
Removal of Heavy Metals from Petroleum Refinery Effluent Using Coconut Shell-Based Activated Carbon

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ABSTRACT

The performance evaluation of locally prepared activated carbon from coconut shell in removing Cr^{3+} , Cu^{2+} , Pb^{2+} and Zn^{2+} ions from Petroleum refinery effluent water was studied. The activated carbon produced was chemically activated utilizing Zinc chloride as activating agent. Batch Adsorption studies were carried out to examine the effect of adsorption dosage, contact time, pH and stirring speed on the adsorption of Cr^{3+} , Cu^{2+} , Pb^{2+} and Zn^{2+} from Petroleum refinery effluent water. In studying the effect of one factor others were kept constant. The adsorbent was contacted with the adsorbate for time intervals between 30 to 60 minutes. The kinetic studies showed that pseudo – second – order reaction model best described the adsorption process, also the Langmuir adsorption isotherm best fit the adsorption data at equilibrium. Based on the results obtained, it can be concluded that Coconut based activated Carbon is a viable alternative for treating industrial effluent water.

Keywords: Activated carbon, adsorption, heavy metals, kinetic, refining waste water

INTRODUCTION

Water pollution is a major problem in the global context. Several industrial wastewater streams may contain heavy metals such as Cr, Cu, Pb, Zn, Ni, etc. including the waste liquids generated by metal finishing or the mineral processing industries [1]. Essentially, industries dealing in electroplating, electronics, batteries and metal treatment/fabrication are the major sources of heavy metal contamination. The presence of heavy metal ions is of major concern due to their toxicity to many life forms. [2], also Petroleum refining industries are other sources of heavy metal contamination as a result of the metals present in the crude oils which are mostly Ni(II) and

VO(II) porphyrins and non-porphyrins. Other metal ions reported from crude oils include: copper, lead, iron, magnesium, sodium, molybdenum, zinc, cadmium, titanium, manganese, chromium, cobalt, antimony, uranium, aluminum, tin, barium, gallium, silver and arsenic. Metalloporphyrins are among the first compounds identified to belong to biological origin.[3]

According to National Environmental Standard and Regulatory Agency (NESRA) most of the rivers are polluted and cannot be used as drinking source. 10 percent are heavily polluted or dead, 63 percent are polluted and only 27 percent are healthy. These figures show the need of waste water treatment before discharging to rivers. Treatment processes for heavy metal removal from wastewater include precipitation, membrane filtration, ion exchange, adsorption, and co-precipitation/adsorption. Studies on the treatment of effluent bearing heavy metals have revealed adsorption to be a highly effective technique for the removal of heavy metals from waste stream and activated carbon has been widely used as an adsorbent. [4].

In recent years, researchers have studied the production of ACs from cheap and renewable precursors, such as nutshells, fruit stones, coir pith, bagasse, bamboo, rice husk, and cotton stalks, *etc.* Coconut shell is a potential precursor for the production of ACs due to its excellent natural structure and low ash content. Conversion of coconut shells into activated carbons which can be used as adsorbents in water purification or treatment of industrial and municipal effluents would add value to these agricultural commodities, help reduce the cost of waste disposal, and provide a potentially cheap alternative to existing commercial carbons. [5], [6]

In this work, removal of heavy metals (Cu, Cr, Pd, and Zn) from WRPC (Warri Refining and Petrochemicals Company) effluent was carried out using coconut shell-based activated carbon. Parameters such as pH, stirring speed, adsorbent dosage and contact time, were investigated at 30°C. While the pseudo first-order and pseudo second-order models were used to analyze the kinetic data. The

Langmuir and Freundlich Isotherm were used to study the interaction between the adsorbent and the adsorbate.

MATERIALS AND METHOD

Production of Activated Carbon

Coconut shell was obtained from a waste dump site located in Ugbomro, Uvwie local government area of Delta state. Dirt was hand removed from samples after which they were washed and sun dried for 2-5 days. Pestle and mortar was used to crush the samples. 300g of the coconut shell was carbonized in a muffle furnace for 1 hr at 400°C. The carbonized samples were then activated using 1M ZnCl₂ at 500°C for 2 to 3 hours. The sample was then brought out of the muffle furnace and cooled in a desiccator. It was then washed several times with distilled water until the pH range between 5 and 6 was obtained. The Activated carbon produced was then dried in an oven at 110°C for 24 hours. [7]

Petroleum Refining Wastewater

The wastewater sample used was collected from the effluent discharge point of Warri refining and petrochemical (WRPC), Delta State. It was carefully bottled in a plastic container and was immediately taken to the laboratory for analysis.

