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COCONUT SHELL-DERIVED ACTIVATED CARBON FOR HEAVY METAL REMOVAL FROM INDUSTRIAL WASTEWATER IN IBADAN, NIGERIA

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Abstract: Activated Carbon produced from coconut shell was used as adsorbent to remove Zinc, Cadmium and Lead from industrial wastewater. In order to effectively evaluate the level of pollutant to be removed by the activated carbon made from coconut shell, the physical and chemical parameters of the activated carbon were evaluated. This was achieved by carrying out the pH value, bulk density, moisture content, ash content, water and acid solubility. Batch adsorption experiment was conducted to examine the effects of adsorbent dosage, contact time, pH and stirring rate on adsorption of Zinc, Cadmium and Lead ions from wastewater. The obtained results showed that the adsorptions of the metal pH were found to be at 1g, 300rpm and pH 6 respectively. Kinetic studies showed the Pseudo-second order reaction. The study also showed that activated Carbon prepared from coconut shell can be effectively used as lowcost alternative for removal of metal ions.

Keywords: Activated Carbon, Adsorption, Heavy Metals, Reagent, Adsorbent.

1.0. INTRODUCTION

Water is a limited natural resource and fundamental for life and health (Dobriyal et al., 2014). With rapid development of science and technology, industrial pollution and natural resource destruction rate is increasing; the human life is gradually affected. Wastewater from numerous industries such as paints and pigments, glass production, mining operations, metal plating and battery manufacturing processes are known to contain contaminate such as heavy metal. Heavy metals such as Pb, Cd, Cr, Ni, Zn, Cu and Fe are present in industrial wastewater, these heavy metals in wastewater are not biodegradable and their existence in receiving lakes and streams causes bioaccumulation in living organisms, which leads to several health problems in animals, plants and human beings such as cancer, kidney failure, metabolic acidosis, oral ulcer, renal failure and damage in for stomach of the rodent (Mehmet et al., 2006)

As a result of the degree of the problems caused by heavy metals pollution, removal of heavy metals from wastewater is important (Chand et al, 1994)

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Investigation into new and cheap methods of metal ions removal has been on the increase lately. Recently, efforts have been made to use cheap and available agricultural wastes such as coconut shell, orange peel, rice husk, peanut husk and sawdust as adsorbents to remove heavy metals from wastewater (Vaishnav et al., 2012). Heavy metals are generally defined as metals with relatively high densities, atomic weight or atomic numbers. Metals are prevalent in the environment. They are derived from both natural and anthropogenic sources. Certain metals are essential for plant growth and for animal and human health. However, when they are present in excessive concentration, they may be toxic (Akhionbare, et al, 2013). Other heavy metals such as Cadmium, Mercury, and Lead are highly toxic. This category would be the focus of this study. Potential sources include mining, industrial waste, agricultural runoff, paints and treated timbers. Activated carbon is a carbonaceous, highly porous adsorptive medium that has a complex structure composed primarily of carbon atoms (Haycarb). Activated carbons are manufactured from coconut shell, walnut shell, hard and soft woods etc. for the preparation of activated carbon the suitable material should contain higher carbon and less ash. Coconut shell falls in the spectrum of such material. As early as 2001 "kim, et al" conducted a study on the performance of granular activated carbon from coconut shells, and analyzed the reaction efficiency with divalent copper ions in the adsorption and removal process.

The result showed that after the coconut activated carbon adsorption process the content of copper ions in the wastewater was up to standard. Water pollution is a major problem in global context. Several industrial waste streams may contain heavy metal such as cadmium, lead, zinc and nickel etc. Heavy metals are toxic and detrimental water pollutants; their presence affects both human animals and vegetation because of their mobility in aqueous environment, toxicity and non-biodegradability. These toxic metals probably exist in high concentration must be effectively treated and removed from waste water before discharging into environment. In recent times the removal of toxic heavy metals from sewage industrial and mining waste effluents has been widely studied. Among the many methods available to reduce heavy metal concentration from waste water the most common once are chemical precipitation, ion exchange, reverse osmosis and adsorption.

