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Removal of of Pb(II), Cd(II), Cu(II) and Ni(II) Ions from Aqueous Solution Using *Pentaclethra Macrophylla* Stem Activated Carbon

N. R. Ekere^{*}, A. B. Agwogie and J. N. Ihedioha,*Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Nigeria.*^{*}Corresponding Author Email: nwachukwu.ekere@unn.edu.ng

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Abstract

Pentaclethra Macrophylla stem activated carbon (PMSAC) was utilized as biomass derived adsorbent for adsorption of Pb(II), Cd(II), Cu(II) and Ni(II) from aqueous solution. The activation was chemically carried out using ZnCl₂ solution. The Physicochemical analysis of PMSAC showed high fixed carbon and pore volume values. The Scanning Electron Microscope (SEM) and Energy Dispersive X-ray were used to characterize the PMSAC. Simultaneous batch adsorptions used to evaluate the optimal operational conditions for the adsorption showed initial metal ions concentration (5 mg/L), solution pH (6), contact time (90 min), adsorbent dose (3.0 g for Cd(II) and 4.0 g for Pb(II), Cu(II) and Ni(II), particle size (30 μm) and carbonization temperature (400 °C). The Langmuir isotherm model gave better fit for the adsorption process. Dubinin-Radushkevich isotherm indicates physical adsorption. The kinetics and thermodynamic parameters were studied.

Keywords: Adsorption, *Pentaclethra macrophylla*, Physisorption, Isotherm, Kinetics.

Introduction

The increased widespread of heavy metals in the environment as a result of anthropogenic activities is posing significant hazard to human health as a result of their toxicity and non-biodegradability in the environment [1]. Industrial wastewaters are major sources of heavy-metal contamination.

Heavy metals are dispersed widely in the environment as a result of human and industrial activities such as paper production, purification of metals, metal finishing, manufacturing of chemicals, mining operations, electroplating, smelting and battery manufacturing. Some metals such as lead, cadmium, nickel, arsenic, and mercury are not useful in human wellbeing and may be toxic and carcinogenic. Even, metals regarded as essential to life may become harmful at very high levels of exposure [2]. Due to the harmful effects of heavy metals in the

environment, treatment of industrial wastewater or effluents before they are discharged is recommended [3, 4].

A range of different methods exist for such effluent treatment. For instance precipitation, ion exchange, electro-coagulation, membrane filtration and packed-bed filtration have been used in removing heavy metals from wastewater [5-9]. Some of these methods have high operational cost, partial metal removal, and requirement of expensive equipment, high energy requirements and toxic sludge disposal problems [10, 11]. For instance when the concentration is low (<100 mg/L), the effectiveness of some of these methods reduces drastically [12]. These conventional technologies are too expensive to use or unable to remove and recover heavy metals to a satisfactory level [13]. Commercial activated carbons are

equally expensive to use in such remediation [14] hence, interest has shifted to the use of locally available biomass to generate activated carbons which are cheap and effective.

Biosorption offers a technically feasible, robust and economically attractive alternative for the removal of heavy metals from aqueous solution [15, 16]. The usefulness of biomaterials in removing metal ions from aqueous solution has been investigated by several researchers and all have shown that the plant based adsorbents are cheap [17-20]. In an effort to deepen the knowledge of the simple technology with low-cost adsorbent, eco-friendly and economical process, the study was taken up to investigate the efficiency of Stem Activated Carbon (SAC) made from a tropical tree, *Pentaclethra Macrophylla*, known in folk medicine to be anti-poison due to metals ingestion, to remove heavy metals from aqueous solutions. The kinetics, isotherms and thermodynamic features of the adsorption process were also investigated.

Experimental

Plant description (pentaclethra macrophylla)

Pentaclethra Macrophylla called the African oil bean is a tropical tree in the family of Leguminosae (Mimosoideae) and grows abundantly in Nigeria and other sub Saharan countries. *Pentaclethra macrophylla* trees grow to about 21 m in height and about 60 cm girth with a low branching and an open crown [21]. Stem form is usually crooked and buttressed although some are straight-stemmed making for good timber. *P. macrophylla* is grown on the fringes of farms mainly for its edible seed [22].

