




Enhanced Removal of Pb(II), Cd(II), and Zn(II) Ions from Aqueous Solutions Using EDTA-Synthesized Activated Carbon Derived from Sawdust

Onyedikachi G. Okpara¹ , Osareme M. Ogbeide¹, Jeremiah N. Nworu¹, Jude I. Chukwuekeh¹, Solomon A. Igoche¹, Friday S. Alich², Okechukwu E. Orinya²

¹Department of Science Laboratory Technology, Federal College of Agriculture, Ishiagu, Nigeria

²Department of Food Science and Technology, Federal College of Agriculture, Ishiagu, Nigeria

Email: dikachi015safety@gmail.com

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Abstract

EDTA synthesized activated carbon derived from sawdust, was utilized as adsorbent for the removal of Pb(II), Cd(II) and Zn(II) ions from aqueous solutions. The adsorptive characteristics and elemental composition of this activated carbon were studied using SEM and EDX techniques respectively, the analysis revealed that SAC-EDTA contained 71.95% by weight of carbon contents which are requisites for the high adsorption capacity. The effect of initial metals ions concentration, adsorbent dose, contact time, and solution pH were examined at equilibrium for optimum values, experimental data were also fitted into two different isotherms: Langmuir and Freundlich, to establish the best fit for the adsorption process. From the results, the studied metals ions were best described by Langmuir with maximum monolayer coverage (q_{max}) of 89.29 $\text{mg}\cdot\text{g}^{-1}$ for Pb(II), 60.24 $\text{mg}\cdot\text{g}^{-1}$ for Zn(II) and 47.85 $\text{mg}\cdot\text{g}^{-1}$ for Cd(II), and R^2 value of 0.981, 0.9732 and 0.9605 respectively. The Freundlich isotherm also gave a favourable performance with K_f values of 16.43, 11.98 and 10.21 $\text{mg}\cdot\text{g}^{-1}\cdot\text{L}^{1/n}\cdot\text{mg}^{-1/n}$, and R^2 values of 0.9919, 0.9867 and 0.9797 respectively. Therefore, this study demonstrates that SAC-EDTA adsorbent could be used to adsorb heavy metals in our environment. Hence, the order of adsorption affinity is $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$.

Subject Areas

Environmental Chemistry, Toxicology, Agricultural Science, Biotechnology

Keywords

Adsorption, Heavy Metals Ions, Isotherms, SEM, Sawdust-Synthesized with EDTA

1. Introduction

Water pollution has been a major concern for environmentalists worldwide. Heavy metals are the most common water pollutants which could be found in a wide variety of organic chemicals and has derivative which are used as intermediates in the synthesis of dyes, pesticides, explosives, insecticides, fertilizers and others [1]. Water contaminated with metallic effluent can cause several health problems. Lead (Pb) for instance, can interfere with enzyme activities and formation of red blood cells. It can as well affect nerves and brain at low concentration. Zinc (Zn) can cause membrane damage mucous, diarrhea, and dizziness [2]. Cadmium (Cd) is responsible for kidney tubular impairment, lung cancer, and proteinuria [3] [4].

Heavy metals such as mercury, Zinc, cadmium and chromium can bio accumulate through the food chain to toxic levels in man [4]. The impact of heavy metal release into our environment is increasing as a result of population explosion, industrial and technological expansion, increased energy utilization and waste generation from domestic and industrial sources [4]. These have rendered many waters hazardous and unfit for drinking for man and other living organisms [5]. The release of these heavy metals poses a significant threat to the environment and public health because of their toxicity, bioaccumulation in the food chain and persistence in nature [6]. In virtue of the high toxicity and poor biodegradability of metallic compounds, it is necessary to remove them before discharging into the water bodies. Thus, various treatment technologies can be applied in the treatment of these pollutants. The techniques includes; filtration, ultrafiltration, electrodialysis, chemical precipitation, ion exchange, reverse osmosis, sedimentation, solvent extraction, electrochemical deposition, coagulation and adsorption [7] [8] [9]. However, these conventional techniques are not economically viable for small and medium size industries due to huge capital required [10]. Therefore it is necessary to search for low-cost alternative methods that may be effective, economical and sludge free [7] [11]. In this case, adsorption using activated carbon, a phase transfer process is suitable and has been widely used in practice to remove organic and inorganic contaminants from fluid phases [12], it had proven economically viable, effective and simple to design. Based on this, researches and projects are embarked upon, on the use of different bio-sorbents such as nut shells, wood, bone, maize cob and husk [13] [14], cassava waste [15] [16], cucumber peel [17], sawdust, coconut shell and fiber [18], etc., for the treatment of heavy metals in aqueous solution [19] [20] [21] [22] [23]. As the world continues to develop new ideas towards recycling or

converting waste products into useful commodity, there is every tendency that the need for activated carbon would also increase, hence, the need for individuals, companies, and countries to be prepared to meet this demand for our economic base as a country.

Sawdust a residual waste product generated from sawmills, which has environmental benefits in terms of the reuse of solid waste [19], has been utilized in several studies [24] [25] [26] [27] [28] to investigate its potential in removing heavy metals from waste or polluted waters likewise from aqueous solutions. In trying further to improve the more the potency of different sawdust materials, synthetic or modification methods have been applied in various research work [29] [30] [31] [32] to generate a better adsorption capacity of sawdust by increasing the surface area, average pore volume, pore diameter, functional groups like polyphenolic and hydroxyl, as well as to convert carboxyl groups to carboxylate groups that serve as the binding sites for heavy metals [32]. This study is aimed to develop an efficient adsorbent from sawdust synthesized with chelating agent EDTA (ethylenediaminetetraacetic acid), and to investigate the feasibility of utilizing this adsorbent for the purpose of adsorption of heavy metals; Pb (II), Cd(II), Zn(II) in aqueous solutions. EDTA-synthesis enhanced the adsorption capacity of sawdust probably due to its chelating ability [33]. Equilibrium and isotherms of metal adsorption on sawdust were studied and described by two different models. The effects of various parameters such as initial concentration, pH, adsorbent dose and contact time were also evaluated.

