the figure 14. All other activation parameters such as impregnation temperature, impregnation ratio, and activation temperature and activation time were kept constant at 120^{0}C, 1:4, 700^{0}C and 1h respectively.

As shown in figure 14, there is no appreciable change in the removal efficiency. However, slight increase in the removal efficiency to 60.1% from 57.2% is observed when the impregnation time is increased up to 1.5h but after then no change in the removal efficiency is recorded. This shows that only specific amount of KOH can penetrate into the interior of the EPPC with respect to time, thus after optimum time, the removal efficiency remains constant.

3.3.5. Effect of the activation time

The effect of the activation time is shown in the figure 15. All other activation parameters such as impregnation temperature, impregnation time, impregnation ratio, activation temperature and activation time were kept constant at 120^{0}C, 1.5h, 1:4, 700^{0}C and 1h respectively.

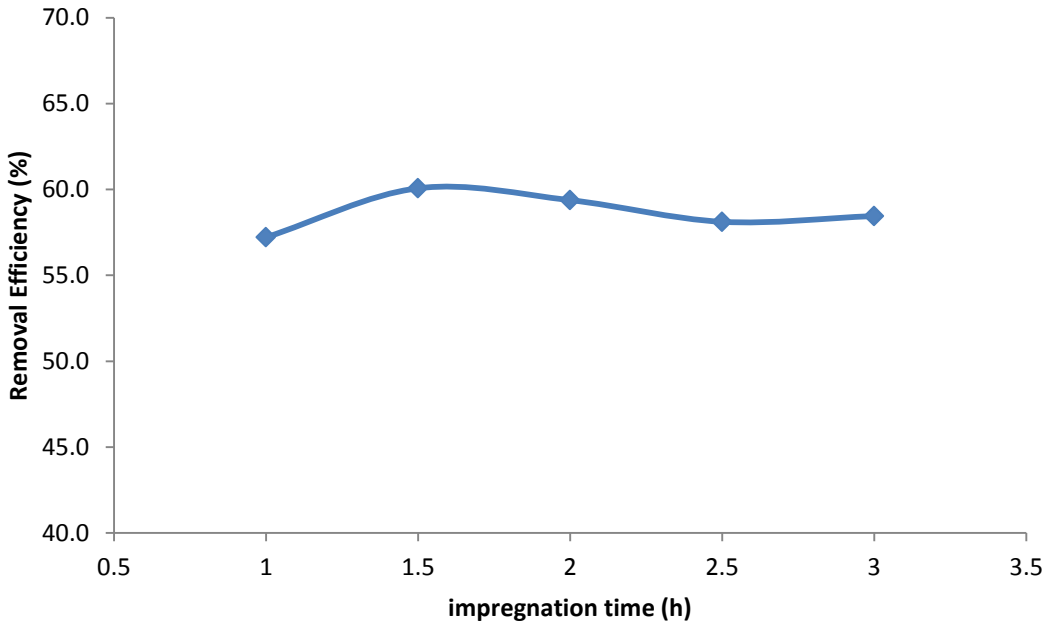

Figure 14: Effect of impregnation time on EPPAC-3 for removal efficiency of lead (II) at initial concentration of lead (II): 300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25±2 ^{0}C.

As the time is increased from 0.5h to 1.0h, the efficiency increases to 60.1% and then with the further increase in time removal efficiency decreases. This is because with the increase in the activation time the previously formed pore structure gets destroyed.

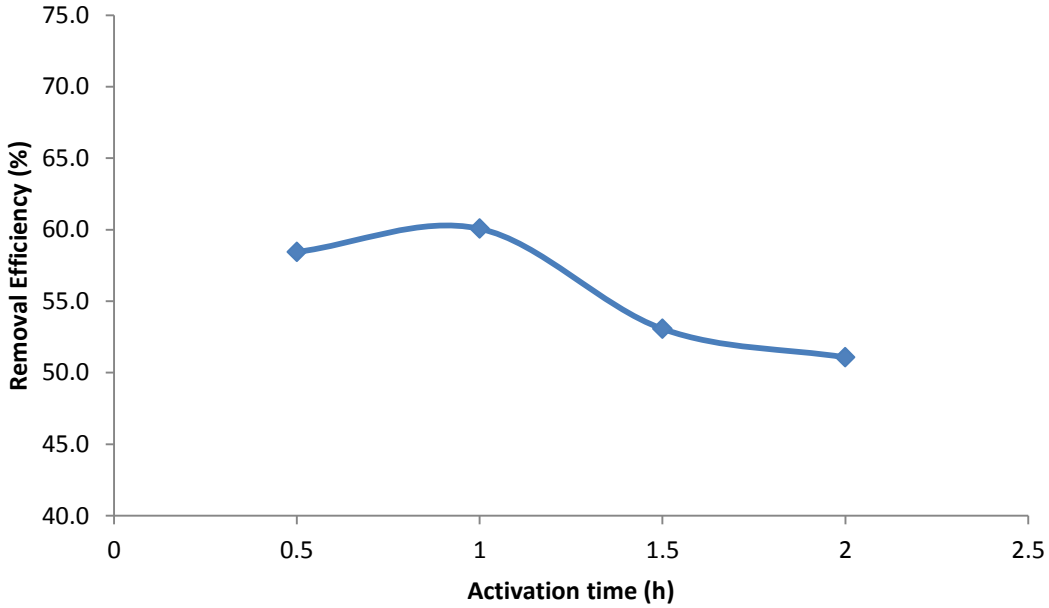

Figure 15: Effect of impregnation time on EPPAC-3 for removal efficiency of Lead (II) at initial concentration of lead (II): 300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25±2^{0}C.

Figure 16 shows the variation in removal efficiency of EPPAC-3 for lead (II) removal caused by activation factors: impregnation time, impregnation temperature, impregnation ratio activation time, activation temperature. As it is obvious from the figure 16 that most significant impact on the removal efficiency of EPPAC-3 is caused by the change in EPPC to KOH impregnation ratio. The variation for EPPC to KOH is 29.25% which is very high as compared to variation in removal efficiency caused by other parameters.

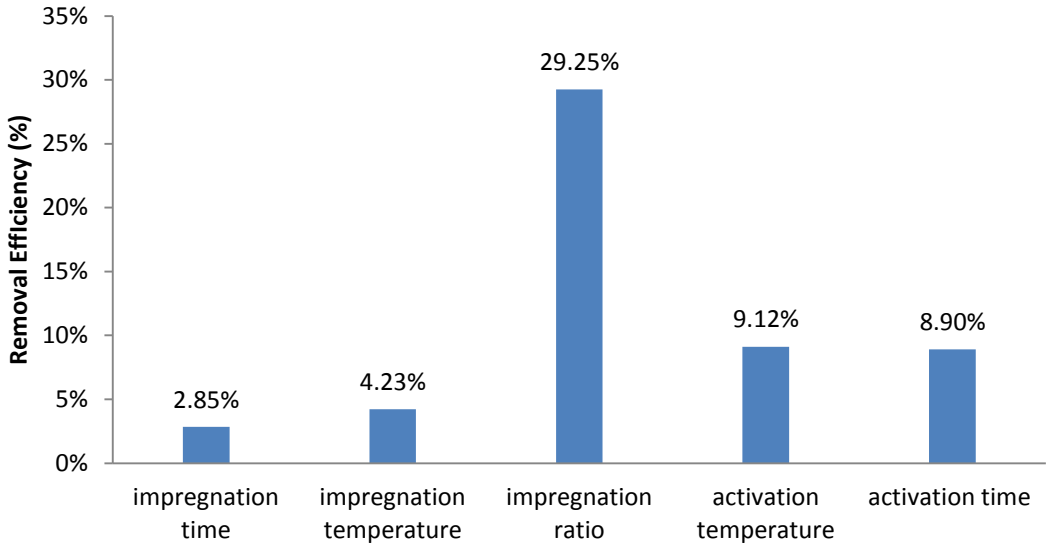

Figure 16: Effect of the activation factors on the removal efficiency of EPPAC-3.

The optimum activation conditions for EPPAC-1, EPPAc-2 and EPPAC-3 are mentioned in table 3.

Table 3: Optimum activation conditions for EPPAC-1, EPPAC-2 and EPPAC-3

Sample ID	**Activation Parameters**					
	Activation time (h)	Activation temperature (^{0}C)	Activation ratio	Impregnation time (h)	Impregnation ratio	Impregnation temperature (^{0}C)
EPPAC-1	2	700^{0}C	1:1	-	-	-
EPPAC-2	2	700^{0}C	1:1	-	-	-
EPPAC-3	1	700^{0}C	-	1.5	1:4 in 10mL	120

3.4. Surface characterization

Characterization of activated charcoal includes the determination of physical and chemical properties such as surface area, pH, and surface structure (scanning electron microscope analysis), elemental composition (SEM/EDS analysis), and ash content and surface groups of the activated charcoal.

3.4.1. Scanning Electron Microscope (SEM) Analysis

The physical morphology of the surfaces of EPPC, EPPAC-1, EPPAC-2 and EPPAC-3 was carried out by using SEM (TESCAN VEGA.3-LMU). The SEM photographs for EPPC, EPPAC-1, EPPAC-2 and EPPAC-3 are shown in figures 17, 18, 19 and 20. For comparison studies all photographs are of 1000X magnification. Figure 17 shows that EPPC has very limited cavities and pores thus it is very slightly porous.

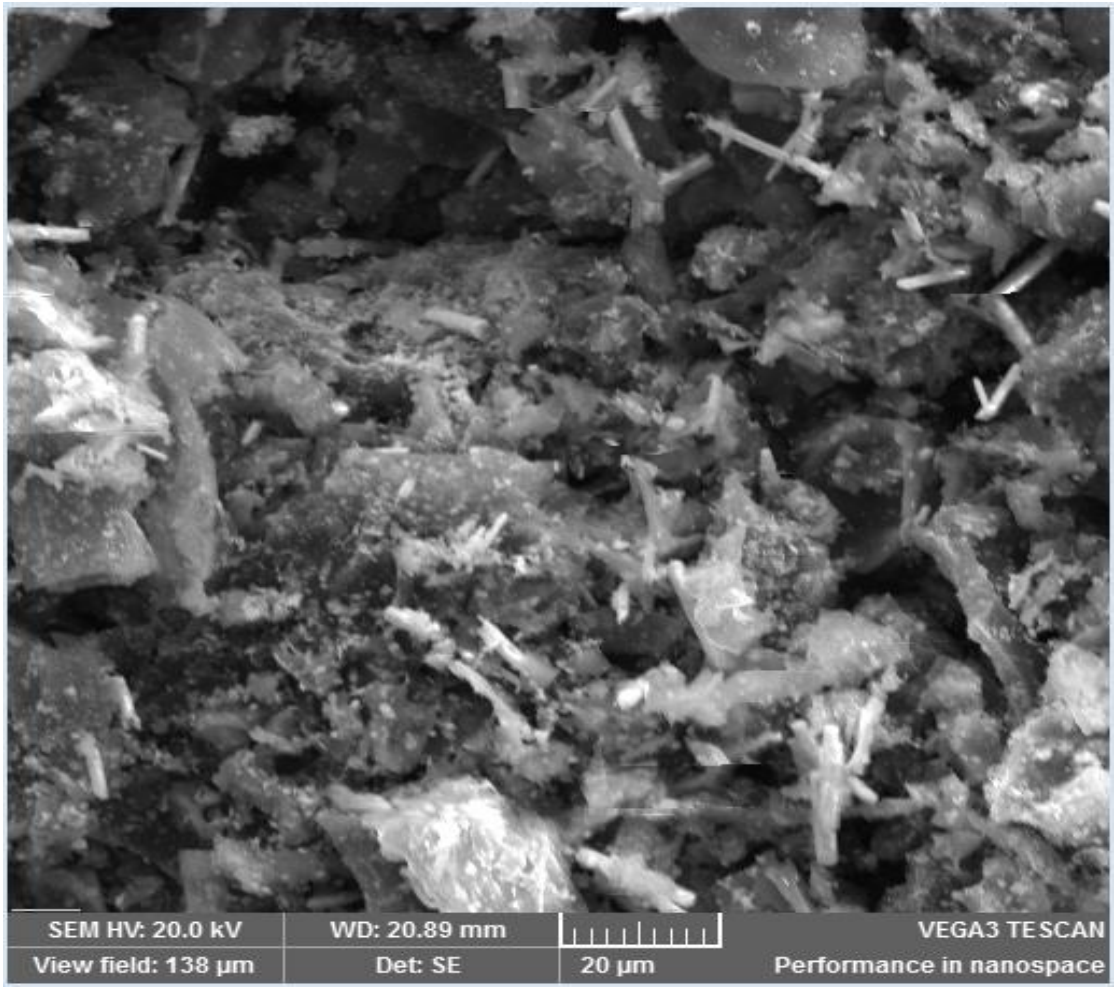

Figure 17: Scanning electron microscope image of EPPC.