Sample collection and preparation

Pentaclethra Macrophylla Stem used for this study was collected from Plant Science and Biotechnology Departmental garden, University of Nigeria Nsukka, Enugu State, Nigeria. A voucher sample was deposited at the herbarium of the Department after authentication by botanist from the same Department. The samples were washed severally with water and air dried for 14 days. They were later oven dried at 105 °C for 3 h. The

sample was ground into powder using stainless grinding mill. The dried powdered *Pentaclethra Macrophylla Stem* was sieved into various sizes using rotary sieve shaker [19]. The sieved fractions were stored in different containers prior to carbonization.

Carbonization of the pentaclethra macrophylla stem powder

The carbonization of the adsorbent was carried out according to the method used by Abdul et al [22]. A 50 g mass each of dried *Pentaclethra Macrophylla Stem Powder* were carbonized in a muffle furnace at different temperature ranges 300 °C, 350 °C, 400 °C, 450 °C and 500 °C for 2 h each. At the end of 2 h, each of the samples was allowed to cool in desiccators for 3 h. Later the samples were put in air tight bottle.

Activation of the carbonized adsorbent

The carbonized *Pentaclethra Macrophylla Stem* (CPMS) was activated via chemical process according to the method of Girgis et al [9] with slight modification. 40 g of each of the CPMS at various temperatures ranges 300 °C, 350 °C, 400 °C, 450 °C and 500 °C were soaked in 250 mL of 25 % ZnCl₂ solution in five different 500 mL beakers for 24 h. The mixture was filtered after 24 h and the residue neutralized with dilute HCl, washed with deionized water to a pH 7.0. The samples were then dried in a thermostatically controlled oven at 105 °C and later removed to cool at room temperature. Each of the *Pentaclethra Macrophylla stem activated carbon* (PMSAC) was stored in an air tight bottle.

Preparation of metal ions solutions

The reagents used in this study were of Analar grade and were supplied by BDH laboratories, Germany. The reagents were used without further purification. The stock solution of concentration 1000 mg/L of Pb(II), Cd(II), Cu(II) and Ni(II) ions each was prepared by dissolving calculated amounts of (Pb(NO₃)₂, Cd(NO₃)₂.4H₂O, Cu(NO₃)₂.3H₂O and NiSO₄.6H₂O) in deionized water. The working solutions were prepared by

dilution of the Stock solutions (1000 mg/L) of the individual metal salt ($\text{Pb}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) with double distilled water to obtain different metal ion concentrations thus 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L, 25 mg/L and 30 mg/L.

Physicochemical analysis

ASTM Standard methods [23] were used to determine moisture, ash, and volatile matter content. Horsfall et al method [24] was utilized to estimate the fixed carbon content, pore volume, porosity and bulk density of the adsorbent. Digital pH meter and Conductimeter were used to determine the pH and conductivity of PMSAC respectively. Also Scanning Electron Microscope (SEM: model: Phenom World ProX) was used to observe the PMSAC surface structures. The adsorbent zero point charge (pH zpc) was estimated by the solid addition method devised by Mall et al. [25]. The energy value was determined using bomb calorimeter, Parr, (model 1281) following the standard method ASTM D1989 – 95 [26].

Batch adsorption studies

Batch adsorption experiments were carried out using 150 mL pretreated plastic bottles. The studied adsorption parameters values were varied to obtain the optimal conditions. The pH effect was studied at pH ranges of 2 -10. The change in adsorption with respect to initial metal ion concentration was examined at ranges from 5 to 30 mg/L of each metal at optimal pH value of 6. The effect of contact time was determined using a duration range of 30 to 150 min. The adsorbent dose was varied between 1.0 and 5.0 g. Particle sizes of PMSAC between 30 and 150 μm were investigated. The effect of carbonization temperature was examined at carbonization temperature ranges from 300 to 500 $^\circ\text{C}$. Also, the effect of solution temperature was investigated at temperature range from 305 to 325 K using a thermostat water bath. A 50 mL volume of the adsorbate was used throughout the adsorption process. Whatman No. 42 filter paper was used to filter the solution. The remaining amount of the metal ions in the filtrate after elution was analyzed with Perkin-Elmer Analyst 300 Atomic Absorption

Spectrometer (AAS). The metal uptake capacity of PMSAC biomass was calculated by simple concentration difference method and percentage removal of the metal ions was estimated by the equations 1 and 2.

$$q_e = (C_i - C_e) \frac{V}{M} \quad (1)$$

q_e = Metal uptake capacity of the metal ions per unit weight of PMSAC at equilibrium (mg/g)

C_i = Initial amount of metal ion in the solution (mg/L),

C_e = Metal ion concentration in the solution at equilibrium

M = Mass of adsorbent (g)

The analytical method was validated by analysis of blank samples in triplicates. The blank samples were made to pass through all processes of analysis. Limit of detection (LOD) and Limit of Quantitation (LOQ) were determined as shown in the following equations:

$$\text{LOD} = X_{b1} + 3S_{b1}$$

$$\text{LOQ} = X_{b1} + 10S_{b1}$$

where X_{b1} is the mean concentration of the blank and S_{b1} is the standard deviation of the blank [26]. The result of the analysis is presented in (Table 1) below. Hence FAAS is a robust technique for the metals determination.