2. Material and Methods

2.1. Materials Used, Reagents and Instruments

The activated charcoal precursor material used in this study was *Gmelina arborea* sawdust obtained from sawmill (timber) area of Abakaliki in Ebonyi State, Nigeria. It was thoroughly washed with distilled water to remove surface impurities and sun dried for 2 days. The sawdust was oven dried at 80°C for 2 h to completely remove any water present, and was later grounded to fine powder, sieved to 0.5 mm particle size and was chemically prepared for activation by soaking in dilute acid solution (HNO₃ 2% v/v) for 24 h at room temperature [4]. Thereafter, it was rinsed with deionized water, oven dried and then stored for further chemical synthesis.

The aqueous solutions of metal ions used in the present investigation were prepared using analytical grade reagents. Individual stock of Pb(II), Cd(II) and Zn(II) solutions of 1000 mg metal ion/L concentration were prepared from CuSO₄·5H₂O and Pb(NO₃)₂, Cd(NO₃)₂·4H₂O and Zn(NO₃)₂·6H₂O respectively. These stock solutions were used to prepare a series of dilute solutions. The pH of solutions in range of 2 - 12 was adjusted by using 1.0 M hydrochloric acid solution and 1.0 M anhydrous sodium acetate solution [31]. The pH-value of resulting solutions was measured using HANNA instruments pH meter (pH 209 model, Portugal). The metal concentrations in aqueous solutions were determined by

flame Atomic Absorption Spectrophotometer FS240AA Agilent U.S.A., with photon hollow cathode lamp system in AAS, and using a calibration curve prepared with standard metal ion solutions.

2.2. Methods

2.2.1. Preparation of EDTA-Synthesized Adsorbent

This synthesis was performed according to the reported method by [34], though little modification. The prepared sample powder was mixed with concentrated orthophosphoric acid, H_3PO_4 , to the ratio of acid to sample ratio of 2:1 wt./wt. stirred manually and intermittently for 45 min. and oven dried at $105^\circ C$ for 3 h. The impregnated sample was carbonized in a heat chamber of electric heat muffle furnace in inert flow of nitrogen gas at a temperature raised to $600^\circ C$ for 1.30 min. The resulting activated carbon (AC-Sawdust) was washed severally with warm deionized water until the pH of the washed water became constant. The sample was filtered and oven dried at $105^\circ C$ for 3h. The AC-Sawdust was synthesized using EDTA; 10 g of the AC-Sawdust was refluxed in a mixture of 200 mL of pyridine and 50 g of EDTA for 3 hours at $70^\circ C$. The mixture was cooled followed by addition of 300 ml of deionized water and then filtered. The filtered AC-Sawdust (EDTA-synthesized) was further washed copiously with deionized water to remove excess EDTA and finally dried at $100^\circ C$ for 24 h. The synthesized adsorbent is denoted as SAC-EDTA (Sawdust activated carbon with EDTA). Another portion of the activated carbon sawdust (AC-Sawdust) was left unsynthesized and also used for the analysis.

2.2.2. Characterization of the AC-Sawdust and SAC-EDTA Adsorbent

Scanning Electron Micrograph (SEM) was employed to study the surface characteristics and the morphological features of the activated sawdust (AC-Sawdust) and synthesized sawdust (SAC-EDTA) samples. Likewise, the elemental analysis of both AC-Sawdust and SAC-EDTA were carried out using Energy Dispersive X-ray (EDX) to determine the elemental compositions in the samples before and after EDTA activation respectively.

2.2.3. Experimental Procedure

Batch adsorption experiments was carried out to study the equilibrium effect of various adsorption parameters such as pH, contact time, dosage of adsorbent, temperature and initial concentration of metal ions on the adsorption capacity of removal of metal ions (Pb^{2+} , Cd^{2+} and Zn^{2+}) using EDTA-Sawdust activated carbon (SAC-EDTA) adsorbent. Different metal ions concentrations over the range; 10, 20, 30, 40, 50 and $60\text{ mg}\cdot\text{L}^{-1}$ of the stock solution, were prepared in different conical flasks containing 50 ml of each concentration and 0.5 g of the SAC-EDTA adsorbent at fixed pH 7.5 and room temperature ($25 \pm 2^\circ C$). The solutions were agitated using a mechanical Gemmy orbit shaker (model: VRN-480, USA) at constant 120 rpm for 30 min to establish equilibrium condition. At the end of the given contact time, the mixture was filtered. The metal ion con-

centration in each of the filtrates was determined by flame Atomic Absorption Spectrophotometer FS240AA Agilent U.S.A., at wavelengths of 283.3, 228.8 and 213.9 nm with aid of photon hollow cathode lamp system.

The amount of metal ion adsorbed by the SAC-EDTA was determined by difference between the initial and final ion concentration of the solutions. The amount of metal ion uptake and percentage removal at equilibrium were calculated using Equation: (1) and (2) respectively:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

$$\%Removal = \left[\frac{(C_o - C_e)}{C_o} \right] \times 100\% \quad (2)$$

where, C_o and C_e are respective initial and equilibrium metal ion concentrations ($\text{mg}\cdot\text{L}^{-1}$), V is the volume of solution (ml), “ m ” is the mass of SAC-EDTA adsorbent (g), and q_e is the amount of dye adsorbed ($\text{mg}\cdot\text{g}^{-1}$).