By comparing the Figures 18, 19 and 20 of EPPAC-1, EPPAC-2 and EPPAC-3 with figure 17 of EPPC, clear transformation in the surfaces of EPPAC-1, EPPAC-2 and EPPAC-3 has been observed. Pores, cavities can be prominently observed in the Figures 18, 19 and 20, which are responsible for the increase in the surface area, adsorption capacities and efficiencies. The generation and formation of these pores and cavities is the result of the evolving volatiles from EPPC [118]. These porous structures are also due the chemical reaction between KOH and EPPC which further results in the augmentation of pores [119]. Also by comparing the structures demonstrated in figures 18, 19 and 20 number of pores and the development of the pores are high in EPPAC-2 as compared to EPPAC-3 and EPPAC-1. The possible reason of this highly pores structure of EPPAC-2 may be because of the efficient and proportionate mixing between the grinded KOH particles and EPPC particles. Cavity development is much more prominent in EPPAC-3 as compared to EPPAC-1 mainly because of the fact that KOH solution can be penetrated to the inside of the surface of EPPC due the slight porous surface of EPPC which results in the development of the cavities on the surface of EPPAC-3 as compared to EPPAC-1.

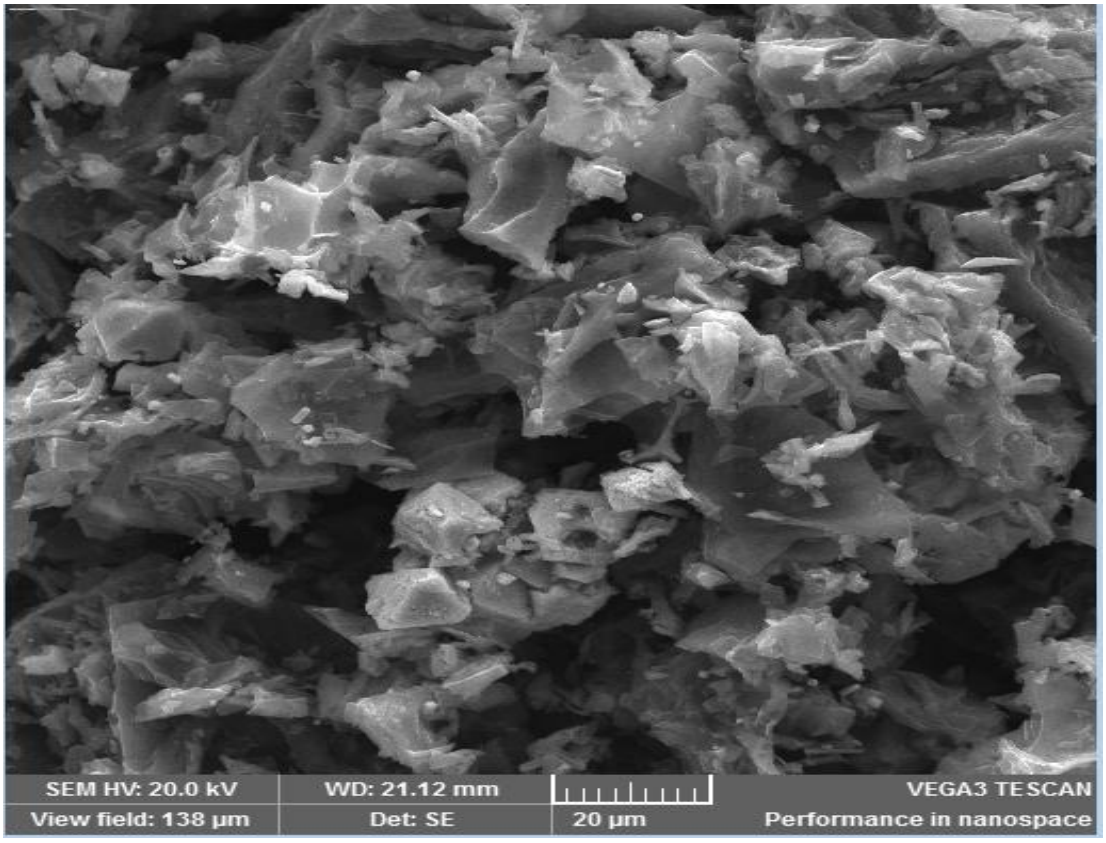

Figure 18: Scanning electron microscope image of EPPAC-1.

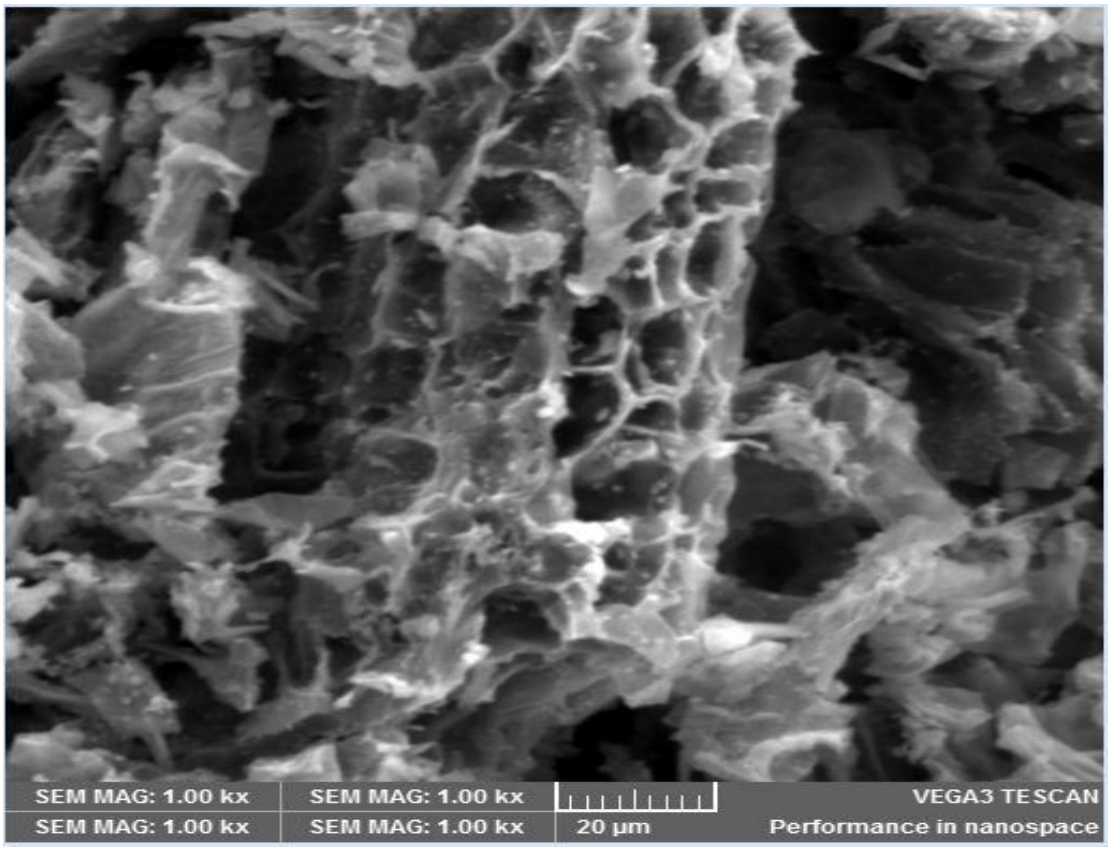

Figure 19: Scanning electron microscope image of EPPAC-2.

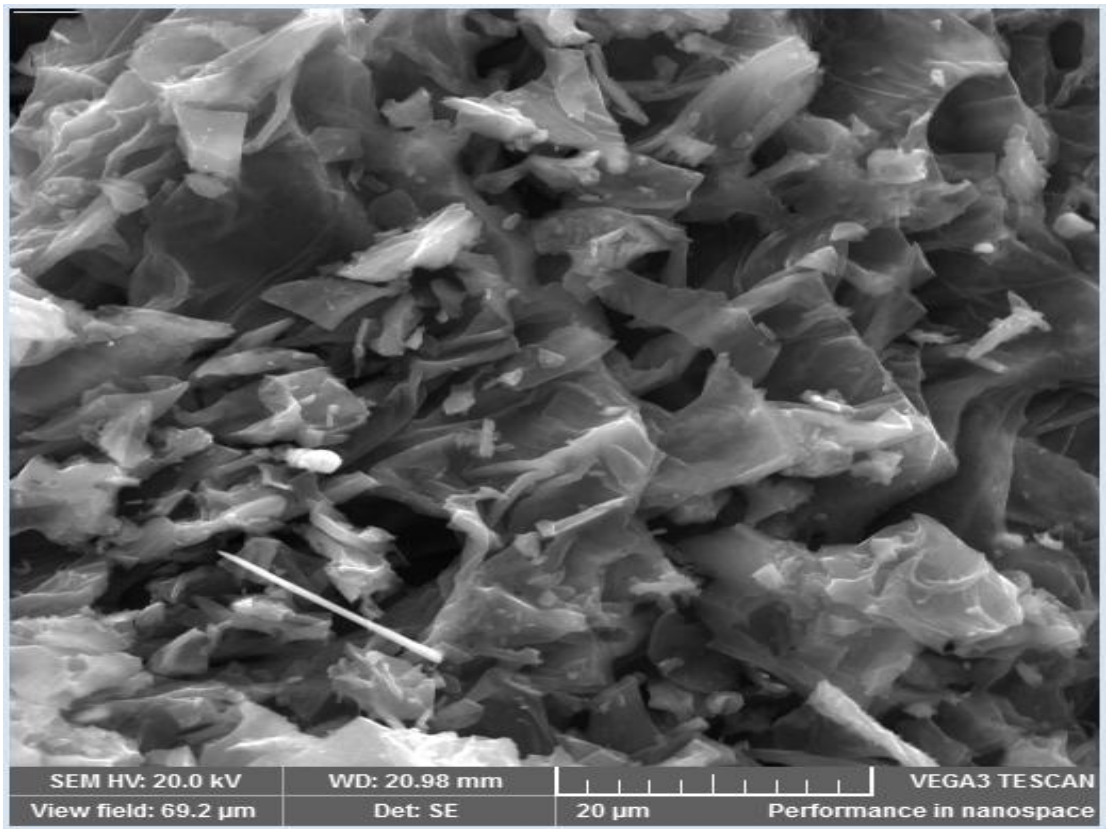

Figure 20: Scanning electron microscope image of EPPAC-3.