Table 1. LODs and LOQs, of analyzed metals.

Metal	LOD	LOQ
	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$
Pb	0.30	0.90
Cu	0.31	0.96
Cd	0.23	0.69
Ni	0.24	0.72

Results and Discussion

Adsorbent characterization

The physicochemical characteristics of the adsorbent are shown in (Table 2). PMSAC had low

percentage values of moisture, ash, and volatile matter, an indication that the adsorbent has relatively small particle density. It is known that high ash content reduces the efficiency of an activated carbon to adsorb metals and good adsorbents usually have lower ash values [27]. The fixed carbon of PMSAC was 82.8 % with pore volume of $4.0 \times 10^{-3} \text{ m}^3/\text{g}$, which was high. Bigger pore volumes are required to adsorb bigger molecules from aqueous media. The bulk density of the adsorbent (PMSAC) was higher than the lower limit of bulk density (0.25 gml^{-1}) according to AWWA [28]. The pH_{zpc} of PMSAC showed that the adsorbent is slightly acidic having pH value of 6.8. Adsorbent with pH values of 6 to 8 are most useful in many applications [29].

Table 2. Physicochemical Properties of PMSAC.

Physical parameters	Values
Moisture	4.2 %
Volatile matter	11.2 %
Ash	1.8 %
Fixed carbon	82.8 %
Pore volume	$4.0 \times 10^{-3} \text{ m}^3/\text{g}$
Bulk density	0.36 gml^{-1}
pH	6.8
Conductivity	$301 \mu\text{S}/\text{cm}$
Energy Value	1.8 KJ/mol

The electrical conductivity of the adsorbent (PMSAC) was $301 \mu\text{S}/\text{cm}$. Conductivity value gives an idea of the presence of leachable materials considered as impurity and undesirable in pure and well prepared adsorbent [25]. The energy value of PMSAC was high (1.8 KJ/mol). Energy content shows the closeness to graphite carbon allotrope the activated carbon is. Higher energy values show efficient carbonization and good activation leading to better quality activated carbon.

Figure 1 shows the SEM image of PMSAC which has irregular and porous surface structure. (Fig. 2) presents the energy dispersive x-ray spectrum of the adsorbent showing that it contains mainly Carbon, Oxygen, and Phosphorus. Carbon has the higher concentration value as shown in (Table 3), indicating that the adsorbent (PMSAC) is mainly of carbon.

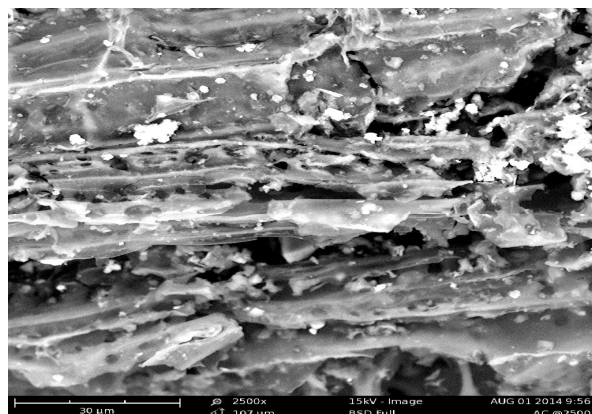


Figure 1. SEM Image of *Pentaclethra Macrophylla* Stem Activated Carbon (PMSAC)

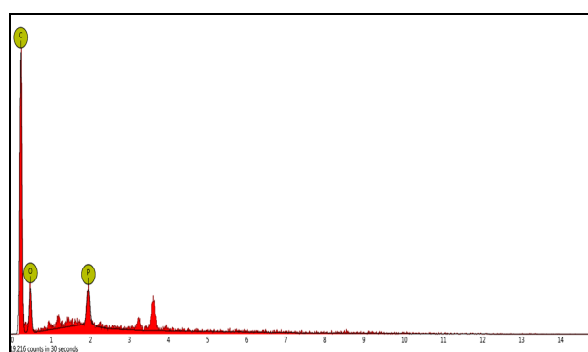


Figure 2. Energy Dispersive X-ray Spectrum of PMSAC

Table 3. Elemental Analysis of PMSAC.