2.2.4. Adsorption Isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the adsorbate phase and adsorbent phase when the adsorption process reaches equilibrium state [35]. The analysis were carried out on the equilibrium data of initial metal ions concentrations by fitting them to different isotherm models in order to find the suitable model that would be favorable for design purposes [36]. Thus, the results were fitted to the commonly used Langmuir and Freundlich isotherm models.

The Langmuir isotherm assumes monolayer adsorption onto a homogenous surface with finite number of adsorption sites. While, the Freundlich isotherm model assumes multilayer adsorption process onto heterogeneous surface. The linear form of the Langmuir isotherm model is given as:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (3)$$

where, q_e is the amount of the metal ions adsorbed on the SAC-EDTA adsorbent at equilibrium ($\text{mg}\cdot\text{g}^{-1}$), C_e is the equilibrium concentration of the Pb(II), Cd(II) or Zn(II) ions in the solution ($\text{mg}\cdot\text{L}^{-1}$), while q_m and K_L are the Langmuir constants. q_m is the maximum monolayer adsorption capacity of the adsorbent ($\text{mg}\cdot\text{g}^{-1}$) and K_L is the energy constant related to the heat of adsorption [5].

The Freundlich isotherm is represented by the Linear Logarithm equation given as:

$$\log_{q_e} = \log_{K_f} + \frac{1}{n} \log C_e \quad (4)$$

where, q_e is the amount of the metal ion adsorbate adsorbed on the SAC-EDTA adsorbent at equilibrium ($\text{mg}\cdot\text{g}^{-1}$); C_e is the equilibrium concentration of the metal ions in the solution ($\text{mg}\cdot\text{L}^{-1}$); K_f and $1/n$ are the Freundlich constants. n is

an indicator of how favorable the adsorption process and $K_f(\text{mg}\cdot\text{g}^{-1})(\text{L}\cdot\text{mg}^{-1})^{1/n}$ is an indicator of adsorption capacity. The slope $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [7]. A value for $1/n$ is said to be favorable when $0 < 1/n < 1$ and $1 < n < 10$, irreversible when $1/n = 1$, and unfavorable when $1/n > 1$ and $n < 1$ [37].

3. Results and Discussion

3.1. Characterization of Activated Carbon Adsorbent

Scanning electron micrograph (SEM) was employed to study the surface characteristics and the morphological features of the activated sawdust (AC-Sawdust) and synthesized sawdust (SAC-EDTA) samples. The results showed that the surface texture of the synthesized activated (SAC-EDTA) was more active with well-developed pores after activation with EDTA, while the resulted activated sawdust (AC-sawdust) before EDTA activation showed some particulate matter in the surface like filament structure, conferring the anisotropic nature of the wood with high lignin in the lamellae between the cell walls. This anisotropy was eliminated by treatment with chelating action of the EDTA as showed in **Figure 1**.

Likewise, the elemental analysis of both AC-Sawdust and SAC-EDTA were carried out using Energy Dispersive X-ray (EDX) to determine the elemental compositions of the samples before and after EDTA activation respectively. The data in **Table 1** revealed the amount of carbon and oxygen contents present in the two samples. The SAC-EDTA was very high in carbon content and significantly low in oxygen content owing to the effects of acid (H_3PO_4) activation on AC-Sawdust. It is also observed in **Table 1**, that the charcoal activated with EDTA (SAC-EDTA), contains the element “Fe” with 6.78 wt%, which could have resulted due to chemical activation. However, since SAC-EDTA is richer in carbon content, it is expected to be an efficient material for this metal ions removal. The lower the oxygen contents the higher the carbon contents of the samples under study, the more efficient the adsorbent.

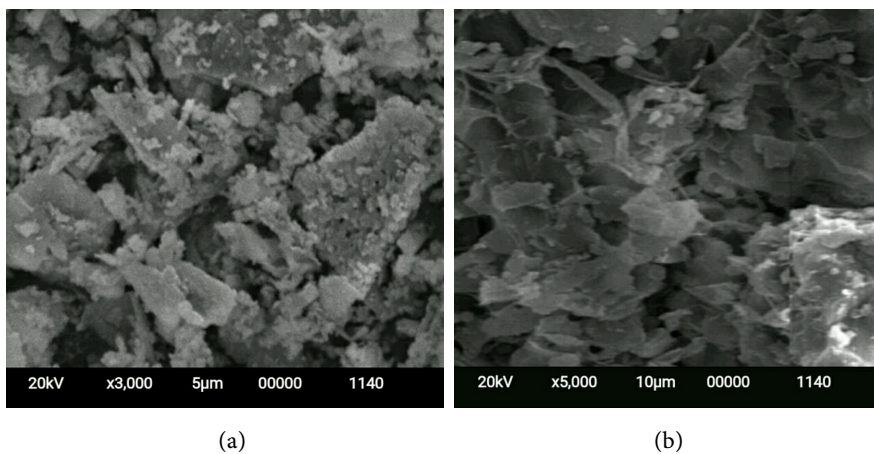


Figure 1. SEM image of the activated sawdusts: (a) AC-Sawdust and (b) SAC-EDTA.

Table 1. Elemental composition of AC-Sawdust and SAC-EDTA adsorbents.

Elements	AC-Sawdust	SAC-EDTA
	(Weight %)	
C	64.67	71.95
O	28.59	15.84
Ca	3.26	2.87
P	1.45	0.68
K	0.84	0.76
S	0.63	0.60
Si	0.56	0.52
Fe	-	6.78
Total	100.00	100.00

where; AC-Sawdust = Activated sawdust, and SAC-EDTA = EDTA-Synthesized sawdust (SAC-EDTA) samples.

3.2. Adsorption Study

The equilibrium experiments were carried out to determine the optimal conditions of pH of solution, contact time and dosage of the adsorbent.