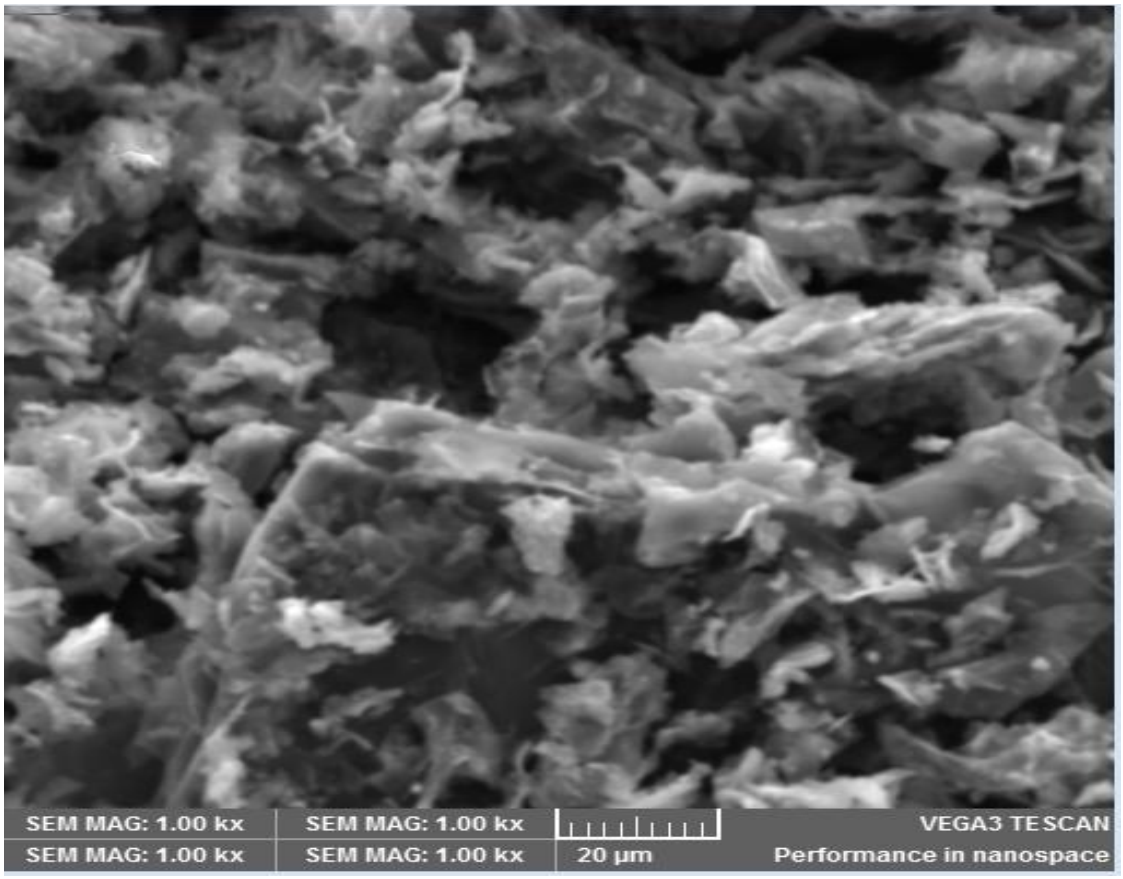

Figure 21: Scanning electron microscope image of lead (II) loaded EPPAC-1.

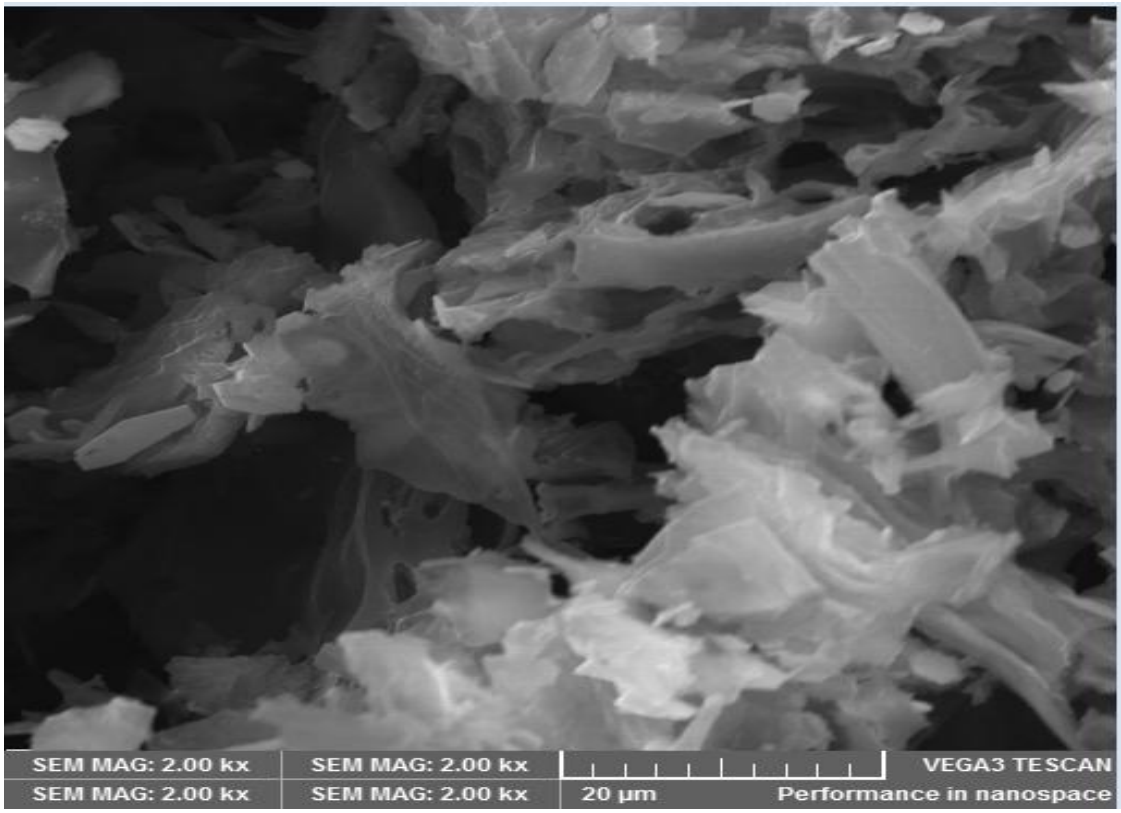

Figure 22: Scanning electron microscope image of lead (II) loaded EPPAC-2.

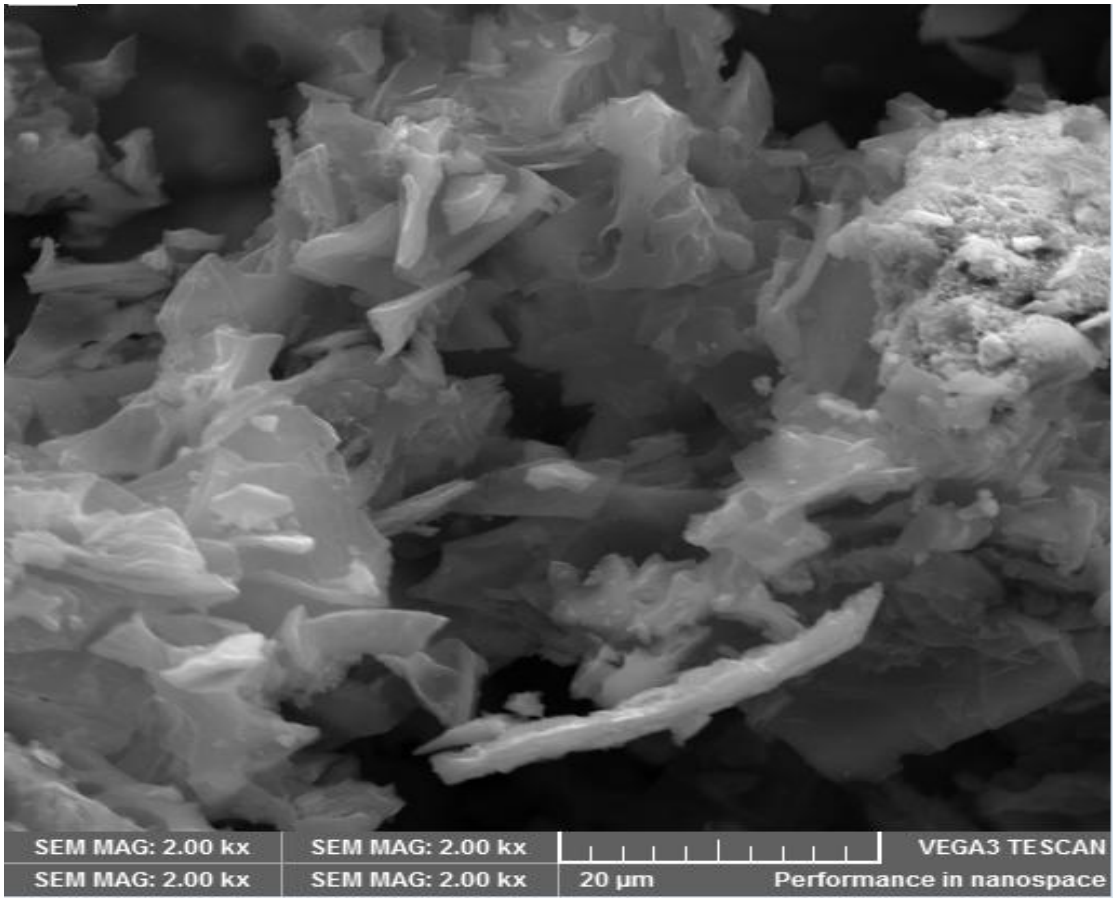

Figure 23: Scanning electron microscope image of lead (II) loaded EPPAC-3.

In EPPAC-1 direct physical mixing of KOH lentils was carried out. Actually at some points the weight ratio of KOH to EPPC can be very high and at other points the ratio can be very low and both cases are responsible for the generation of structure as shown in figure 20, since high or low KOH to EPPC ratio at pacific points can result in the suppressing of pores and distortion of the structure [118]. The SEM images of loaded EPPAC-1, EPPAC-2 and EPPAC-3 are also shown in figures 21, 22 and 23 respectively.

3.4.2. Surface area measurements

The surface areas of EPPAC-1, EPPAC-2 and EPPAC-3 have been measured by using NOVA quanta-chrome instrument version 11.02. The BET (Brunaeur-Emmet-Teller) multipoint method has been employed for the determination of surface area using nitrogen gas. The surface areas of EPPAC-1, EPPAC-2 and EPPAC-3 are $607m^2/g$, $739m^2/g$ and $631m^2/g$.

3.4.3. Energy Dispersive X-ray spectrometry (EDS) analysis

EDS patters for EPPC, EPPAC-2 and lead (II) loaded EPPAC-2 are shown in figures 24, 25 and 26.

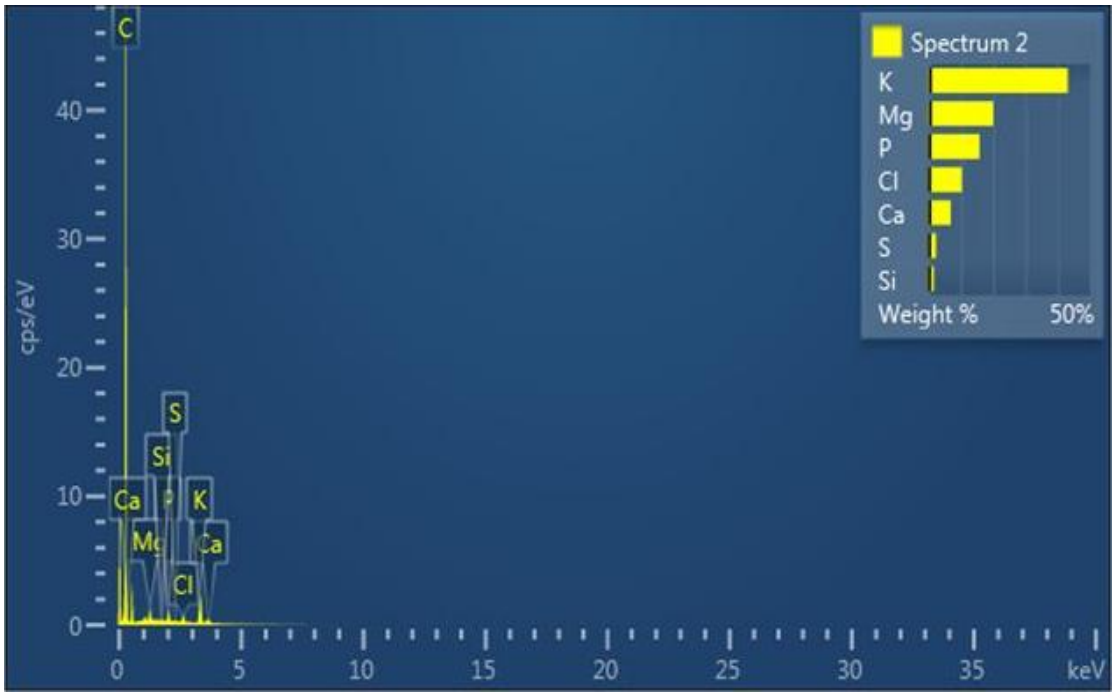

Figure 24: Energy dispersive X-ray spectroscopy (EDS) analysis of EPPC.

Figure 25: Energy dispersive X-ray spectroscopy (EDS) analysis of EPPAC-2.