Analysis

The heavy metals present in the wastewater sample were analyzed using the atomic absorption spectrophotometer. It detected the concentrations of Cr³⁺, Cu²⁺, Zn²⁺, Pb²⁺. The initial concentrations of the metal ions present in the waste water are shown in table 1.

Table 1: Initial Concentration of Metal ions in Wastewater

Heavy Metals	Initial Concentration(mg/L)
Cu ²⁺	0.005
Cr ³⁺	1.225
Zn ²⁺	0.45
Pb ²⁺	0.47

Adsorption Study

Adsorption experiment was done by measuring 50 mL of the wastewater sample and poured into a 100 mL conical flask. 2 g of the previously prepared activated carbon was added to the wastewater. The conical flask containing the adsorbent and the wastewater was placed on a rotary shaker and shook at 150 rpm at a room temperature of (30°C) for a period of 60 min to ensure equilibrium. The suspension was filtered use Whatman filter paper. Atomic adsorption spectrophotometer (AAS) was used to analyze the concentrations of the different metal ion present in the filtrate.[8] The amount of metal ions adsorbed by the adsorbent was evaluated using equation (1):

$$q_t = \frac{(C_0 - C_t)v}{w} \quad (1)$$

The mass balance equation was used to determine the adsorption capacity (q_e) from equation (2) [9]:

$$q_e = \frac{(C_0 - C_t)V}{w} \quad (2)$$

Where, C_0 and C_t are the initial and final concentrations of the heavy metals present in wastewater before and after adsorption, for a period of time t (mg/L) respectively, C_e represent the concentration of heavy metals in wastewater (mg/L) when equilibrium was attained, the volume of wastewater used for adsorbent is V (ml); while w represent the mass (g) of the adsorbent used. The percentage of metal ions removed was obtained from equation (3) [10]:

$$R(\%) = \frac{(C_0 - C_t) \times 100}{C_0} \quad (3)$$

Where $R(\%)$ is the ratio of difference in metal concentration before and after adsorption.

The Effect of Contact Time on Removal of Heavy Metals

Some quantity of the activated carbon was weighed and placed in a 120ml plastic bottle. 50ml of the effluent sample was measured and poured into a 120ml plastic container containing 1g of the activated carbon. The mixture was agitated with an electronic mechanical shaker at 150rpm, for 30, 40, 50 and 60 minutes respectively and allowed to settle. The settled mixture was then filtered through a

filter paper into a conical flask. The effluent-adsorbent filtrate was analyzed to determine the concentration of heavy metals using the AAS (Atomic Absorption Spectrophotometer) at each agitation time. (II)

The Effect of Adsorbent Dosage on Removal of Heavy Metals

Different dosages of the adsorbent (1 - 4g) were added into different conical flasks containing 50ml of effluent water, corked and agitated in an electronic mechanical shaker for 30 minutes at a constant speed of 150 rpm at a room temperature of 30°C. The content of each flask was then filtered and analyzed after the agitation time. [13]

The Effect of pH Variation on Removal of Heavy Metals

Over a pH range of 4 – 8, the effect of pH on adsorption of metal ions was studied. For this particular work, 50ml of effluent sample was measured into different 250ml conical flasks and 1g of the adsorbent added and agitated at 150 rpm for a period of 30 minutes. The whatman filter paper was used to filter the mixture and the filtrate analyzed to determine the concentration of the metal ions

The Effect of Shaking Speed on Removal of Heavy Metals

Shaking speed was varied for 150rpm, 200rpm, 250rpm and 300 rpm respectively, to study the effect of shaking speed on the adsorption of metal ions. 1g of the adsorbent was each added to different conical flasks containing 50ml of effluent sample, corked and agitated in a shaker for a period of 30 minutes at room temperature of 30°C. The content of each flask was then filtered and analyzed after agitation time. [14]

Kinetic Analysis

The Adsorptive capacity of activated carbon on wastewater at different time intervals was studied by the kinetics of adsorption. The pseudo –first order and pseudo – second – order model equations were fitted to model the kinetics of heavy metal adsorption onto activated carbon.[15] The linearity of each model when plotted indicates whether the model suitably described the adsorption process or not.