3.2.1. Effect of Concentration

The effect of changing initial metals ions concentration on the biosorption of lead, cadmium and zinc ions onto SAC-EDTA adsorbent over a range of 10 - 60 mg·L⁻¹ was investigated at constant adsorption parameters. Rapid increase in adsorption of each of the metals ion as initial Pb(II), Cd(II) and Zn(II) concentration was observed for about 30 min. From **Figure 2**, the percentage removal increased with increasing metals ion concentration, perhaps due to high availability of the sorption sites which gradually decreased when the surface sites became saturated at equilibrium. For lead and Zinc, the maximum removal (90.22% and 84.22%) was at concentration of 50 mg·L⁻¹, then decreased to 91.68% and 84.16% respectively at concentration of 60 mg·L⁻¹. For Cadmium, maximum removal (79.16%) was at concentration of 60 mg·L⁻¹. Thus, the optimum adsorption of Pb(II) and Zn(II) at 50 mg·L⁻¹, and that of Cd(II) at 60 mg·L⁻¹ concentration depicts higher efficiency of the SAC-EDTA adsorbent.

3.2.2. Effect of Adsorbent Dosage

The influence of adsorbent dose on lead, Cadmium and Zinc removal was studied by varying the adsorbent dose from 0.1 to 1.1 g into a number of flasks each containing 50 mL of aqueous solutions at initial lead and zinc concentration of 50 mg·L⁻¹, and cadmium concentration of 60 mg·L⁻¹. Increased adsorbent dosage implied a greater surface area and a greater number of binding sites available for the constant amount of adsorbate ions. For lead, Cadmium and zinc, the minimum percentage removal was 42.56%, 36.93% and 39.75% for the dose of 0.1 g

and it increased to maximum value of 98.46%, 90.65% and 94.56% respectively

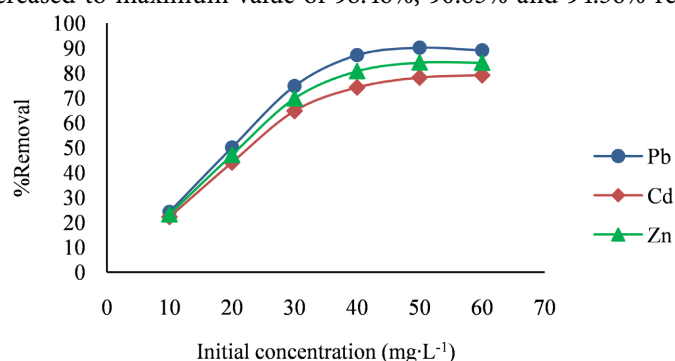


Figure 2. Effect of initial concentration on adsorption of Pb(II), Cd(II) and Zn(II).

for dose of 1.1g as shown in **Figure 3**. It there means that the increase in adsorption with increasing adsorbent dosage is due to increasing number of adsorbent particles thus more surface (unsaturated) sites were available for metal ions attachment [31]. It can be concluded that by increasing the adsorbent dose, the availability of the exchangeable sites or surface area increases and the removal efficiency SAC-EDTA adsorbent increases. Hence, an adsorbent dose of 1.1g was chosen as an optimum value for subsequent experiments.

3.2.3. Effect of Contact Time

The effect of contact time on the adsorption of lead, cadmium and zinc ions onto SAC-EDTA adsorbent was studied at different times range from 10 to 60 min and optimum parameters. From **Figure 4**, the removal percentage of the three metal ions increases rapidly with increasing contact time (high adsorption rate). For lead, cadmium and zinc, the minimum percentage removal was 42.23%, 42.11% and 42.17% at time of 10 min and it increased to maximum (optimal) value 90.22%, 72.28% and 81.25% at time of 50 min. After optimal time, increasing in contact time is not effective in the adsorption process. As the surface adsorption sites become exhausted, the adsorption reached equilibrium as a result of the reduction of available sites which are difficult to be occupied due to repulsive forces between metal ions onto the adsorbent surface and the bulk phase [31] [38].

3.2.4. Effect of Initial solution pH

The effect of pH on removal of metal ions by SAC-EDTA adsorbent was studied by changing the initial pH (2 - 12) of 50 ml of metal aqueous solution of lead, cadmium and zinc at concentration 50 mg·L⁻¹ by adjusting the value of pH with 1.0 M HCl and 1.0 M sodium acetate solution. **Figure 5** shows the removal of lead, cadmium and zinc as a function of pH, where the adsorption takes place slightly at lower pH values (pH = 2 - 6) then the removal of lead and zinc ions increases with increasing pH of the solution, given the optimum value at pH 10 and 12 for Zn(II) and Pb(II) ions with removal percentage 87.94% and 99.14% respectively. At higher pH value of 8 for Cd(II), a sharp decrease in adsorption

curve was observed which later rise. The active groups are protonated reducing

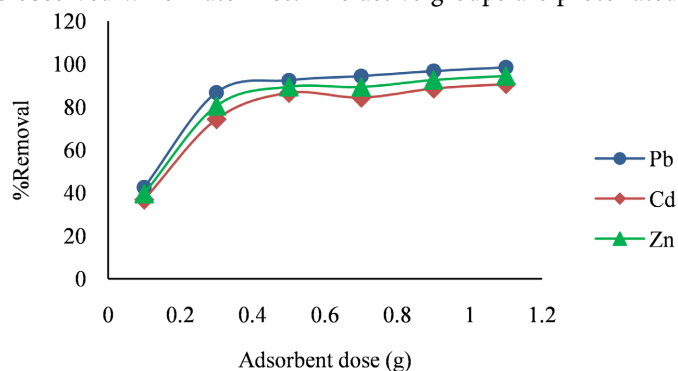


Figure 3. Effect of adsorbent dosage on adsorption of Pb(II), Cd(II) and Zn(II).