The aim of this study was to determine the performance of a low-cost adsorbent in the removal of heavy metals from industrial waste water; which was achieved by: preparing and carbonizing the coconut shell, characterizing the activated carbon from the coconut shell, evaluating the physiochemical properties of the adsorbent, and determining the effects of time, temperature, pH and adsorbent dose on the adsorbent.

2.0.   STUDY AREA

The study area is at the hinterland of Ibadan located in Akinyele, Lagelu and Ibadan North

Local Government Area of Oyo State. It is between latitude 7026′45.0″N and longitude 3055′53.4″E with altitude of 223m (Akinyele), latitude 7026′42.0″N and 3056′39.8″E (Lagelu) with altitude of 241m. Ibadan, city in South-Western Nigeria, capital of Oyo State, located about 110km northeast of Lagos. Figure 1 shows a map of Nigeria indicating the location of Ibadan city in Oyo state. Ibadan is located between longitude 30 451N and 40001E and latitude 70151N and 70301E and is reputed to be the largest indigenous city in Africa, South of Sahara. It is naturally drained by four rivers with many tributaries; Ona River in the North and West; Ogbere River towards the East; Ogunpa River flowing through the city and

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Kudeti River in the central part of the metropolis. The map and satellite image of the study area are shown in Figure 1 and 3 respectively.
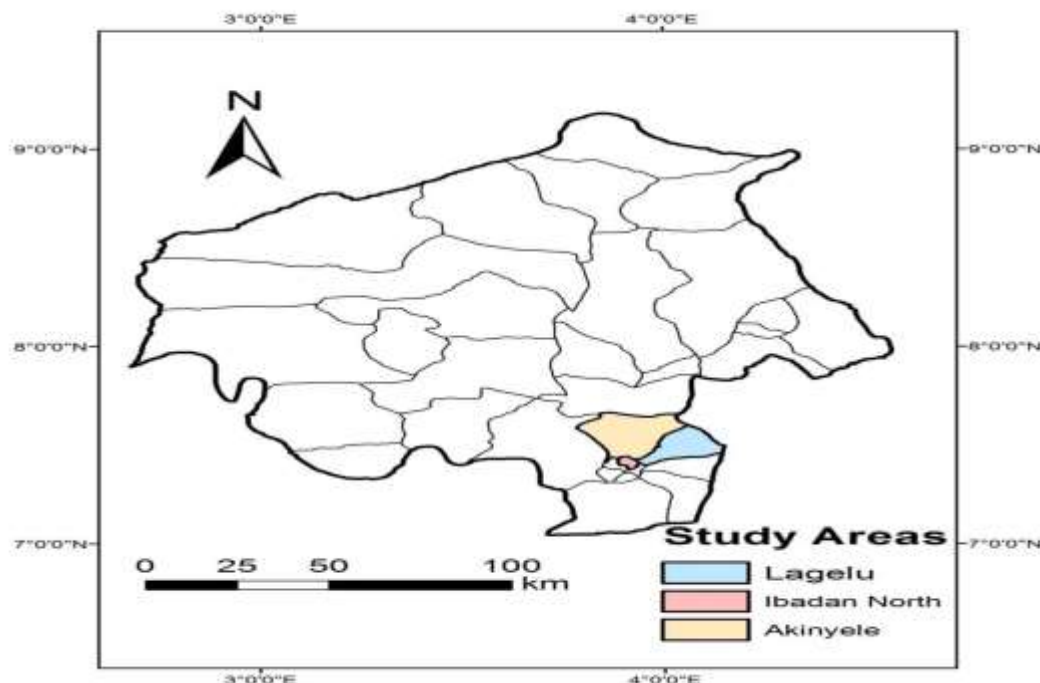
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Figure 2: Satellite image of the Study Area

3.0. METHODOLOGY

3.1. Chemicals/Reagents

All chemicals used were analytical reagent grade, they include: Phosphoric acid, Hydrogen Chloride, Zinc metal, Lead in Nitrate, Cadmium chloride, Sodium hydroxide, Distilled water, Hydrochloric acid and Sodium hydroxide.