The general expression for pseudo – first –order equation model is shown in equation model is shown in the equation (4) and (5):

$$\frac{dq_t}{dt} = (q_e - q_t) \quad (4)$$

The sorption capacities at equilibrium and at time t , are represented by q_e and q_t respectively (mgg^{-1} and k is the pseudo – first order sorption rate constant (Lmin^{-1}). Applying boundary conditions after integrating, from $t=0$ to $t=t$ and $q_t = 0$ to $q_t = q_t$, the integrated, form of equation (4) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.0303} t \quad (5)$$

The pseudo – second order chemisorption kinetic rate equation is expressed as shown in equation (6)

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

The sorption capacities at equilibrium and at time t , are represented by q_e and q_t (mgg^{-1}) respectively and k_2 is the rate constant of the pseudo – second order sorption ($\text{g.mg}^{-1} . \text{min}^{-1}$)

Adsorption Equilibria

Generally adsorption process proceeds through varied mechanisms such as external mass transfer of solute onto sorbent followed by intraparticle diffusion. Adsorption equilibrium is a dynamic concept achieved when the rate at which molecules adsorb onto a surface is equal to the rate at which they desorb. The physical chemistry involved may be complex and no single theory of adsorption has being put forward to explain all the systems. Fortunately, engineer requires only data at equilibrium conditions.[16]

Langmuir Isotherm

Langmuir isotherm is concerned with the monolayer (single layer) coverage of the solid surface by the adsorbate. It assumes that the surface consists of "sites" onto which the adsorbate can accommodate one entity at a time. The binding energy at each site is also assumed to be equivalent [17]. When used to describe the adsorption of solutes from solution, the Langmuir equation is as follows:

$$n = \frac{\alpha c}{1 + \beta c} \quad (7)$$

Or

$$\frac{c}{x/m} = \frac{1}{\alpha} + \frac{\beta}{\alpha} c \quad (8)$$

At the equilibrium time

$$\frac{C_e}{q_e} = \frac{1}{\alpha} + \frac{\beta}{\alpha} C_e \quad (9)$$

α and β are constants, C_e is concentration at equilibrium, q_e is the adsorptive capacity at equilibrium

Freundlich Isotherm

Herbert Max Finley Freundlich, a German physical chemist, presented an empirical adsorption isotherm for non-ideal sorption on heterogeneous surfaces as well as multilayer sorption [18] and is expressed by the equation:

$$q_e = K_f C_e^{1/n_f} \quad (10)$$

$$\log q_e = \log K_f + \quad (11)$$

C_e and q_e are concentration and adsorptive capacity at equilibrium

RESULTS AND DISCUSSION

Effect of Contact Time on Removal of Heavy Metals

The relationship between contact time and the percentage removal of heavy metals from effluent with activated carbon produced from coconut shell is shown in figure-1. The effect of contact time was studied at a room temperature of 30°C, at intervals of 10 min from 30 to 60 minutes. From the obtained result, it is evident that the removal of metal ions increased as contact time increases. Cr^{3+} , Cu^{2+} , Pb^{2+} and Zn^{2+} were removed using the produced adsorbent. The percentage metal ions removal reached equilibrium within 60 minutes for Cr, 30 minutes for both Cu(II), Pb(II) and Zn(II) with Cr(III) recording 14.61% removal, Cu(II) 100%, Pb 60.85% and Zn(II) 50.67% removal. Consequently, there is a trend of $Cu^{2+} > Pb^{2+} > Zn^{2+} > Cr^{3+}$.

After which further increase in time did not bring about any further improvement for the metal ions, but resulted in desorption of some of the metal ions (lead and zinc) from the adsorbent surface. This experiment shows that the different metal ions attained equilibrium at different times. Cu (II) had 100% in all cases removal as a result of its minute concentration of 0.005mg/L.