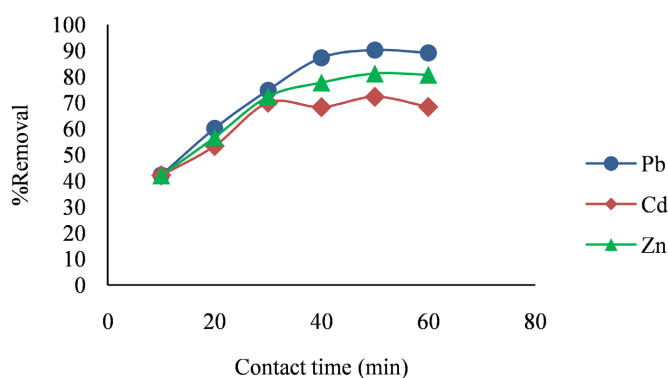


Figure 4. Effect of contact time on adsorption of Pb(II), Cd(II) and Zn(II).

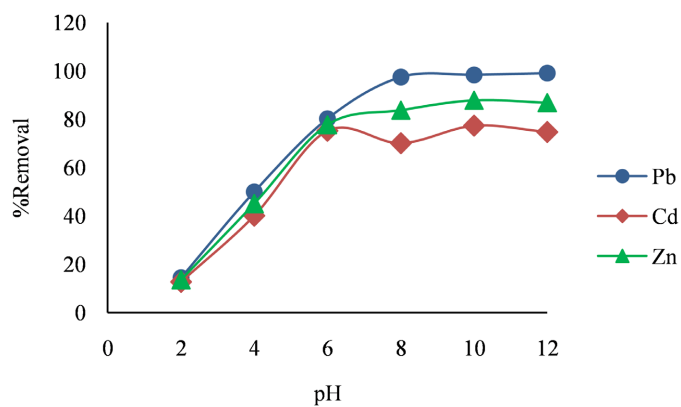


Figure 5. Effect of solution pH on adsorption of Pb(II), Cd(II) and Zn(II).

the number of binding sites available for metal ions removal. Thus, weak adsorption occurred due to strong electrostatic repulsive force between the protonated surface of SAC-EDTA adsorbent and positively-charged metal ions [37].

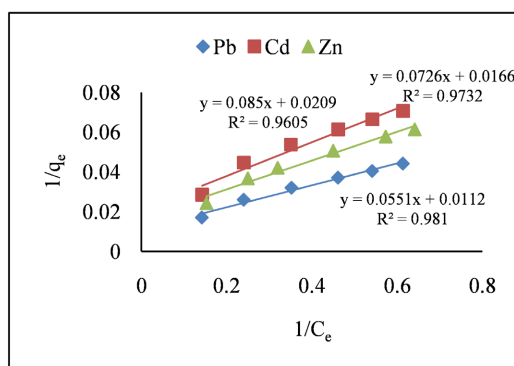
3.3. Adsorption Isotherms

The equilibrium relationship between adsorbent and adsorbate are described by adsorption isotherms. This was studied using the optimum parameters and varying initial metal ions concentrations (10 - 60 mg·L⁻¹) at constant temperature. **Figure 6(a)** shows Langmuir models for the three metals ions by plotting $1/q_e$ versus $1/C_e$. Monolayer adsorption capacity q_{max} was calculated from slope and K_L was obtained from intercept. Also, the essential characteristics of this Langmuir isotherm model can be expressed in terms of a dimensionless separation factor for equilibrium parameter, R_L [5] which is defined as:

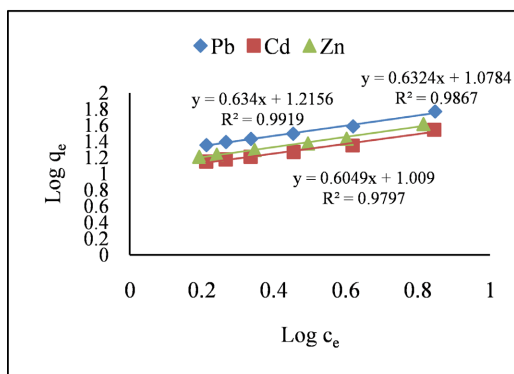
$$R_L = \frac{1}{(1 + K_L C_o)} \quad (5)$$

where, K_L is the Langmuir constant which indicates the nature of adsorption (L/mg), C_o is the initial metal ion concentration (mg·L⁻¹). The separation factor R_L indicates the isotherm shape base on the favorability in the given criteria; Linear ($R_L = 1$), Unfavourable ($R_L > 1$), Favourable ($0 < R_L < 1$), and Irreversible ($R_L = 0$) [5]. For the C_o range (10 - 60 mg·L⁻¹) used in the study, R_L lies between 0.0038 - 0.0098 for Pb(II), 0.0013 - 0.0032 for Cd(II) and 0.0011 - 0.0028 for Zn(II), indicating that these metals ions adsorption are favoured on the SAC-EDTA adsorbents.

Figure 6(a) & **Figure 6(b)** shows the plot of Langmuir and Freundlich isotherms for the Pb (II), Cd(II) and Zn(II) ions uptake onto SAC-EDTA adsorbent.



(a)



(b)

Figure 6. Isotherm models for adsorption of Pb(II), Cd(II)

and Zn(II) ions onto SAC-EDTA adsorbent: (a) Langmuir and (b) Freundlich isotherms.

The adsorption parameters obtained from Langmuir and Freundlich isotherm plots are presented in **Table 2**. The best equilibrium was obtained on the basis of these parameters and linear regression correlations (R^2). From **Table 2**, the maximum monolayer coverage capacity (q_{\max}) for Pb (II), Cd(II) and Zn(II) ions from Langmuir isotherm model was determined to be 89.29 $\text{mg}\cdot\text{g}^{-1}$, 47.85 $\text{mg}\cdot\text{g}^{-1}$ and 60.24 $\text{mg}\cdot\text{g}^{-1}$, while the constant (K_L) was calculated to be 0.203 $\text{L}\cdot\text{g}^{-1}$, 0.246 $\text{L}\cdot\text{g}^{-1}$ and 0.229 $\text{L}\cdot\text{g}^{-1}$ respectively.