3.2 Instrumentation

Instruments	Functions
Analytical Balance	Weight Measurement
pH meter	Measurement of pH
Sieve	Sieving into desired sizes
Atomic Absorption spectrophotometer FS 240 varian	Estimation of metal ion concentration
Water bath	Regulating temperatures
Cyclic vibrator (PEC 360rpm)	Agitation
Oven/ furnace	Drying samples

Other materials include;

Beakers, Conical flask, 50ml bottle, Magnetic stirrer hot plate, Whatman filter paper, Funnel, Pipette and Measuring cylinder.

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3.3   Sample Collection and Preparation

3.3.1. Sample collection

The wastewater sample used for the purpose of this study was collected from Fabex paint industry located at Samonda in Ibadan, Oyo South Western, Nigeria. The sample was collected from the production and washing of paint production materials, and bottled in a sample bottle.

The coconut shell used as adsorbent for this study was obtained from fruit selling source in Mokola Ibadan South western Nigeria.

3.3.2.   Preparation of adsorbent

The coconut shell was washed with detergent and rinsed with de-ionized water, and allowed to dry.

3.3.2.1.   Carbonization Process

•   100g of the sample was weighed and introduced into a Muffle furnace at 400^0C for 30 minutes.

•   This was brought out after 30 minutes and allowed to cool.

•   It was ground using a mortar and pestle.

3.3.2.2. Activation process

This process was done according to the method described by Abechi et al (2013) with slight modification.

•   100g of the carbonized sample was mixed with 0.5M phosphoric acid and allowed to soak overnight.

•   The treated sample was heated to form a paste and dried at 120^0C.

•   The dried sample was then pyrolyzed at a predetermined temperature of 250^0C and activation time of 30minutes in the furnace.

•   The activated carbon was washed with de-ionized water repeatedly until the washing solution nearly attained pH of 7.0.

•   The prepared activated carbon was dried at 120^0C overnight.

•   The sample was brought out the following day, cooled and sieved into particle size of between 300μm - 425μm.

•   The sample was then stored in a sealed plastic container for this study.

3.3.2.3 Characterization / analysis of the activated carbon

In order to effectively evaluate the level of pollutant to be removed by the activated carbon made from the coconut shell, the physical and chemical parameters of the activated carbon were evaluated. The following analyses were carried out to achieve this:

a. Determination of pH value

•   2g of the sample was poured into a clean dry 25ml beaker

•   13ml of the hot distilled water was added to the sample in the beaker and stirred slowly.

•   The sample was cooled in a cold-water bath to 25°C.

•   The pH electrode was standardized with a buffer solution and immersed into the sample   and the pH recorded.

b. Determination of pore volume and porosity

•   2g of the sample was weighed and transferred into a measuring cylinder to get the total volume of the particles.

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•   This sample was then poured into a beaker containing 20ml of distilled water and was boiled for 5 minutes to displace air in the sample.

•   The content in beaker was filtered, superficially dried and weighed.

•   The pore volume of the sample was gotten by dividing the change in weight by the density.

•   Porosity was calculated by dividing the pore volume of the particle with the total volume of the particle.

c. Determination of the bulk density

•   10g of samples was weighed with a weighing balance.

•   The sample was transferred into 50 ml measuring cylinder.

•   The sample and the measuring cylinder were then weighed

•   The bulk density was calculated by dividing the weight of the sample and the cylinder by the volume of the sample.

d. Determination of moisture content

•   The plastic dishes were washed and dried in the oven at 110°c.

•   After drying they were into the desiccator to cool and each dish was weighed.

•   10g of the sample was weighed and put into the pre-treated dish, and the weight of the sample plus the dish was recorded.

•   The sample was introduced into the oven at 70°-80°Cfor 2 hours and at 100-135°C for the next 4 hours or until weight is constant.

•   The sample was cooled in the desiccator and weight of the dry sample plus dish were recorded.

•   The moisture content was obtained with the equation below:

$$\% \text{ Moisture} = \frac{W_2 - W_3}{W_2 - W_1} \times 100$$

Where; W_1 = Initial weight of empty crucible W_2 = Weight of crucible + sample before drying.