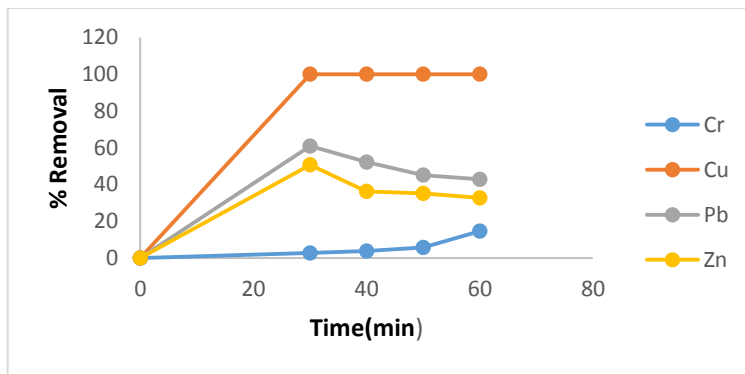


Figure -1

The effect of contact time on adsorption of heavy metals by activated carbon from coconut shell (PH = 4, agitation speed = 150rpm, mass = 1g Temp = 30°C)

Effect of Adsorbent Dosage

It can be seen that adsorbent dosage controls the availability and accessibility of sites for adsorption. Adsorbent dosage was varied from 1g to 4g, under the specific conditions (initial pH of 4, contact time of 30 minutes, 150 rpm shaking speed and at room temperature of 30°C). Figure-2, shows that increased adsorbent loading led to increased percentage removal of the heavy metals. For Cr, the maximum removal was attained at 2g with 17.96% removal. The removal of Cu(II) attained maximum removal even at a lower adsorbent dosage of 1 g with 100% removal while Pb had its optimal removal at a maximum dosage of 4g with 75.53%removal. As for Zn, the maximum removal of 43.3% was reached at 2g where any further increase in adsorbent dosage resulted to the desorption of Zn. From the foregoing, any further increase in adsorbent dosage brought no increase in adsorption, which was as a result of overlapping of adsorption sites due to overcrowding of adsorbent particles [19]. Consequently, for further investigation of the work, 2 g was chosen as the optimum adsorbent dosage for removal of Cu (II), 2g for

adsorption of Cr (III) and Zn (II), then 4g chosen as optimum dosage for Pb(II) metal ions.

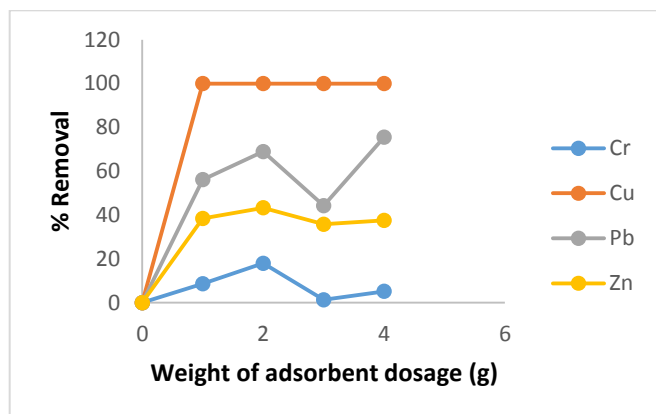


Figure 2

The effect of adsorbent dosage on the adsorption of heavy metals by activated carbon from coconut shell (Time = 60 min, PH = 4 agitation speed = 150rpm, Temp = 30°C

Effect of pH on Adsorption of Heavy Metals

The pH of the effluent is one of the important factors governing the rate of adsorption of the metal ions. Essentially, the pH of the untreated effluent solution is 7.5. The effect of pH was studied from a range of 4 to 8 under the precise conditions (at contact time of 30 minutes, 150 rpm shaking speed, with 1 g of the adsorbents used, and at a room temperature of 30°C). From Figure-3, with activated carbon from coconut shell used as adsorbent, it was observed that with increase in the pH (4-8) of the effluent, the percentage removal of metal ions increased differently up to the pH 8 as shown. At pH 4, maximum removal was obtained for Cr with 27.59% removal. At pH 6, maximum adsorption for Pb occurred with 34.89% removal; while at pH 8, optimal removal of Zn was achieved with 41.56% removal. While 100% removal of Cu(II) ion was achieved even at a low pH of 4 because of the low concentration of Cu(II) ion present in the effluent. The increase in percentage removal of the metal ions may be explained by the fact that at higher pH the adsorbent surface is deprotonated and negatively charge; hence attraction between the positively charged metal cations occurred. [19]