The adsorption intensity $1/n$, indicates both the relative distribution of energy and the heterogeneity of the adsorbent sites, it was determined from the slope and K_f was calculated from intercept. The K_f values obtained from Freundlich isotherm demonstrate that a physical process was reasonably part of the sorption process. The higher the value of K_f , the higher the adsorption capacity. The “ n ” values were used to measure the linear deviation of the adsorption and the adsorption types [39]. In this study, the “ $1/n$ ” values were less than 1 ($0 < 1/n < 1$) suggesting a favorable adsorption process.

Comparing the maximum adsorption capacities values for the two isotherms on the three metals ions, one may conclude that Langmuir isotherm described the adsorption process most with maximum monolayer coverage (q_{\max}) for each metals ions as shown in **Table 2**. However, when observed the correlation (R^2) values and other parameters for the two isotherms, one can say that equilibrium data fitted well to the two models, but gave a better fit to the Langmuir model. The suitability of both in representing the equilibrium data of Pb(II), Cd(II) and Zn(II) ions indicates that a monomolecular layer of metal ions formed on the surface of the SAC-EDTA adsorbent [40]. The order of adsorption affinity on the adsorbent is $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$, which according to [19] is related to the differences in electronegativity of the atoms.

4. Conclusion

The need to clean-up heavy metal contaminated environment cannot be over emphasized. The present investigation evaluated the fact that the chemically synthesized sawdust by ethylenediaminetetraacetic (EDTA) is effective adsorbent for the removal of heavy metals ions from aqueous solutions. The Synthetic treatment of raw sawdust with perchloric acid (H_3PO_4) followed by EDTA modified its composition, properties, and characteristics as verified by EDX and

Table 2. Langmuir and Freundlich isotherm parameter for adsorption of Pb(II), Cd(II) and Zn(II) ions SAC-EDTA adsorbent.

Metal ion	Langmuir isotherm				Freundlich isotherm		
	K_L	Q_{\max}	R_L	R^2	K_f	$1/n$	R^2
Pb(II)	0.203	89.29	0.0073	0.9810	16.43	0.6324	0.9919

Cd(II)	0.246	47.85	0.0024	0.9605	10.21	0.6049	0.9797
Zn(II)	0.229	60.24	0.0021	0.9732	11.98	0.6324	0.9867

SEM. This changes in the SAC-EDTA adsorbent resulted in higher uptake of the metals ions with an increase in percentage removal. The effects of some parameters on the adsorption of these Pb(II), Cd(II) and Zn(II) ions were also studied at optimal experimental conditions. The results showed that 1.1 g·L⁻¹ of the synthesized adsorbent is required for the removal of about 98.46% Pb(II), 90.65% Cd(II) and 94.56% of Zn(II) respectively from initial concentrations of 10 mg·L⁻¹. This is better than some of the previously reported results [30] [31] [32] obtained with other sawdust activated adsorbents. Isotherm studies also confirmed that synthesized sawdust (SAC-EDTA) is a suitable adsorbent and can be used for treatment of effluents containing heavy metals.

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Conflicts of Interest

The authors declare no conflicts of interest.

References

- [1] Rodriguez-Mirasol, J., Gonzalez-Serrano, E., Cordero, T., Cotoruelo, L. and Rodriguez, J.J. (2004) Removal of Water Pollutants with Activated Carbons Prepared from H₃PO₄ Activation of Lignin from Kraft Black Liquors. *Water Research*, **38**, 3043-3050. <https://doi.org/10.1016/j.watres.2004.04.048>
- [2] Ghazi, M.B.H.I., Ngai, C.W., Abdul, H.R. and Azazi, N.Z. (2013) Freundlich Isotherm Equilibrium Equations in Determining Effectiveness a Low Cost Absorbent to Heavy Metal Removal in Wastewater (Leachate) at Teluk Kitang Landfill, Pengkalan Chepa, Kelantan, Malaysia. *Journal of Geography and Earth Science*, **1**, 1-8.
- [3] Shafiq, M., Alazba, A.A. and Amin, M.T. (2018) Removal of Heavy Metals from Wastewater Using Date Palm as a Biosorbent: A Comparative Review. *Sains Malaysiana*, **47**, 35-49. <https://doi.org/10.17576/jsm-2018-4701-05>
- [4] Ghazi, Z.A., Khattak, A.M., Iqbal, R., Ahmad, R., Khan, A.A., Usman, M., Nawaz, F., Ali, W., Felegari, Z., Jan, S.U., Iqbal, A. and Ahmad, A. (2018) Adsorptive Removal of Cd²⁺ from Aqueous Solutions by a Highly Stable Covalent Triazine-Based Framework. *New Journal of Chemistry*, **42**, 10234-10242. <https://doi.org/10.1039/C8NJ01778F>
- [5] Ogbeide, O.M., Ezech, E.E. and Okpara, O.G. (2019) Isotherms, Kinetics and Equilibrium Studies of Adsorption of Lead (II) Ions from Aqueous Solutions Using Polymer-Modified Coconut Shell Activated Carbon (MCSAC). *IOSR Journal of Environmental Science, Toxicology and Food Technology*, **13**, 28-43.
- [6] Ceribasi, H.I. and Yetis U. (2001) Biosorption of Ni (II) and Pb (II) by *Phanaerochate chrysosporium* from a Binary Metal System-Kinetics. *Water SA*, **27**, 15-20.