According to EDS analysis of EPPC and EPPAC-2 no characteristic signal of lead (II) has been detected which shows that EPPC and EPPAC-2 do not have any lead in their elemental composition. But for the lead (II) loaded EPPAC-2, clear signals have been obtained at 2.3, 9.1, 10.5, 11.3, 12.6 and 14.8 keV respectively. Thus the EDS spectrum confirms the adsorption of lead (II) by EPPAC-2. The elemental analysis of the EPPC, EPPAC-2 and lead (II) loaded EPPAC-2 has been carried out by the energy dispersive X-ray spectroscopy (EDS) detector (Oxford instruments INCA-Xact) attached to the scanning electron microscope.

Full area EDAX scan of EPPC, EPPAC -2 and lead (II) loaded EPPAC-2 has been done and important conclusions have been drawn regarding the detection of certain elements. Table 4 shows that EPPC is composed of elements such as magnesium, phosphorous, sulphur, chlorine, potassium, calcium and silicon. However, EPPAC-2 is only composed of chlorine. Lead and chlorine have been detected in EPPAC-2 loaded with lead (II) by EDAX scan.

Almost similar elements have been detected in pyrolysed date pits as that of EPPC [117]. In this study carbon cannot be detected because of the non-availability of the silicon bases necessary for the detection of carbon.

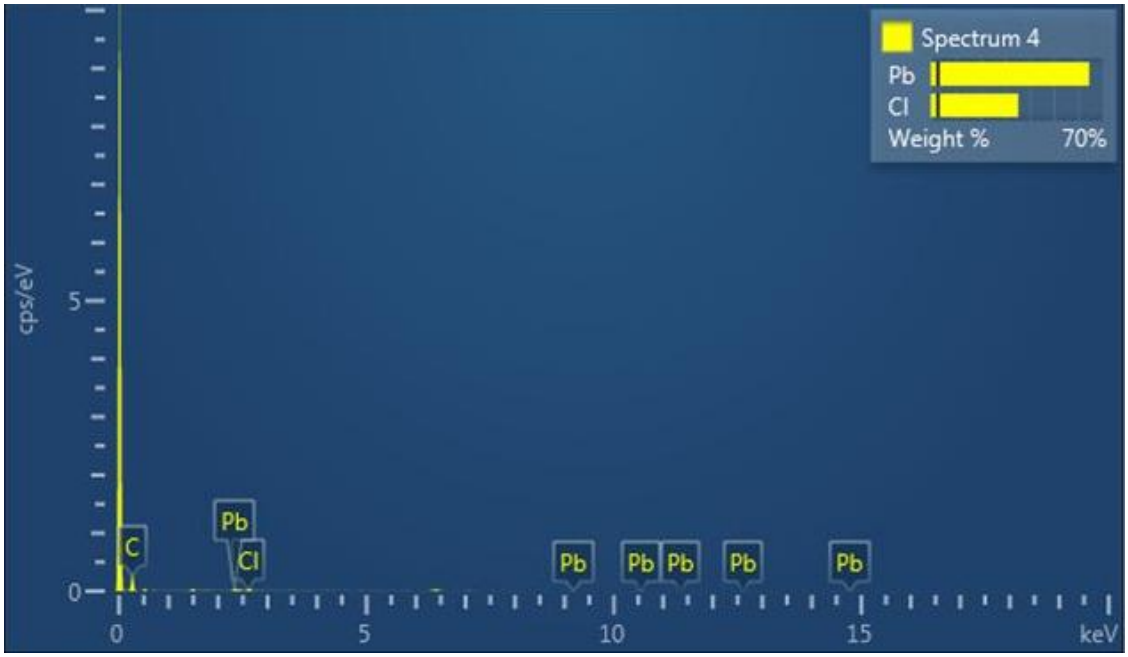

Figure 26: Energy dispersive X-ray spectroscopy (EDS) analysis of EPPAC-2.

3.4.4. pH measurements and Boehm titration

EPPAC-2 (0.4g) was added to 20mL double distilled water and the resulting suspension mixture was stirred at 200 RPM for 24h. After then the solution was filtered and pH of the filtrate was measured. The pH was found out to be 7.8. Boehm titration method has been used to determine the amount of surface groups on EPPAC-2. One gram of EPPAC-2 was added to 50mL of 0.05M solutions of HCl and NaOH. The resulted solutions were sealed and they were shaken for 24h. Then 5mL of each solution was pipetted and excess of acid or base was titrated with NaOH and HCl. The end points were determined by using phenolphthalein indicator for acid titrated with NaOH and methyl orange for base titrated with HCl. The amount of acidic sites was calculated on the basis of assumption that NaOH neutralizes acidic groups (carboxylic, phenolic and lactonic). Similarly the amount of basic sites was calculated on the basis that HCl neutralizes basic groups [120]. The amount of acidic and basic groups is shown in table 5. The presence of acidic groups such as carboxylic and phenolic groups is responsible for the complexation properties of adsorbents [117]. In this study the good adsorption capacity of EPPAC-2 is certainly due to presence of these acidic sites.

3.4.5. Ash contents

EPPAC-2 (0.2g) was loaded in porcelain crucible covered with lid and then put in furnace at 650^0C for 20 minutes. Thus weighing before loading and after heating, EPPAC-2 yielded 2.5% ash contents. The physical and chemical properties of EPPAC-2 are mentioned in table 5.

Table 4: Physical and chemical properties of EPPAC-2

Properties	Values
BET Surface area (m^2/g)	739
Ash content (%)	2.5
pH	7.8
Acidic groups (mmol/g)	0.85
Basic groups (mmol/g)	1.34

3.5. Adsorption studies

Adsorption is a process which takes place on the surface. It depends upon the physical and chemical properties of adsorbent and adsorbate. Effect of various parameters like initial concentration of the adsorbate, adsorbent dose, contact time and initial pH were studied.

Adsorption studies were carried out by using stock solution of 1000 mg/L Pb (II) prepared from lead nitrate $Pb(NO_3)_2$. By using this stock solution other dilute standard solutions were prepared of different lead (II) concentrations 100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L, 500 mg/L, 600 mg/L, 700 mg/L, 800 mg/L and 900 mg/L. Throughout the experimental work, 250 mL of Erlenmeyer flasks were used. Each of flask contained 100 mL of lead solution of required concentrations. Desired pH was adjusted by using 0.1 M HNO_3 and 0.1 M NaOH with specific amount of adsorbent (EPPAC-2) in each flask. All the experiments were carried out at 25±2 ^{0}C. Flasks containing samples were agitated by using Wise shake flask shaker at 120 RPM for all experiments. The samples were filtered by using whatman filter papers and supernatant was analyzed for lead (II) by AA240FS fast sequential atomic absorption spectrometer. The blank adsorption experiments were also carried out. The equilibrium adsorption capacity, removal efficiency and adsorption capacity at time t were determined by using:

$$q_e = \frac{(C_o - C_e)V}{M} \tag{18}$$

$$Removal\ efficiency = \frac{C_o - C_e}{C_o} \times 100 \tag{19}$$

$$q_t = \frac{(C_o - C_t)V}{M} \tag{20}$$

Where q_e (mg/L) is the equilibrium adsorption capacity, q_t is adsorption capacity at time t, C_o (mg/L) is the initial concentration of lead ions in the solution, C_e (mg/L) is

the equilibrium concentration of the lead ions in the solution, C_t is the concentration of lead ions in the solution at time t, V (L) is the volume of the lead solution, M (g) is weight of the adsorbent.

3.5.1. Effect of Contact time

Figure 27 shows the effect of contact time on the removal efficiency of lead (II) ions from aqueous solution of concentrations 300 mg/L and 1000 mg/L respectively. As the contact time is increased to 24h, the adsorption of lead increases which is indicated by increase in the removal efficiency of lead (II) ion to 70% for 300 mg/L and to 38% for 1000 mg/L. After 24h the adsorption of lead (II) ions becomes slow and very small change in the removal efficiency was detected after 24h. All other parameters such as initial pH (5.1), adsorbent dose (0.32 g), and shaker RPM (120), adsorbent particle size (150 micron) and temperature (25 ± 2^0C) were kept constant. The equilibrium time is considered to be 24h for all the experiments.

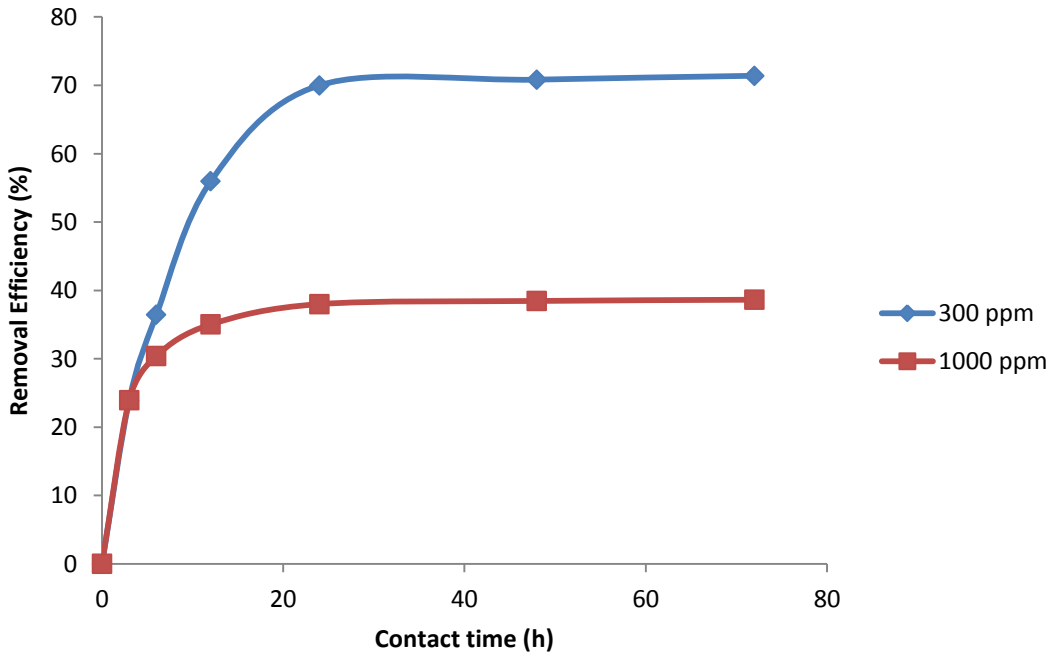

Figure 27: Effect of contact time on the adsorption of lead (II) by EPPAC-2. Initial concentrations: 300mg/L, 1000mg/L; adsorbent particle size: 150 micron; temperature: 25 ± 2 ^{0}C; adsorbent dose: 0.32g/100mL; initial pH; 5.1; shaker RPM: 120.

3.5.2. Effect of Initial pH

Figure 28 shows the effect of initial pH on the adsorption of lead (II) ions on the eggplant peel activated charcoal (EPPAC-2) at temperature of 25 ± 2^0C, adsorbent dose

of 0.15 g/ 100 mL, contact time of 24h, lead concentration of 300 mg/L, adsorbent particle size 150 micron and shaker RPM of 120. All the initial pH runs have been carried out at pH $\leq$ 8.0 because $Pb(OH)_2$ plays an important and vital role in removing Pb (II) ions [3]. At lower pH the removal efficiency of adsorbent is low; however as pH increases, removal efficiency of the adsorbent also increases. The optimum pH is 5.1 with removal of 48.1% lead (II) from the solution with the initial lead concentration of 300 mg/L. As the pH is further increased from 5.1 there is no appreciable change in the removal efficiency. At lower pH, competitive adsorption occurred between H^+ ions and Pb (II) ions for occupying adsorption sites, which is responsible for the decrease in the removal efficiency.