Element Number	Element Symbol	Element Name	Confidence	Concentration	Error
6	C	Carbon	100.0	62.1	3.8
8	O	Oxygen	100.0	31.4	1.5
15	P	Phosphorus	100.0	6.5	4.1

Effect of solution pH

The pH of a solution alters the surface charge of the biosorbent and the extent of ionization of the adsorbate. The effect of pH on simultaneous adsorption Pb(II), Cu(II), Cd(II) and Ni(II) by PMSAC is shown in (Fig. 3). It can be seen that there was a peak adsorption at pH of 6. The pH value of 6.0 was chosen to be the optimal pH in this study for all other experiments. Several reports indicated pH of 5 – 6 as optimum for adsorption of Pb(II), Cu(II) and Zn (II) from aqueous solutions. [20, 30-33]. The adsorption reduced as the pH values was lowered. This is due more protonation of the active sites thereby

making them less available to retain the studied metal ions. When pH increases, formation of hydroxylated complexes of the metal ions which are soluble compete with the active sites hence decreasing metal retention in the adsorbent [34, 19].

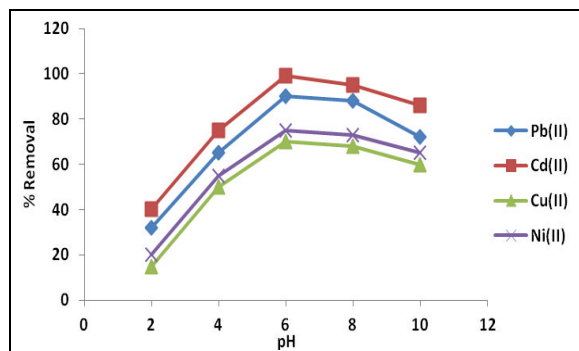


Figure 3. Adsorption of Pb(II), Cd(II), Cu(II) and Ni(II) by PMSAC at different pH values.

Initial metal ions concentration

The rate of metal ions adsorption by adsorbent depends on the initial metal ions concentration. The influence of initial metal ion levels on the adsorption by PMSAC is presented in (Fig. 4). The percentage removal for all the studied metal ions decreased with increase in the amount of metal ions from 5 to 20 mg/L. The percentage removal was of the order: Pb(II) > Cd(II) > Ni(II) > Cu(II) at equal concentrations. The decrease in the percentage adsorption could be accounted for by the fact that biosorbents have already fixed number of active sites which get saturated at higher concentrations leading to lower percentage removal of the metal ions by PMSAC [34].

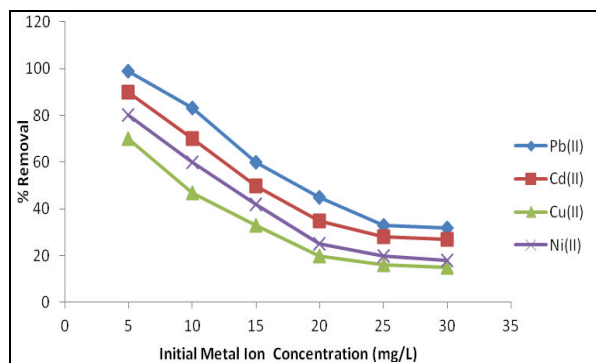


Figure 4. Adsorption of Pb(II), Cd(II), Cu(II) and Ni(II) by PMSAC at different initial metal ion concentrations

Contact time

The effect of contact time on the removal of Pb(II), Cd(II), Cu(II) and Ni(II) was investigated at various contact time ranging from 30 to 150 minutes and the result is presented in (Fig. 5). The optimal simultaneous removal of Pb(II), Cd(II), Cu(II) and Ni(II) was reached at 90 minutes. At this time, the maximum amount of the metal ions was adsorbed. The decreased uptake of the metal ions was probably due to reduced available active sites for adsorption as a result of saturation of the active surface sites of PMSAC with metal ions [2].