- [7] Okpara, O.G., Ogbeide, O.M., Ezeh, E.C., Chukwuekeh, J.I., Nwankwo, O.D. and Igwilo, C.N. (2020) Kinetic and Thermodynamic Studies on Adsorption of Lead (II) Ions from Aqueous Solutions Using Polymer-Modified Coconut Shell Activated Carbon (MCSAC). *International Journal of Chemical Science*, **4**, 1-8.
- [8] Hameed, B.H., Tan, I.A. and Ahmad, A.L. (2009) Preparation of Oil Palm Empty Fruit Bunch-Based Activated Carbon for Removal of 2,4,6-Trichlorophenol: Optimization Using Response Surface Methodology. *Journal of Hazardous Materials*, **164**, 1316-1324. <https://doi.org/10.1016/j.jhazmat.2008.09.042>
- [9] Mohan, D., Singh, K.P. and Singh, V.K. (2008) Wastewater Treatment Using Low Cost Activated Carbons Derived from Agricultural Byproducts—A Case Study. *Journal of Hazardous Materials*, **152**, 1045-1053. <https://doi.org/10.1016/j.jhazmat.2007.07.079>
- [10] Eruola, A.O. and Ogunyemi, I.O. (2014) Evaluation of the Adsorption Capacity of the Coconut Shell and Palm-Kernel Shell Adsorbents Powder for the Sorption of Cadmium (II) Ions from Aqueous Solution. *IOSR Journal of Environmental Science, Toxicology and Food Technology*, **8**, 55-63. <https://doi.org/10.9790/2402-08635563>
- [11] Mandina, S., Chigondo, F., Shumba, M., Nyamunda, B.C. and Sebata, E. (2013) Removal of Chromium (VI) from Aqueous Solution Using Chemically Modified Orange (*Citrus sinensis*) Peel. *IOSR Journal of Applied Chemistry*, **6**, 66-75. <https://doi.org/10.9790/5736-0626675>
- [12] Rashed, M.N. (2013) Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater. In: Rashed, M.N., Ed., *Organic Pollutants-Monitoring, Risk and Treatment*, IntechOpen, London, 168-194. <https://doi.org/10.5772/55953>
- [13] Igwe, J.C. and Abia, A.A. (2003) Maize Cob and Husk as Adsorbents for Removal of Cadmium, Lead and Zinc Ions from Wastewater. *The Physical Scientist*, **2**, 210-215.
- [14] Igwe, J.C., Okpereke, O.C. and Abia, A.A. (2005) Sorption Kinetics and Intraparticle Diffusivities of Co, Fe, and Cu, Ions on EDTA Modified Maize Cob. *Indian Journal of Chemistry*, **15**, 187-191.
- [15] Abia, A.A., Horsefall, Jr.M. and Didi, O. (2003) The Use of Chemically Modified and Unmodified Cassava Waste for the Removal of Cd, Cu and Zn Ions from Aqueous Solution. *Bioresource Technology*, **90**, 345-348. [https://doi.org/10.1016/S0960-8524\(03\)00145-7](https://doi.org/10.1016/S0960-8524(03)00145-7)
- [16] Horsfall, M.J., Abia, A.A. and Spiff, A.I. (2003) Removal of Cu (II) and Zn (II) Ions from Wastewater by Cassava (*Manihot esculenta* Cranz) Waste Biomass. *African Journal of Biotechnology*, **2**, 360-364. <https://doi.org/10.5897/AJB2003.000-1074>
- [17] Basu, M., Guha, A.K. and Ray, L. (2017) Adsorption of Lead on Cucumber Peel. *Journal of Cleaner Production*, **151**, 603-615. <https://doi.org/10.1016/j.jclepro.2017.03.028>
- [18] Igwe, J.C., Nwokennaya, E.C. and Abia, A.A. (2005) The Role of pH in Heavy Metal Detoxification by Bio-Sorption from Aqueous Solutions Containing Chelating Agents. *African Journal of Biotechnology*, **4**, 1109-1112.
- [19] Lim, J., Kang, H.M., Kim, L.H. and Ko, S.O. (2008) Removal of Heavy Metals by Sawdust Adsorption: Equilibrium and Kinetic Studies. *Environmental Engineering Research*, **13**, 79-84. <https://doi.org/10.4491/eer.2008.13.2.079>
- [20] Jang, A., Seo, Y. and Bishop, P.L. (2005) The Removal of Heavy Metals in Urban Runoff by Sorption on Mulch. *Environmental Pollution*, **133**, 117-127. <https://doi.org/10.1016/j.envpol.2004.05.020>
- [21] Vijayaraghavan, K., Jegan, J., Palanivelu, K. and Velan, M. (2005) Biosorption of Copper, Cobalt and Nickel by Mirine Green Alga *Ulva Reticulate* in a Packed Column.