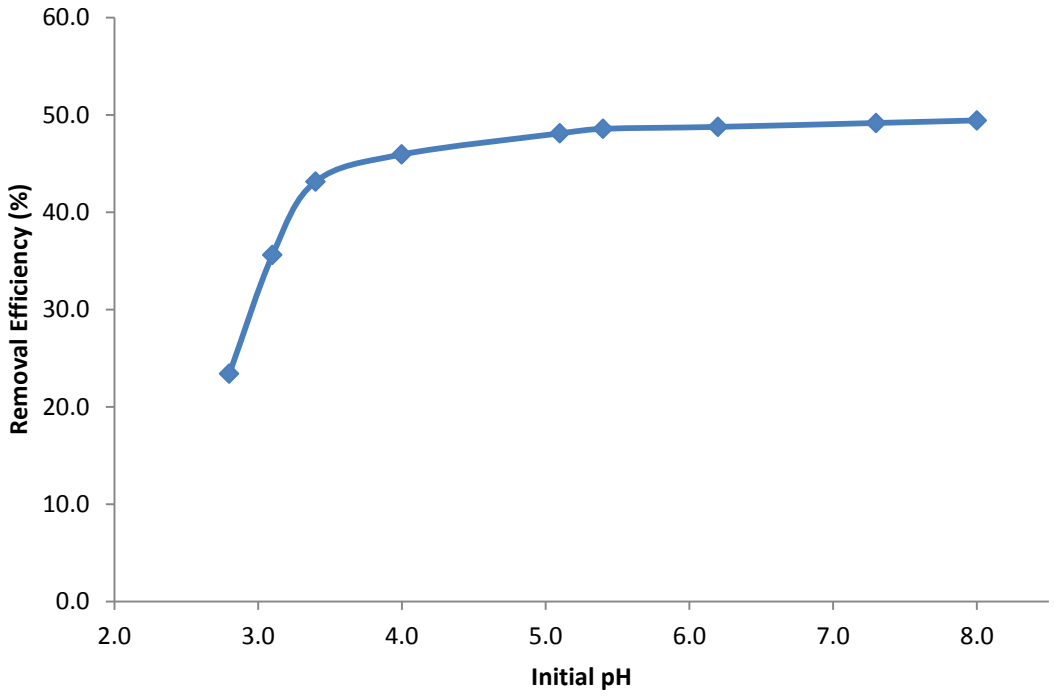

Figure 28: Effect of initial pH on the adsorption of lead (II) by EPPAC-2. Initial concentration: 300mg/L; adsorbent particle size: 150 micron; temperature: 25±2 ^{0}C; adsorbent dose: 0.15g/100 mL; contact time: 24h; shaker RPM: 120.

Figure 29 shows final pH values as function of initial pH values, the final pH values are higher than initial pH values for initial concentration of lead (II) 300 mg/L. The behavior of the final pH in figure 29 is almost similar to removal efficiency trend in figure 28. As the initial pH is increased from 2.8 to 5.1, removal efficiency also increases sharply along with final pH. With the increase in removal efficiency of lead (II) ions, greater will the number of OH^- ions in the solution, greater will the final pH.

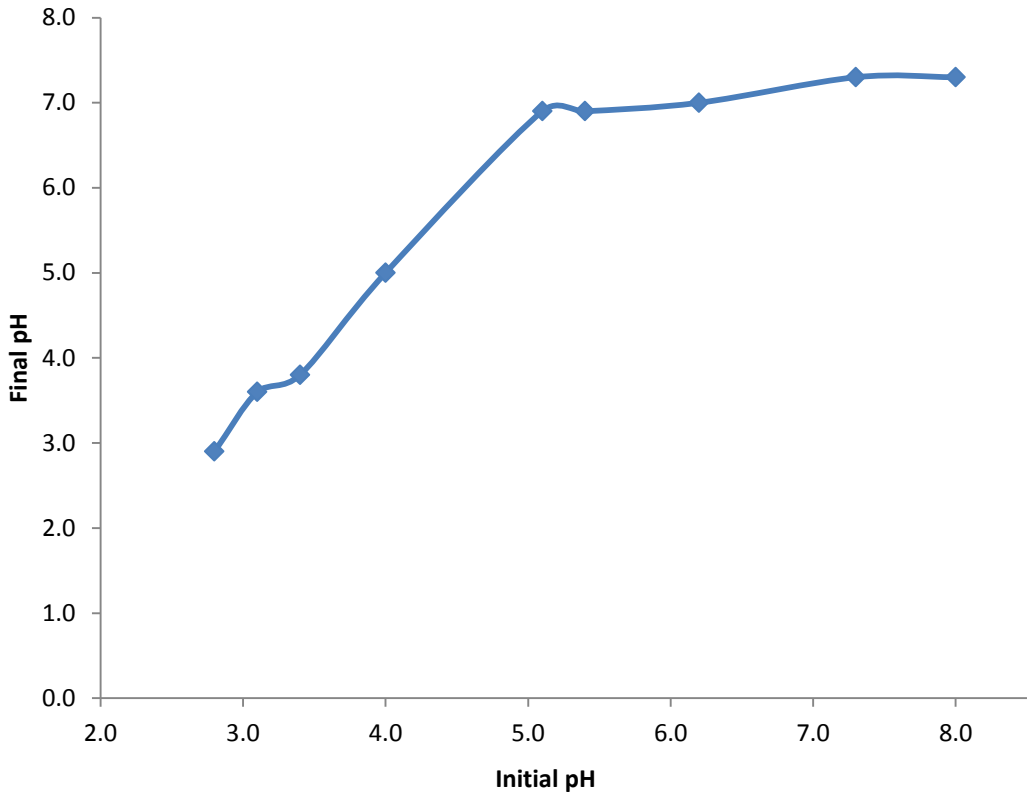

Figure 29: Final pH as function of initial pH. Initial concentration: 300mg/L; adsorbent particle size: 150 micron; temperature: 25±2 ^{0}C; adsorbent dose: 0.15g/100 mL; contact time: 24h; shaker RPM: 120.

3.5.3. Effect of Adsorbent dose

Figure 30 shows the effect of increase in the adsorbent dose on the removal efficiency of lead (II) ion for initial lead (II) concentration of 100 mg/L. Therefore, as the adsorbent dose is increased from 0.08 g / 100 mL to 0.32 g/ 100 mL, removal efficiency of lead (II) is increased from 14.6% to 94%. At the removal efficiency of 94%, adsorbent dose of 0.32g is taken as optimum adsorbent dose of EPPAC-2 because no appreciable change in the removal efficiency occurs at higher doses greater than 0.32 g.

All other parameters such as initial concentration of lead (II) in the solution (100 mg/L), initial pH (5.1), contact time (24 h), shaker RPM (120), adsorbent particle size (150 micron) and temperature (25±2 ^{0}C) were kept constant.

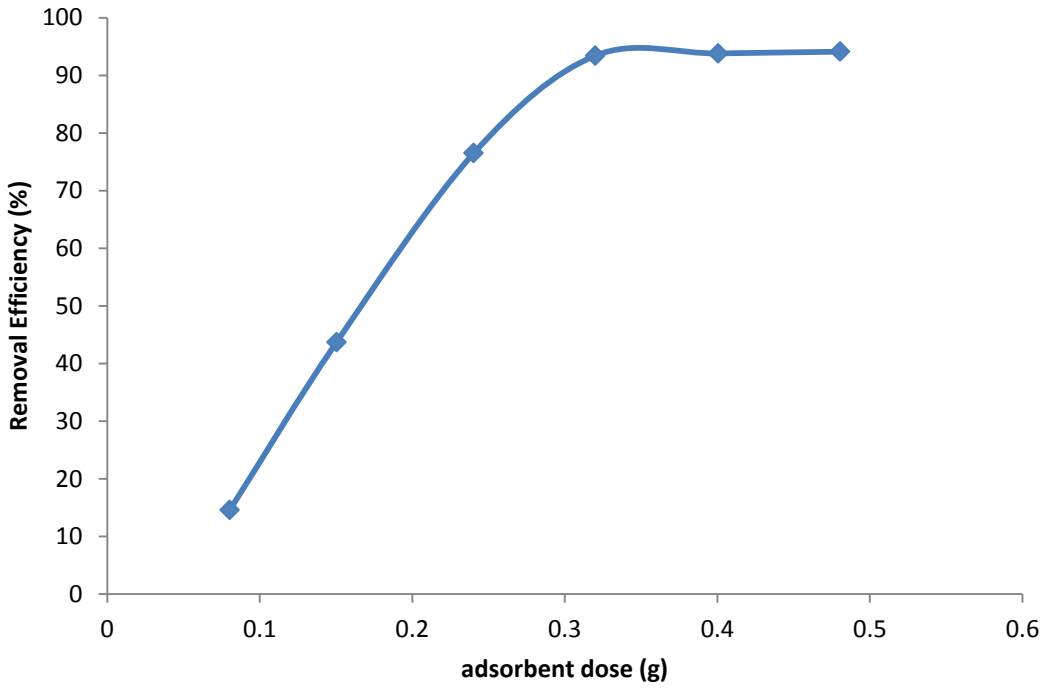

Figure 30: Effect of EPPAC-2 dose on the adsorption of lead (II): initial lead concentration: 100 mg/L; initial pH: 5.1; contact time: 24 h; adsorbent particle size: 150 micron; Shaker RPM: 120; temperature: 25±2 ^{0}C**.**

3.5.4. Effect of Initial concentration

Solutions of different lead (II) concentrations were prepared (100 mg/L, 200mg/L, 300 mg/L, 400 mg/L, 500 mg/L, 600 mg/L, 700 mg/L, 800 mg/L and 900 mg/L) from stock solution of 1000 mg/L. All solutions were of one hundred milliliters each. However other parameters like adsorbent dose (0.32 g), contact time (24 h), initial pH (5.1), adsorbent particle size (150 micron), shaker RPM (120) and temperature (25±2 ^{0}C) were kept constant for all the solutions of different concentrations. Figure 31 shows that as the initial concentration of lead (II) in the solution is increased, percentage removal efficiency of the lead (II) decreases. The percentage removal efficiency of lead (II) decreases from 93.4% to 38% as the initial concentration is increased from 100 mg/L to 1000 mg/L. Since the initial concentration of lead (II) is increased while maintaining a constant amount of adsorbent dose 0.32g, so as a result fewer sites are available for each higher concentration of lead (II).

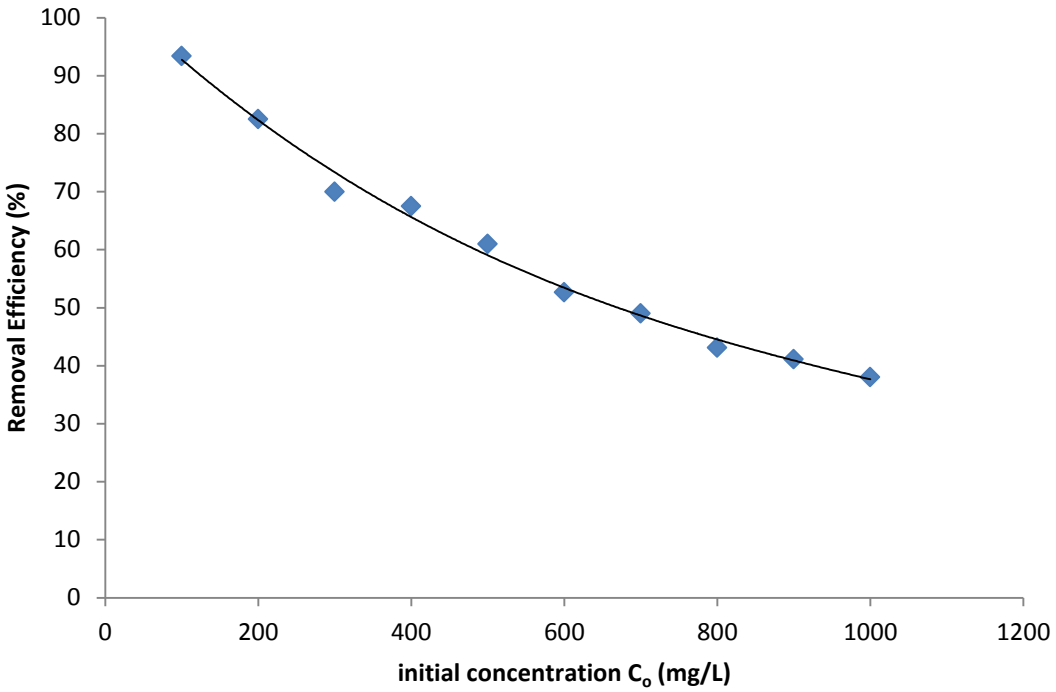

Figure 31: Effect of the initial concentration on lead (II) removal by EPPAC-2. Adsorbent dose: 0.32 g/100 mL; initial pH: 5.1; temperature: 25±2 ^{0}C; adsorbent particle size: 150 micron; contact time: 24 h; shaker RPM: 120.