  W_3 = Final weight of crucible + sample after drying.

e. Determination of water and acid solubility

The grounded fine sample was collected with a small spatula enough to cover the tip of the spatula. The sample was transferred into small test tube

For water solubility; approximately 6 drops of water was added into the test tube and the mixture was stirred with a glass stirring rod. The solubility was recorded.

For acid solubility; 6 drops of 1M of HCL was added into the test tube and the mixture was stirred using a glass stirring rod and the solubility was recorded. **f. Determination of Ash Content**

•   5g of the finely grounded sample was added into porcelain crucible.

•   The sample was charred using Bunsen flame inside fume cupboard.

•   The sample was transferred into a pre-heated muffle furnace at 550°C for 2 hours.

•   The sample was then cooled in desiccators and weighed again.

•   The ash content was calculated with the equation below:

$$\% \text{ Ash (wet basis)} = \underline{\text{Weight of ash}} \quad \times \quad 100$$

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Weight of original sample

3.4. Adsorption Determination

In investigating the adsorption potential of activated carbon from coconut shell, the effect of adsorbent dose, contact time, temperature and pH on the percentage removal of cadmium, lead and zinc was examined.

3.4.1. Effect of adsorbent dose

The effect of adsorbent dose was studied by varying the adsorbent dose used for adsorption. The dosages of interest in grams were 0.4, 0.6, 0.8 and 1.0. The experiment was carried out by measuring 50 ml of the raw waste water into a 250ml conical flask and required adsorbent dose was introduced into the conical flask. The solution was stirred for 60minutes at 300rpm and 60^0C using a magnetic stirrer hot plate. The mixture was filtered immediately with whatman filter paper. The filtrate was then corked in a 50ml bottle, and analyzed with a 240FS Varian Atomic Absorption spectrophotometer (AAS).

3.4.2. Effect of contact time

The effect of contact time was studied by varying the agitation time. The following agitation time in minutes was tested; 30, 40, 50 and 60. The experiment was carried out by measuring 50 ml of the raw waste water into a 250ml conical flask. The optimum adsorbent dose (1.0g) was transferred into this conical flask and stirred on a magnetic stirrer for the specified time at 300rpm and temperature of 60^0C respectively for each time. The mixture was filtered immediately with a Whatman filter paper. The filtrate was then corked in a 50ml bottle, and analyzed with a 240FS Varian Atomic Absorption spectrophotometer (AAS).

3.4.3 Effect of temperature

The effect of temperature was studied by varying the temperature at which the reaction takes place at optimized conditions of adsorbent dose (1.0g), and contact time (30mins). The temperature of interest were; 30^0C, 40^0C, 50^0C and 60^0C. The reactor was a 250ml conical flask; the mixture was stirred with a magnetic stirrer hot plate for 30mins. The mixture was filtered immediately with a Whatman filter paper and the filtrate was then corked in a 50ml bottle, and analyzed with a 240FS Varian Atomic Absorption spectrophotometer (AAS).

3.4.4 Effects of pH

The effect of pH was examined by varying the pH of the raw waste water. The considered pH values were; 2, 4, 6, and 10. The experiment was carried out by measuring 100ml of the raw waste water into a conical flask and the pH of the sample was adjusted using 1M of HNO_3 or HCL. 1.0g of the adsorbent was added into the conical flask. The resultant mixture was stirred using a magnetic stirrer at 300rpm for 30mins. The mixture was filtered immediately and the filtrate was then corked in a 50ml bottle, and analyzed with a 240FS Varian Atomic Absorption spectrophotometer (AAS).

3.5. Data Analysis

The adsorption capacity Q_e was calculated by mass balance relationship equation shown

$$Q_e = (C_0 - C_e) \times V/m$$

Where

V = The volume of the solution

M = The mass of adsorbent (g)

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The percentage of metal ions adsorbed from solutions was calculated by the following equation;

%adsorbed $= (C_0-C_e)/C_0 \times 100$

C_0=Initial concentration of heavy meal

C_e=Final concentration of heavy metal

Langmuir Isotherm: The Langmuir isotherm is expressed as:

$C_e/Q_e = C_e(1/Q_m) + 1/bQ_m$

Where,

Q_e= the equilibrium value of the metal ions adsorbed per unit weight of adsorbent C_e= The equilibrium concentration of the adsorbate

b= Relates the affinity between the adsorbent and the adsorbate

The favorability of the isotherm depends on the dimensionless constant factor R_1 which is given by:

$R_L = 1/1 + K_L * C_0$

C_0=Initial concentration

If R_L=0, it shows that the adsorption isotherm is irreversible and if $0 < R_L < 1$ then it shows that Langmuir adsorption isotherm is favorable.