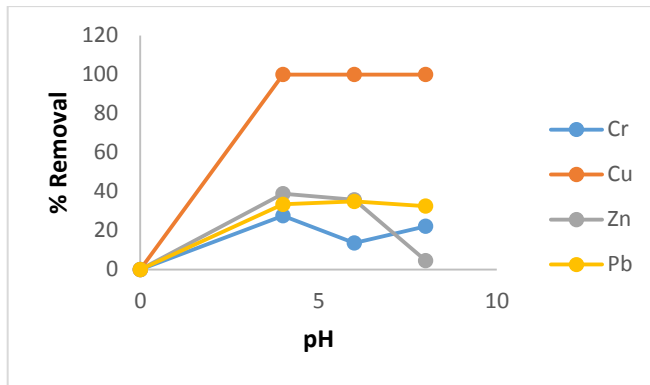


Figure -3

Effect of pH on the adsorption of heavy metals by activated carbon from coconut shell (Time = 60min, agitation speed = 150rpm, mass = 2g and Temp = 30°C)

Effect of Stirring Speed on Adsorption of Heavy Metals

The effect of stirring speed was investigated under the specified conditions (at optimum contact time of 30 minutes, with 2g of the adsorbents used, at pH 7.5 and at a room temperature of 30°C) with activated carbon from coconut shell used as adsorbent. It was observed that with increase in shaking speed from 150 to 300 rpm of the effluent solution, the percentage removal of metal ions under study increased up to 200 rpm as shown in fig.4. Hence maximum recoveries were made for Zn and Cr at 200 rpm with 39.56% removal and 60.73% removal respectively. Also at a lower shaking speed of 150 rpm, Cu (II) and Pb(II) attained maximum removal of 100% and 56.81% respectively. Essentially, the increase in shaking speed resulting to increase in metal ions percentage removal, was due to the fact that, increase in stirring rate enhanced the metal ions diffusion to the surface of the adsorbent; and also caused reduction in the film boundary layer around the adsorbent. That of 350 rpm could not actually be exactly determined owing to inconsistency and disturbances from the swirling or revolution of the electronic shaker.

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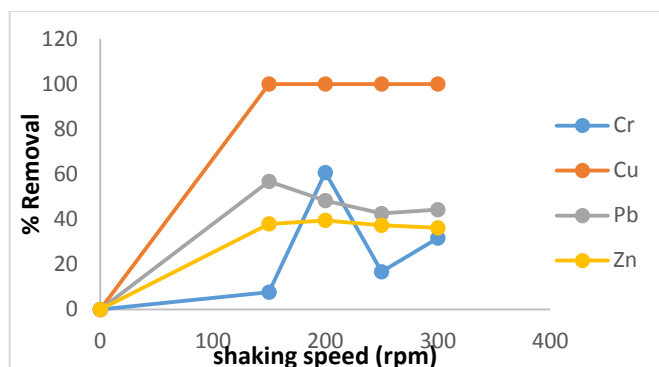


Figure -4 Effect of shaking speed on the adsorption of heavy metals by activated carbon from coconut shell (Time = 60 min, pH = 4 mass 2g and Temp = 30°C)

Kinetics Study of the Removal of Heavy Metals from Wastewater by Activated Carbon from Coconut Shell

The adsorption kinetic results from the fitted data in fig. 5 and Fig. 6 shows that the pseudo –second – order reaction model (Ho model) yield a relatively straight lines compared to the pseudo – first –order reaction model, which was significantly scattered (non – linear). The adsorption of Cu (II) ion shows a perfect linearity for pseudo – second – order reaction model. This is as a result of chemisorption. In Chemisorption (chemical adsorption), the heavy metals stick to the adsorbent surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface [20].

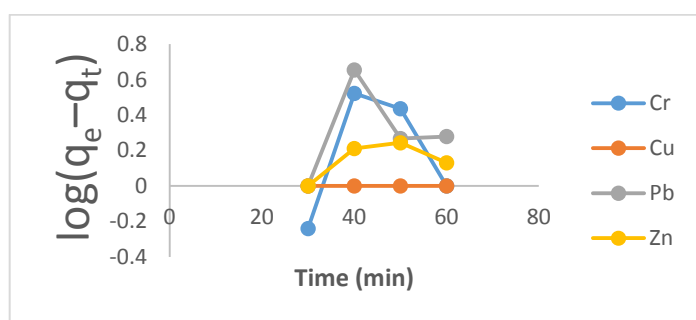


Figure – 5 Pseudo –first – order reaction model for adsorption of heavy metals on activated carbon from coconut shell