3.5.5. Adsorption kinetic models

The adsorption of the lead (II) from wastewater was tested by using pseudo-first-order and pseudo-second-order kinetic models. Mathematically pseudo-first-order is expressed as:

$$log(q_e - q_t) = logq_e - k_1 t \quad (21)$$

where q_e is the equilibrium adsorption capacity (mg/g), q_t is the adsorption capacity at time t, k_1 is pseudo-first-order rate constant (g/mg h) which can be evaluated by plot between $log(q_e - q_t)$ and t.

Mathematically pseudo-second-order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (22)$$

where q_e the equilibrium adsorption capacity (mg/g) is, q_t is the adsorption capacity at time t, k_2 is pseudo-second-order rate constant (g/mg h) which can be evaluated by plot between $\frac{t}{q_t}$ and t.

The adsorption kinetics for the lead (II) removal was studied for the contact time of 72h. The graph as shown in figure 32 which is between q_t and contact time shows that as the contact time increases, adsorption capacity also increases and then adsorption capacity becomes constant after 24h. So the experimental equilibrium adsorption capacity is 140 mg/g according to figure 32. The plots for the pseudo-first and pseudo-second order kinetic models are presented in figure 33 and figure 34.

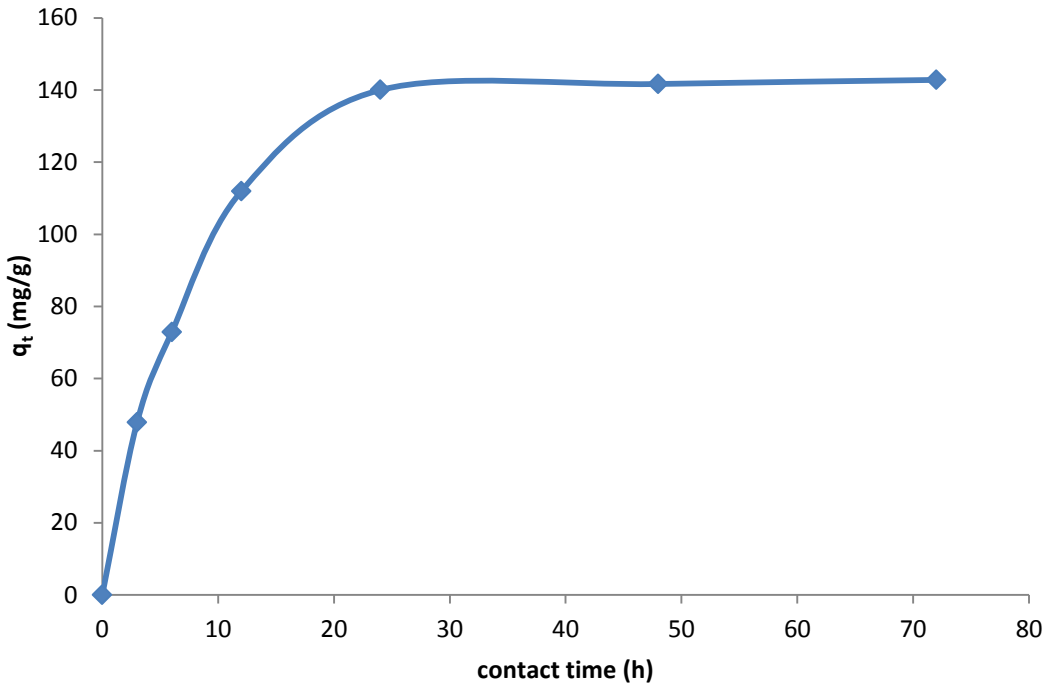

Figure 32: Effect of the contact time on adsorption capacity of EPPAC for lead (II) removal. Adsorbent dose: 0.32 g/100 mL; initial pH: 5.1; temperature: 25±2 ^{0}C; adsorbent particle size: 150 micron; contact time: 72 h; shaker RPM: 120

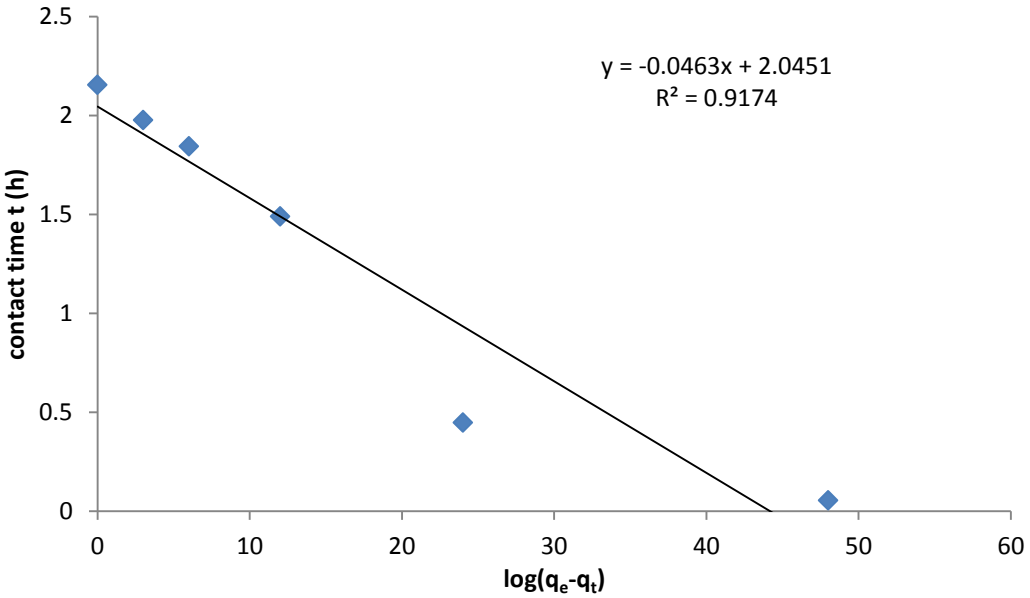

Figure 33: Pseudo-first-order kinetic model for lead (II) adsorption on EPPAC-2. Adsorbent dose: 0.32 g/100 mL; initial pH: 5.1; temperature: 25±2 ^{0}C; adsorbent particle size: 150 micron; contact time: 72 h; shaker RPM: 120.

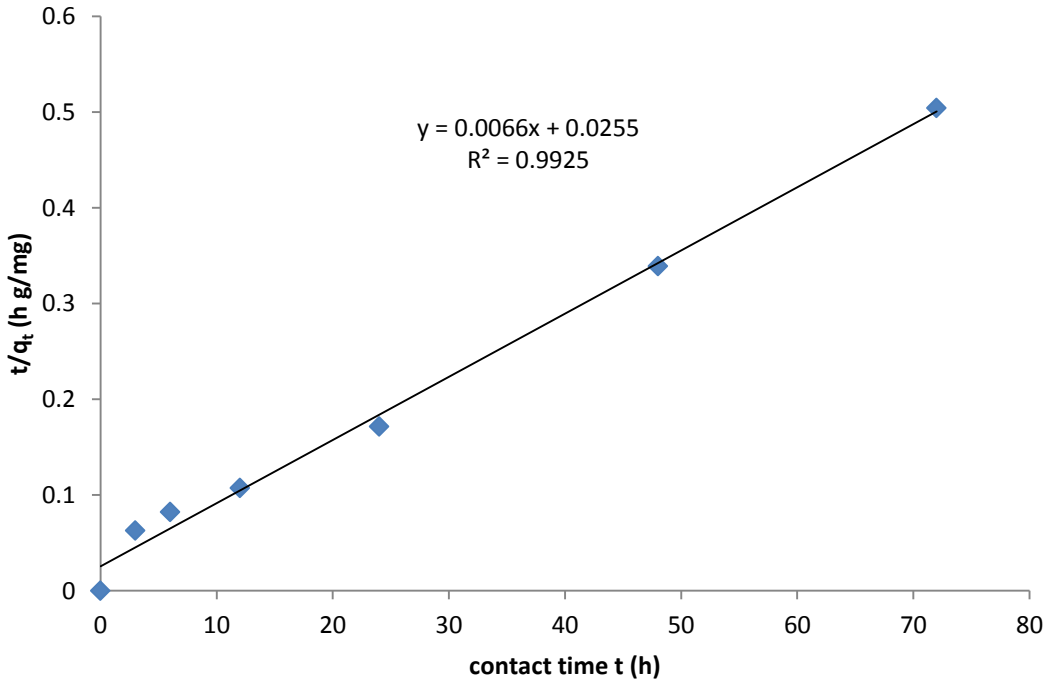

Figure 34: Pseudo-second-order kinetic model for lead (II) adsorption on EPPAC-2. Adsorbent dose: 0.32 g/100 mL; initial pH: 5.1; temperature: 25±2 ^{0}C; adsorbent particle size: 150 micron; contact time: 72 h; shaker RPM: 120.

Table 6 shows each model parameters values such as k_1 pseudo-first-order rate constant (g/mg h), $q_{e(cal)}$ calculated equilibrium adsorption capacity, k_2 pseudo-second-order rate constant (g/mg h) and R^2 regression coefficient. For the first order kinetics, there is a huge difference in the calculated value of adsorption capacity $q_{e(cal)}$ 110.94 mg/g and the experimental adsorption capacity 140 mg/g. But for the second order kinetics the difference in the calculated value of adsorption capacity $q_{e(cal)}$ 151.51 mg/g and the experimental adsorption capacity 140 mg/g is much less a compared to difference for the first order kinetics. Also the comparison of R^2 values for both kinetic models shows that pseudo-second-order kinetic model best describes the adsorption of lead (II) in current studies. The R^2 for second order kinetic model is 0.9925 which is higher than that of first order kinetic model 0.9174. This concludes that in the current adsorption studies for the for lead (II) removal, the concentrations of both adsorbent (EPPAC-2) and adsorbate (lead ions) are involved in the rate determining step which may be chemical adsorption [121].

Table 5: Kinetic model parameters for the adsorption of lead (II) ions using EPPAC-2

Kinetic model	**Parameters**	**Values**
pseudo-first-order	k_1(g/mg h)	0.0463
	$q_{e(cal)}$(mg/g)	110.94
	R^2	0.9174
pseudo-second-order	k_2 (g/mg h)	0.0017
	$q_{e(cal)}$(mg/g)	151.51
	R^2	0.9925

3.6. Adsorption isotherm models

At fixed temperature the ratio of the quantity adsorbed to that remaining in the solution is called adsorption isotherm and it best describes the relationship between the adsorbent and the adsorbate [122].

The equilibrium data was correlated by using different isotherms; Langmuir, Freundlich, Dubinin-Radushkevich, Toth, Langmuir-freundlich and Temkin isotherms.

3.6.1. Langmuir isotherm model

Mathematically its linear form of equation (1) is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{k_a q_m} + \frac{C_e}{q_m} \tag{23}$$

where q_e is the amount of the metal adsorbed for the complete monolayer (mg/g), k_a is the Langmuir adsorption equilibrium constant. The plot of $C_e\ /q_e$ versus C_e enables the determination of isotherm constants. The plot is shown in figure 35. Langmuir isotherm is also used to calculate the dimensionless constant known as separation constant or equilibrium parameter (R_L) which gives information about the favorability of the adsorption of meal ions on the adsorbent. Mathematically it is expressed as:

$$R_L = \frac{1}{1+k_a C_o} \tag{24}$$

Where R_L is the separation factor, k_a is the Langmuir adsorption equilibrium constant and C_o (mg/L) is the initial concentration the lead (II) ions.