Freundlich Isotherm: The Freundlich isotherm was expressed by the equation: $\log Q_e = \log k_f + 1/n \log C_e$

Where,

k_f=The adsorption coefficient which characterize the strength of adsorption

C_e=the equilibrium concentration of the adsorbate

Q_e=the equilibrium value of the adsorbed per unit weight

RESULT PRESENTATION AND DISCUSSION

The results of the study of adsorption of Cd, Pb, and Zn using activated carbon from coconut shell are presented in Tables 1 – 6.

Table 1: Physicochemical properties of raw and carbonized coconut shell.

PARAMETERS	RESULTS

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Physical Moisture (%) Volatile solid (%) Ash content (%) pH i. Raw ii. Carbonized Bulk density g/cm^3 i. Raw ii. carbonized pore volume and porosity **Chemical** Solubility in water (%) Solubility in 1m of HCL (%) Calcium mg/g Zinc mg/g Cadmium mg/g Lead mg/g	7.96 90.10 2.90 5.03 4.68 0.51 0.61 1.8675 and 0.25 respectively. 1.20 7.3 0.15 0.04 Nil Nil

Water and Acid solubility: Table 1 indicated that the solubility of coconut shell in water and acid were found to be 1.2 and 7.3% respectively.

Metal concentrations: From Table 1, results of digestion (wet digestion method) of the sample show that 1g of coconut shell contains 0.15mg/g of Calcium and 0.04mg of Zinc.

Pore volume and porosity: From Table 1, the value of the pore volume and porosity of the sample were 1.8675 and 0.25 respectively.

4.1 Effect of Adsorption Parameters

Table 2: Initial Concentrations of the Heavy Metal in the Raw Effluent

Parameters	Result
Zinc, mg/l Zn	15.22
Iron, mg/l Fe	2.04
Lead, mg/l Pb	16.28
Cadmium, mg/l Cd	16.00

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Table 3: Effect of Temperature on Zinc, Lead and Cadmium adsorption using coconut shell

Volume = 0.05l, Mass = 1.0g						
	Zinc		Lead		Cadmium	
Temp	Qe	% adsorbed	Qe	% adsorbed	Qe	% adsorbed
30°C	0.591	78	0.619	76	0.593	74
40°C	0.580	76	0.604	74	0.581	73
50°C	0.515	68	0.562	69	0.548	69
60°C	0.475	62	0.515	61	0.484	61

4.3.1 Effect of Temperature on the Adsorbent (Coconut Shell)

The temperature dependence of the adsorption process is related with several thermodynamic parameters. The effect of temperature on the removal of Cadmium, Zinc and Lead was studied in the range of 30-60^{0}C. The results indicate that low temperatures are in favour for the removal of these metals from the waste water. This may be due to the tendency for the metal to escape from the solid phase with an increase in temperature of the solution.

Table 4: Effect of adsorbent dose on the adsorption of Zn, Cd and Pb using coconut shell

Volume = 0.05l						
	Zinc		Cadmium		Lead	
Quantity(g)	Qe	% adsorbed	Qe	% adsorbed	Qe	% adsorbed
0.4	1.265	67	0.434	54	1.310	64
0.6	0.926	73	0.499	62	0.948	70
0.8	0.745	78	0.569	72	0.755	74
1.0	0.611	81	0.607	76	0.627	77

4.3.2 Effect of adsorbent dose on the adsorbent (coconut shell)

Increase in adsorbent dosage increases the percentage removal of Cd, Zn and Pb as shown in the table s and figures below. It is due to increased adsorbent surface area and availability of more adsorption.