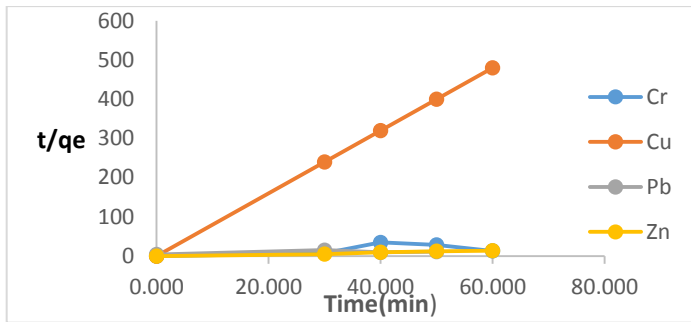


Figure – 6
 Pseudo –second –order reaction model for adsorption of heavy metals on activated carbon from coconut shell

Equilibrium Adsorption Isotherm

From the result of the fitted data, in fig.7 and fig. 8 it is clear that the equilibrium curve relating q_e and C_e determines the nature of the sorption process. The Langmuir isotherm fits the adsorption data at equilibrium as it yield a very good straight line compared to Freundlich isotherm which was significantly scattered (non - linear). This shows that the adsorption of Heavy metals by activated carbon from coconut shell can be explained by Langmuir isotherm.

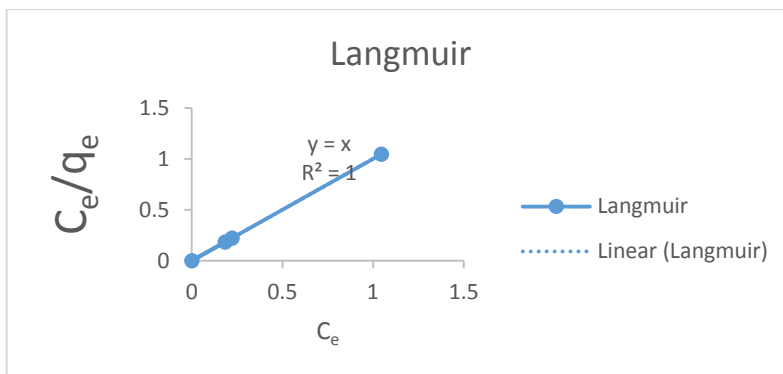


Figure – 7
 Langmuir adsorption isotherm for the removal of heavy metal by activated carbon from coconut shell

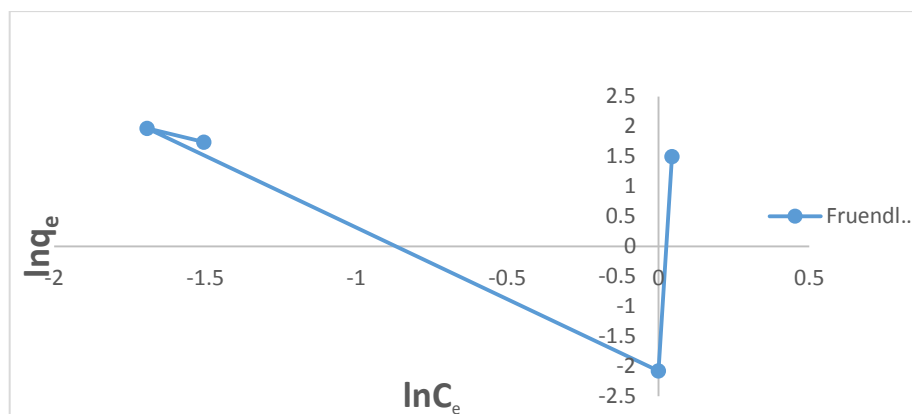


Figure -8

Freundlich adsorption isotherm for the removal of heavy metal by activated carbon from coconut shell

CONCLUSION

The obtained results from this work indicate that activated carbon produced from coconut shell is a good adsorbent for removal of Chromium, Copper, Lead and Zinc ions. Batch experiments were conducted which showed that the adsorption of Chromium Lead, Copper and Zinc ions are contact time-dependent, adsorbent dosage dependent, pH dependent, and stirring speed dependent. From the results obtained, kinetic studies showed that pseudo-second-order reaction model best described the adsorption process. The Langmuir Isotherm model gave a better fit of the experimental data with a regression co-efficient (R^2) of unity compared to Freundlich isotherm. Coconut shell as an agricultural waste material is cheaply and readily available. However the surface morphology of the activated carbon was not examined. Therefore, this adsorption study provides a cost effective means for removing metal ions from effluents.

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