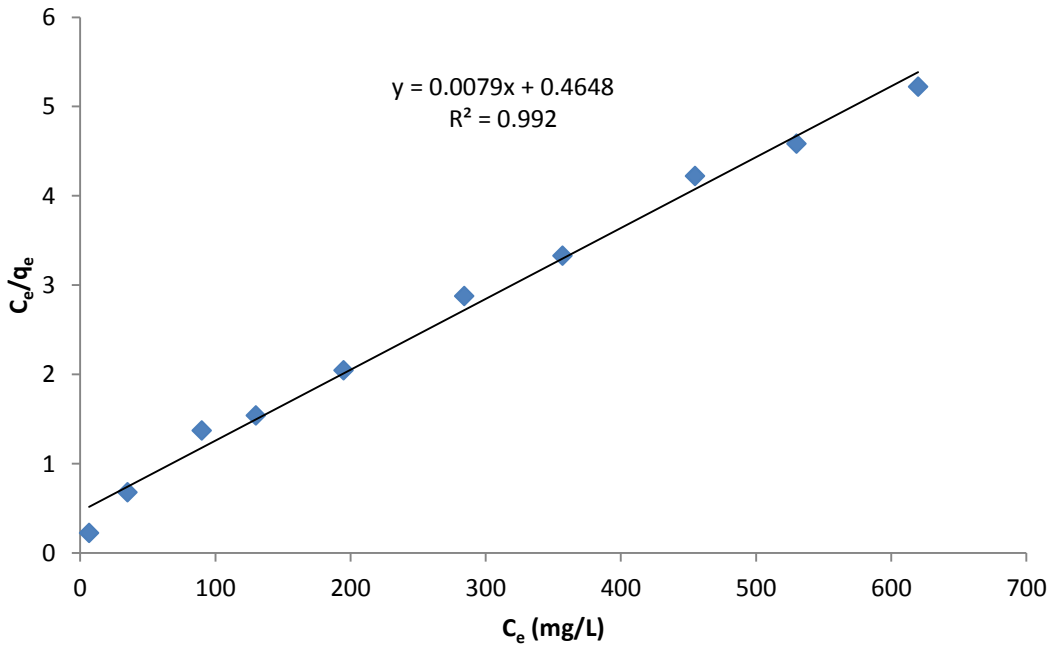

Figure 35: Langmuir adsorption isotherm for adsorption of lead (II) on EPPAC-2. Initial pH: 5.1; temperature: 25±2 ^{0}C; adsorbent dose: adsorbent particle size: 150 micron; 0.32g/100 mL; contact time: 24h; shaker RPM: 120.

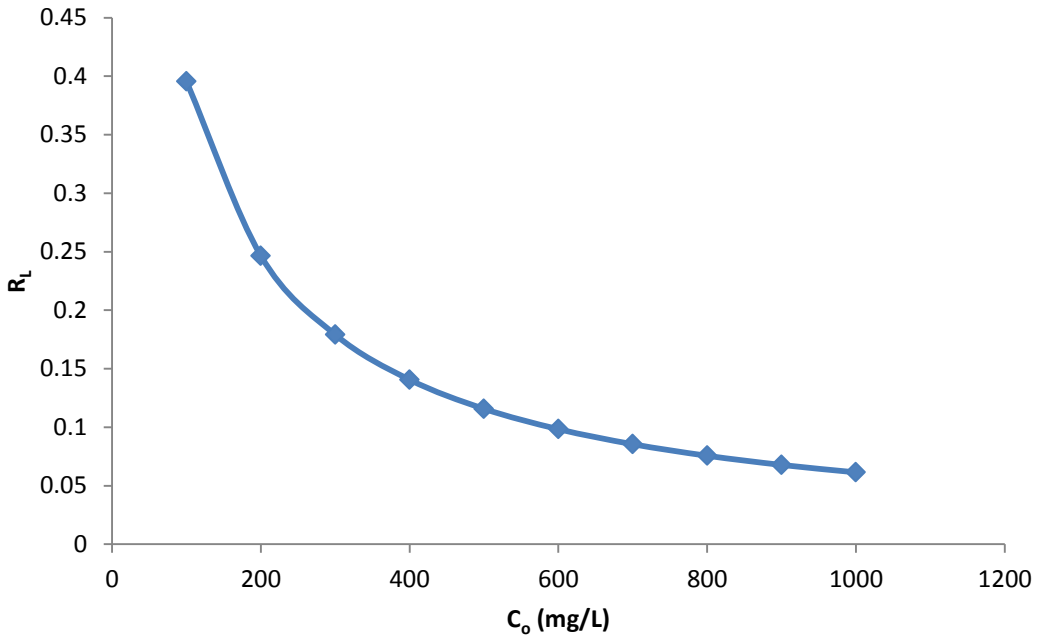

Figure 36: The calculated separation factor R_L against the lead (II) initial concentration C_o.

The values of R_L indicate the type of Langmuir isotherm. If $R_L = 0$, isotherm is reversible, $0 < R_L < 1$ isotherm is favorable, $R_L = 1$ isotherm is linear, $R_L > 1$ isotherm is unfavorable [123]. The values of R_L were calculated at different concentrations of lead (II). Figure 36 shows the plot between C_o (mg/L) and R_L values which shows that with the increase in initial concentration C_o, the R_L values are decreasing which shows that the adsorption of lead (II) ions even at higher concentration is still favorable.

3.6.2. Freundlich isotherm model

Mathematically the linearized form of equation (2) is expressed as:

$$log\, q_e = logk_f + \frac{1}{n} log\, C_e \qquad (25)$$

Where k_f and n are the Freundlich constants and they are related to adsorption capacity and intensity respectively. The plot of $logq_e$ versus $logC_e$ enables the determination of isotherm constants. Figure 37 shows Freundlich isotherm. The equilibrium data is not well fitted in this isotherm as compared to Langmuir isotherm.

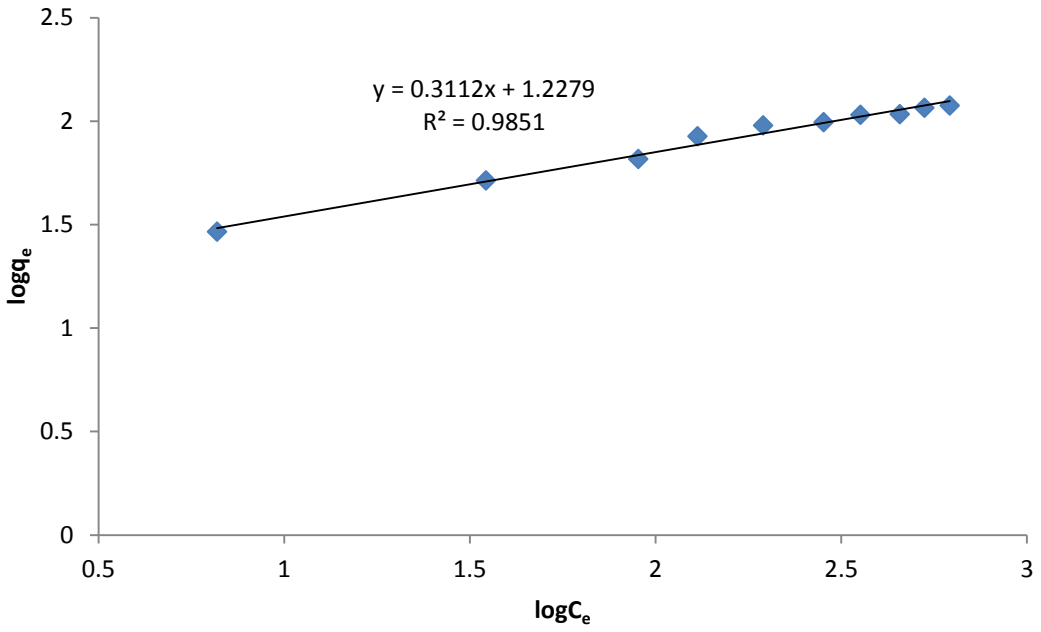

Figure 37: Freundlich adsorption isotherm for adsorption of lead (II) on EPPAC-2. Initial pH: 5.1; temperature: 25±2^{0}C; adsorbent dose: 0.32g/100 mL; adsorbent particle size: 150 micron; contact time: 24h; shaker RPM: 120.

3.6.3. Dubinin-Radushkevich isotherm model

The linear form of Dubinin-Radushkevich isotherm mentioned in equation (3) is presented as follows:

$$lnq_e = lnq_D - 2B_D RTln(1 + \frac{1}{C_e}) \quad (26)$$

where q_D is the Dubinin-Radushkevich constant, B_D is the free energy of the adsorption per mole of adsorbate [124]. The isotherm plot is shown in figure 38.

The equilibrium data is not well fitted as compared to Langmuir and Freundlich isotherm models since its regression coefficient value R^2 0.8018 is very less as compared to R^2 values of Langmuir and Freundlich isotherms which are 0.9920 and 0.9851 respectively.

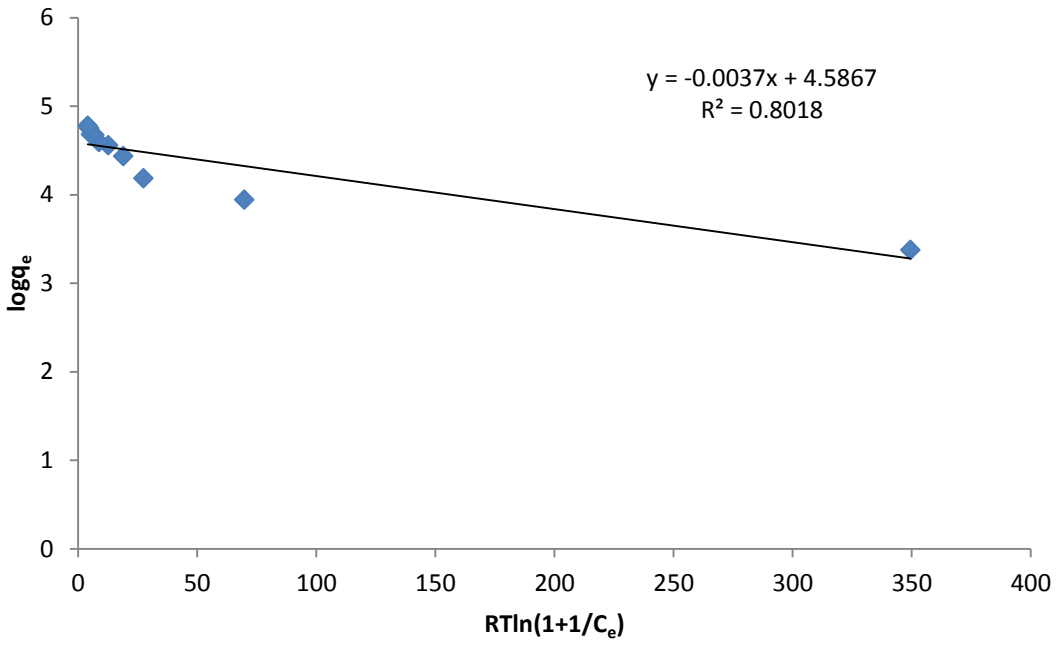

Figure 38: Dubinin-Radushkevich adsorption isotherm for adsorption of lead (II) on EPPAC-2. Initial pH: 5.1; temperature: 25±2 ^{0}C; adsorbent dose: 0.32g/100 mL; adsorbent particle size: 150 micron; contact time: 24h; shaker RPM: 120.

3.6.4. Temkin isotherm model

Initially, Temkin isotherm was used to explain the adsorption of hydrogen gas on the electrodes of platinum [67]. Mathematically its linear form is expressed by equation (4). The plot of q_e versus $logC_e$ enables the determination of isotherm constants. Figure 39 shows Temkin isotherm. In present study of adsorption of lead (II) from aqueous solution, Temkin isotherm is reasonably suitable for this adsorption equilibrium data (R^2 = 0.9719) but has regression coefficient value less in comparison with Freundlich isotherm (R^2 = 0.9851) and Langmuir isotherm (R^2 = 0.9920). When it is compared with Dubinin-Radushkevich adsorption isotherm, it gives better fitting, since there is large difference in the values of regression coefficients.