Table 5: Effect of pH on the zinc, cadmium and lead adsorption using coconut shell

Volume = 0.05l mass = 1.0g						
	Zinc		Cadmium		Lead	
Quantity(g)	Qe	% adsorbed	Qe	% adsorbed	Qe	% adsorbed
2	0.421	55	0.440	55	0.454	56
4	0.509	67	0.523	65	0.540	66

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| 6 | 0.571 | 75 | 0.586 | 73 | 0.609 | 75 |
| 10 | 0.518 | 68 | 0.540 | 67 | 0.454 | 56 |

4.3.3 Effect of pH on the adsorbent (coconut shell)

The pH of the effluent has significant impact on the uptake of metals, since it determines the surface charge of the adsorbent, the degree of ionization, and specification of the adsorbent. The variation of pH affects the effectiveness as hydrogen ion itself is a tough competing adsorbate. Cadmium, Lead, and zinc exist in different forms in solution and the stability of these forms is dependent of the pH system. The tables below show the relationship between pH and adsorption.

4.3.4 Effect of contact time on the adsorbent (coconut shell)

Table 6: The Effect of contact time on zinc adsorption using coconut shell

Volume = 0.05l mass = 1.0g						
	Zinc		Cadmium		Lead	
Quantity(g)	Qe	% adsorbed	Qe	% adsorbed	Qe	% adsorbed
30	0.451	56	0.434	54	0.464	57
40	0.521	68	0.499	62	0.531	65
50	0.590	78	0.569	72	0.597	73
60	0.619	81	0.607	76	0.654	80

It was observed that, increase in contact time from 30 to 60 minutes significantly enhanced the percentage (%) removal of the metals from the wastewater using the adsorbents (coconut shell). As observed from the tables above.

4.0. SUMMARY

Heavy metals are discharged into water from various industries. They can be toxic or carcinogenic in nature and can cause severe problems for human and aquatic ecosystems. Thus, the removal of heavy metals from wastewater is a serious problem. The adsorption process is widely used for the removal of heavy metals from wastewater because of its low cost, availability and eco-friendly nature. The wastewater sample used for the purpose of this study was collected from Fabex paint industry located at Samonda in Ibadan, South- Western, Nigeria. The sample was collected from the production and washing of paint production materials, and bottled in a sample bottle.

The coconut shell used as adsorbent for this study was obtained from fruit selling source in Mokola Ibadan South western Nigeria. Activated Carbon produced from coconut shell was used as adsorbent to remove Zinc, Cadmium and Lead from industrial wastewater. In order to effectively evaluate the level of pollutant to be removed by the activated carbon made from coconut shell, the physical and chemical parameters of the activated carbon were evaluated. This was achieved by carrying out the pH value, bulk density, moisture content, ash content, water and acid solubility. Batch adsorption experiment was conducted to examine the effects of adsorbent dosage, contact time, pH and stirring rate on adsorption of Zinc,

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Cadmium and Lead ions from wastewater. The obtained results showed that the adsorptions of the metal pH were found to be at 1g, 300rpm and pH 6 respectively. Kinetic studies showed the Pseudosecond order reaction. The study also showed that activated Carbon prepared from coconut shell can be effectively used as low-cost alternative for removal of metal ions.

5.0.   CONCLUSION

A review of various processes and adsorbents for heavy metal removal shows that adsorption process has great potential for the elimination of heavy metals from industrial wastewater using low-cost adsorbents. Following the results obtained, it is evident that activated carbon produced from coconut shell is a good adsorbent for removal of Zinc, Cadmium and Lead ions. Batch experiments were conducted and showed that the adsorption of Zinc, Cadmium and Lead ions are time dependent, adsorbent dosage dependent, pH dependent, and stirring speed dependent. Coconut shell (a waste) is inexpensive and readily available; thus, this study provides a costeffective means for removing metal ions from contaminated water.

6.0.   RECOMMENDATION

Based on the conclusion of this study, the following recommendations are made:

The recommendation here is that more studies should be carried out for low-cost adsorption process to promote large scale use of non-conventional adsorbents. Low-cost adsorbents should be used to minimize cost and maximize heavy metal removal efficiency.

7.0.   REFERENCES

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