- Chemosphere*, **60**, 419-426. <https://doi.org/10.1016/j.chemosphere.2004.12.016>
- [22] Ekpete, O.A., Kpee, F., Amadi, J.C. and Rotimi, R.B. (2010) Adsorption of Chromium (VI) and Zinc (II) Ions on the Skin of Orange Peels (*Citrus sinensis*). *Journal of Nepal Chemical Society*, **26**, 31-39. <https://doi.org/10.3126/jncs.v26i0.3628>
- [23] El-Sayed, G.O., Yehia, M.M. and Asaad, A.A. (2014) Assessment of Activated Carbon Prepared from Corncob by Chemical Activation with Phosphoric Acid. *Water Resources and Industry*, **7-8**, 66-75. <https://doi.org/10.1016/j.wri.2014.10.001>
- [24] Kalavathy, M.H., Karthikeyan, T., Rajgopal, S. and Miranda, L.R. (2005) Kinetic and Isotherm Studies of Cu (II) Adsorption onto H₃PO₄-Activated Rubber Wood Sawdust. *Journal of Colloid and Interface Science*, **292**, 54-362. <https://doi.org/10.1016/j.jcis.2005.05.087>
- [25] Yu, B., Zhang, Y., Shukla, A., Shukla, S.S. and Dorris, K.L. (2001) The Removal of Heavy Metals from Aqueous Solutions by Sawdust Adsorption—Removal of Lead and Comparison of Its Adsorption with Copper. *Journal of Hazardous Materials B*, **84**, 83-94. [https://doi.org/10.1016/S0304-3894\(01\)00198-4](https://doi.org/10.1016/S0304-3894(01)00198-4)
- [26] Taty-Costodes, V.C., Fauduet, H., Porte, C. and Delacroix, A. (2003) Removal of Cd (II) and Pb (II) Ions, from Aqueous Solutions, by Adsorption onto Sawdust of *Pinus sylvestris*. *Journal of Hazardous Materials B*, **105**, 121-142. <https://doi.org/10.1016/j.jhazmat.2003.07.009>
- [27] Taty-Costodes, V.C., Fauduet, H., Porte, C. and Ho, Y.S. (2005) Removal of Lead (II) Ions from Synthetic and Real Effluent Using Immobilized *Pinus sylvestris* Sawdust: Adsorption on a Fixed-Bed Column. *Journal of Hazardous Materials B*, **123**, 135-144. <https://doi.org/10.1016/j.jhazmat.2005.03.032>
- [28] Nwifo, B.T., Isaac, N.D. and Onche, E.U. (2014) Preparation and Characterization of Sawdust (Cellulose) as an Adsorbent for Oil Pollution Remediation. *International Journal of Natural Science Research*, **2**, 97-102.
- [29] Singh, J., Mishra, N.S., Banerjee, U.S. and Sharma, Y.C. (2011) Comparative Studies of Physical Characteristics of Raw and Modified Sawdust for Their Use as Adsorbents for Removal of Acid Dye. *Bioresources*, **6**, 2732-2743. <https://doi.org/10.15376/biores.6.3.2732-2743>
- [30] Rajak, V.K., Kumar, S., Thombre, N.V. and Mandal, A. (2018) Synthesis of Activated Charcoal from Saw-Dust and Characterization for Adsorptive Separation of Oil from Oil-in-Water Emulsion. *Chemical Engineering Communications*, **205**, 897-913. <https://doi.org/10.1080/00986445.2017.1423288>
- [31] El-Saied, F.A., Abo-Elenan, S.A. and El-shinawy, F.H. (2017) Removal of Lead and Copper Ions from Polluted Aqueous Solutions Using Nano-Sawdust Particles. *International Journal of Waste Resources*, **7**, Article ID: 1000305. <https://doi.org/10.4172/2252-5211.1000305>
- [32] Kong, S., Kamga, E.T., Fossog, V. and Nanseu-Njiki, C.P. (2016) Removal of Mercury (II) from Aqueous Solution by Modified *Triplochyton scleroxylon* Sawdust. *Journal of Chemical and Pharmaceutical Research*, **8**, 342-353.
- [33] Oviedo, C. and Rodríguez, J. (2003) EDTA: The Chelating Agent under Environmental Scrutiny. *Química Nova*, **26**, 901-905. <https://doi.org/10.1590/S0100-40422003000600020>
- [34] Pam, A.A., Abdullah, A.H., Ping, T.Y. and Zainal, Z. (2018) Batch and Fixed Bed Adsorption of Pb (II) from Aqueous Solution Using EDTA Modified Activated Carbon Derived from Palm Kernel Shell. *Bioresources*, **13**, 1235-1250. <https://doi.org/10.15376/biores.13.1.1235-1250>

- [35] Bello, O.S., Adelaide, O.M., Hamed, M.A, and Popoola, O.M.M. (2010) Kinetic and Equilibrium Studies of Methylene Blue Removal from Aqueous Solution by Adsorption on Treated Sawdust. *Macedonian Journal of Chemistry and Chemical Engineering*, **29**, 77-85. <https://doi.org/10.20450/mjce.2010.181>
- [36] Haghseresht, F. and Lu, G. (1998) Adsorption Characteristics of Phenolic Compounds onto Coal-Reject-Derived Adsorbents. *Energy Fuels*, **12**, 1100-1107. <https://doi.org/10.1021/ef9801165>
- [37] Okpara, O.G., Ogbide, O.M., Ike, O.C., Menechukwu, K.C. and Ejike, E.C. (2020) Optimum Isotherm by Linear and Nonlinear Regression Methods for Lead (II) Ions Adsorption from Aqueous Solutions Using Synthesized Coconut Shell-Activated Carbon (SCSAC). *Toxin Reviews*, **40**, 901-914. <https://doi.org/10.1080/15569543.2020.1802596>
- [38] Haider, S. and Park, S.Y. (2009) Preparation of the Electrospun Chitosan Nanofibers and Their Applications to the Adsorption of Cu (II) and Pb (II) Ions from an Aqueous Solution. *Journal of Membrane Science*, **328**, 90-96. <https://doi.org/10.1016/j.memsci.2008.11.046>
- [39] Bello, O.S., Alabi, E.O., Adegoke, K.A., Adegboyega, S.A., Inyinbor, A.A. and Dada, A.O. (2020) Rhodamine B Dye Sequestration Using *Gmelina aborea* Leaf Powder. *Heliyon*, **6**, e02872. <https://doi.org/10.1016/j.heliyon.2019.e02872>
- [40] Kantasamy, N. and Siti, M.S. (2016) Equilibrium and Thermodynamic Studies of Anionic Dyes Removal by an Anionic Clay-Layered Double Hydroxide. *Malaysian Journal of Analytical Sciences*, **20**, 358-364. <https://doi.org/10.17576/mjas-2016-2002-19>