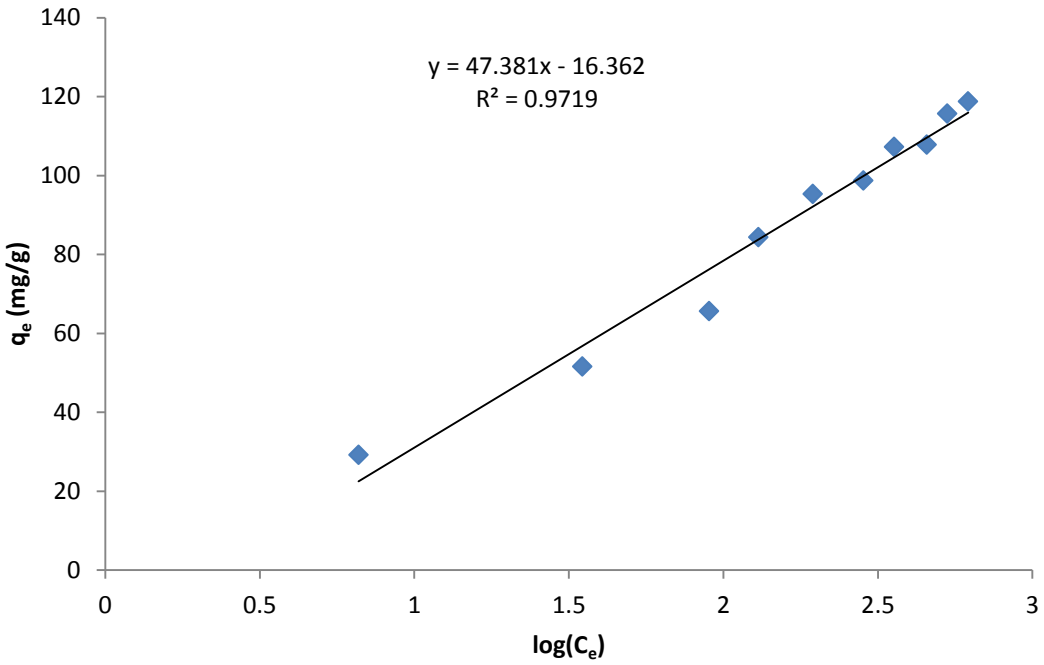

Figure 39: Temkin adsorption isotherm for adsorption of lead (II) on EPPAC-2. Initial pH: 5.1; temperature: 25±2 ^{0}C; adsorbent dose: 0.32g/100 mL; adsorbent particle size: 150 micron; contact time: 24h; shaker RPM: 120.

3.6.5. Toth and Langmuir-Freundlich isotherm models

Toth and Langmuir-Freundlich isotherm models have also been used for the measurement of the maximum adsorption capacities of EPPAC-2 for lead (II) adsorption. Fittings of the both isotherms are shown in figure 40 and 41. Adsorption capacities of EPPAC-2 estimated by Toth and Langmuir-Freundlich isotherm models for adsorption of lead (II) ions are 138 mg/g and 137.704 mg/g respectively. The values of other parameters of both Toth and Langmuir-Freundlich isotherm models are 5.4, 0.579 and 0.040, 1.330 respectively. Adsorption capacity given by linearized Langmuir adsorption isotherm model is 140.84 mg/g which is greater than Toth and Langmuir-Freundlich adsorption capacities. Also the current equilibrium adsorption data is best fitted by Langmiur isotherm as compared to all other isotherms such as Freundlich, D-R, Temkin, Toth and Langmuir-Freundlich, since the regression coefficient value R^2 is greatest for Langmuir (0.9920) in comparison with R^2 values of other isotherms which are 0.9851, 0.9719, 0.8081, 0.9630 and 0.9730 for Freundlich, Temkin, D-R, Toth and Langmuir-Freundlich isotherms respectively.

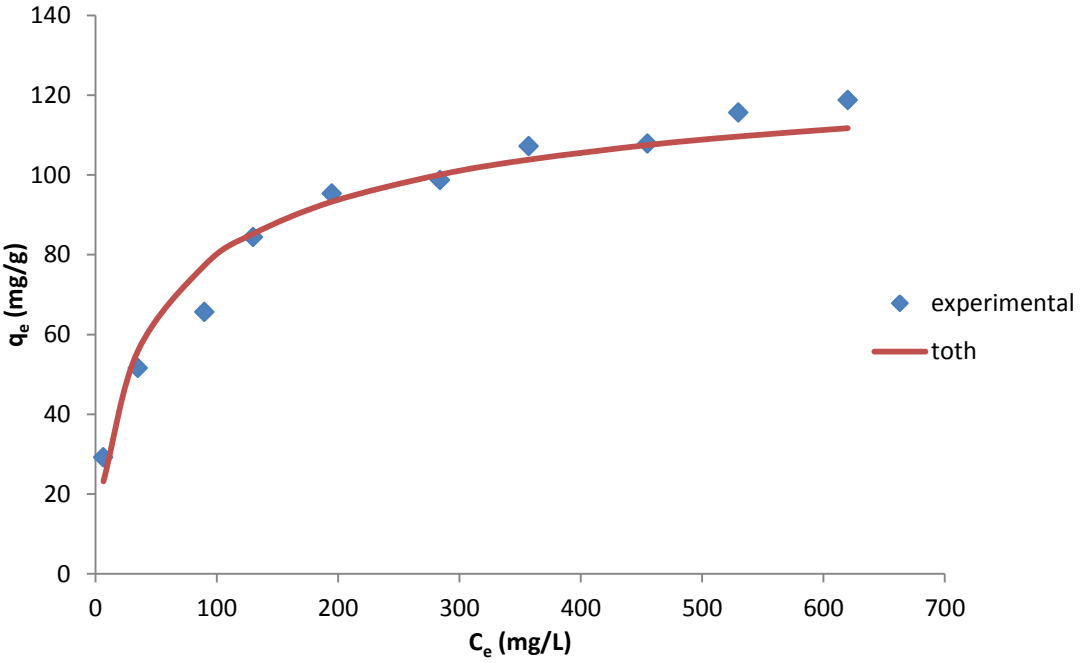

Figure 40: Toth adsorption isotherm for adsorption of lead (II) on EPPAC-2. Initial pH: 5.1; temperature: 25±2 ^{0}C; adsorbent dose: 0.32g/100 mL; adsorbent particle size: 150 micron; contact time: 24h; shaker RPM: 120.

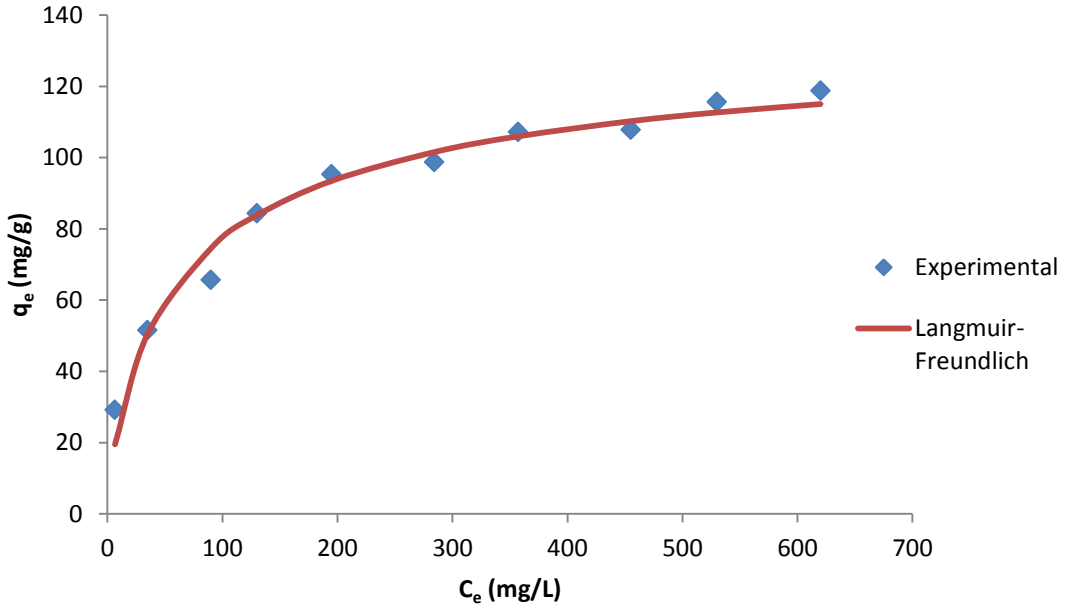

Figure 41: Langmuir-Freundlich adsorption isotherm for adsorption of lead (II) on EPPAC-2. Initial pH: 5.1; temperature: 25±2 ^{0}C; adsorbent dose: 0.32g/100 mL; adsorbent particle size: 150 micron; contact time: 24h; shaker RPM: 120.

The adsorption capacities of various adsorbents for lead (II) removal are mentioned in table 7. The parameters of all the isotherms are mentioned in the table 8.

Table 6: Various adsorbents and their adsorption capacities for lead (II) removal

Adsorbents	**Adsorption Capacities (mg/g)**	**References**
Melocanna baccifera activated charcoal	53.76	[123]
Aspergillus niger	34.69	[124]
Dried activated sludge	131.60	[125]
Tea Waste	65.00	[126]
Rose waste biomass	151.51	[127]
Distillery sludge	71.43	[128]
Pre-treated arca shell biomass	30.39	[129]
Peat	27.80	[130]
Lignin	89.51	[131]
Sugar beet pulp	0.37	[132]
Mustard Husk	30.48	[133]
Coconut shell activated carbon	21.88	[134]
Eggplant peel activated charcoal	140.84	This study

Table 7: Equilibrium adsorption parameters of six isotherms for the removal of lead (II) from wastewater by using EPPAC-2

Isotherm model	**Parameters**	**Values**
Langmuir	q_m (mg/g) k_a (L/mg) R^2	140.84 0.0153 0.9920
Freundlich	k_f (mg/g) n R^2	16.900 3.213 0.9851
Dubinin	q_D (mg/g) B_D R^2	98.169 0.0037 0.8018
Temkin	B (L/g) k_t R^2	47.381 0.4515 0.9719
Toth	K_T (mg/g) a_T t R^2	138.239 5.4 0.579 0.9630
Langmuir-Freundlich	q_{LF} (mg/g) K n_{LF} R^2	137.2 0.042 1.335 0.9730

CHAPTER 4
CONCLUSIONS AND RECOMMENDATIONS

4.1. Conclusions

In this study three different methods have been used to produce eggplant peel charcoals EPPAC-1, EPPAC-2 and EPPAC-3 from eggplant peel charcoal EPPC. The following conclusions can be drawn from this study:

a) The results show that the method of mixing affects the adsorption characteristics and hence the lead (II) removal efficiency of the respective eggplant peel activated charcoal.
b) Results have shown that new method (without using inert gas from external source) seems effective for the production of eggplant peel activated charcoal from EPPC.
c) For both EPPAC-1 and EPPAC-2 (physical mixing methods) EPPC to KOH ratio is the dominant factor in effecting their respective lead (II) removal efficiencies whereas, for EPPAC-3 (impregnation) impregnation ratio effects the removal efficiency of EPPAC-3 to greater extent as compared to other activation parameters.
d) EPPAC-2 obtained by physical mixing of grinded KOH and EPPC is considered to be the most efficient with the removal efficiency of 70% as compared to EPPAC-1 and EPPAC-3 with removal efficiencies 57.7 % and 60.1% under same adsorption conditions: initial concentration of lead (II): 300 mg/L, initial pH: 5.1, adsorbent dose: 0.32g/100 ml, contact time: 24h and temperature: 25 ± 2^{0}C.
e) The optimum conditions of EPPAC-2 are: activation time 2h, activation temperature 700^{0}C and activation ratio 1:1.
f) Scanning Electron Microscope (SEM) analysis shows that EPPAC-2 is highly porous and has cavities responsible for high removal efficiency of lead (II) from wastewater.
g) EPPAC-2 is composed of acidic and basic groups which serve as one of the important factors in enhancement of the adsorption capacity of EPPAC-2.
h) The removal efficiency of Eggplant peel activated charcoal (EPPAC-2) decreases with the increase in the initial concentration of lead (II) ions.

i) The optimum dose, initial pH and equilibrium time for the adsorption of lead (II) ions by EPPAC-2 are 0.32g, 5.1 and 24h respectively.

j) Pseudo-second order kinetic model fits best which shows that chemical adsorption has major influence in the current adsorption studies.

k) Langmuir adsorption isotherm fits best for the adsorption of lead (II) by EPPAC-2 as compared to Freundlich, D-R, Temkin, Langmuir-Freundlich and Toth isotherms. Maximum adsorption capacity of 140.84 mg/g for EPPAC-2 has been obtained by Langmuir model for the lead (II) removal.

l) Batch adsorption studies for lead (II) removal by EPPAC-2 indicate that EPPAC-2 is effective and efficient for lead (II) removal and thus it can be significantly used as low cost adsorbent for water treatment.

4.2. Recommendations for Future Work

The following are few recommendations for the future work:

a) To investigate the effect of heating rate (activation parameter) for obtaining further optimized activated charcoal.

b) To carry out the regenerative studies of the activated charcoal.

c) To carry out adsorption experiments for the removal of other toxic heavy metals such as copper, mercury.

d) To carry out the adsorption studies using commercial wastewater.

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Vita

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