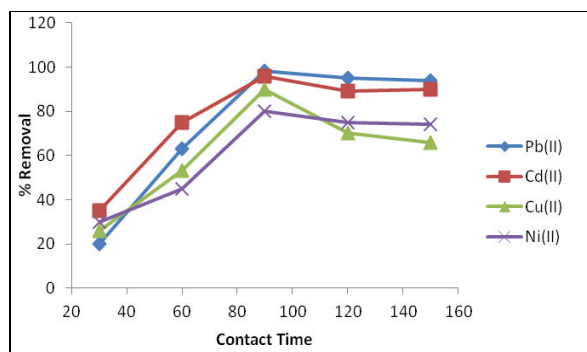


Figure 5. Adsorption of Pb(II), Cd(II), Cu(II) and Ni(II) by PMSAC at different contact time.

Adsorbent dosage

Increase in mass of PMSAC from 1.0 to 4.0 g led to a corresponding increase in the amount of the metal ions. This resulted from an increase in available active sites on the surface of the PMSAC. The uptake of Pb(II), Cu(II) and Ni(II) was maximum at adsorbent dose of 4 g and 3 g for Cd(II). Thereafter no significant increase was observed.

Particle size

The influence of the adsorbent particle sizes on the adsorption of the metal indicated an increase in percentage removal as the particle size increased from 30 to 150 μm . This could be attributed to increased total surface area which provided more active sites for adsorption [2]. With higher particle sizes, the active sites decrease [30].

Carbonization temperature

The results showed that adsorption of metal ion by PMSAC increase with increase in carbonization temperature and fairly decrease at carbonization temperature above 400 °C. It was earlier reported that the temperature of carbonization affects the molecular arrangement of the material by opening up more internal pores [19].

Adsorption isotherm

The adsorption isotherms provide useful information on sorption mechanism, surface properties and affinity of the adsorbent [34]. The Langmuir, Freundlich and Dubinin-Radushkevich isotherms models were used to analyze the equilibrium data. The results of the tests are shown in Table 4. The Langmuir isotherm model assumes that uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules [34, 35]. The linear form of the Langmuir isotherm model is:

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

Where q_e represents adsorption capacity of the adsorbent (mg/g), K_L is the Langmuir adsorption constant (L/mg) and q_L is the maximum adsorption capacity of adsorbent (mg/g). The constants q_L and K_L can be determined from the slope and the intercept of the linear plot of C_e/q_e against C_e .

The essential features, separation factor (R_L) of the Langmuir isotherm is expressed as:

$$R_L = \frac{1}{1 + K_L C_i} \quad (4)$$

Where C_i is the initial metal ion concentration (mg/L) and K_L is the Langmuir equilibrium constant (L/mg). The R_L value gives idea of the nature of the adsorption process. Hence, adsorption is termed irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) [34]. From Table 3, the correlation coefficient (R^2) for Langmuir isotherm gave a good fit.

The Freundlich isotherm model is mostly used to non-ideal sorption on heterogeneous surfaces. The linear form of the model equation is [36]:

$$\log q_e = \log K_f + \left[\frac{1}{n} \right] \log C_e \quad (5)$$

where K_f (mg/g) and n are Freundlich adsorption constants relating to adsorption capacity and amount of the adsorbents respectively. A linear plot of $\log q_e$ versus $\log C_e$ estimates the constants. In Freundlich isotherm model, if the value of n lies between 1 and 10, it is a favorable adsorption [35]. In this study, the value of n obtained for adsorption of metal ions by the adsorbent (PMSAC) where in the range 1.417 to 2.382 indicating a favorable adsorption process.

Dubinin-Radushkevich (D-R) isotherm model was also applied in the analysis of the experimental data. The linear form of the D-R isotherm model is:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (6)$$

where β relates to the mean free energy of adsorption per mol of the adsorbate (mol²/J²), q_m is equal to the theoretical saturation capacity (mg/g) and ε is the Polanyi potential expressed as:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

Given that R (J/mol K) is the gas constant at absolute temperature T (K). The D-R constants q_m and β were estimated from the linear plot of $\ln q_e$ versus ε^2 .

The energy values obtained were below 8 KJ/mol (1.581 – 3.536 KJ/mol). Dubinin-Radushkevich (D-R) isotherm model interpretation is that adsorption with energy value below 8 KJ/mol occurs via physisorption [35]. All the studied metal ions on adsorption onto PMSAC were through physisorption process.

Although the Freundlich and Langmuir isotherms gave the best fit to the experimental data having regression coefficient (R^2) values closer

to 1, Dubinin-Radushkevich (D-R) isotherm was best fit for Cd(II) and Cu(II) ions adsorption by PMSAC.

Table 4. Result of isotherm models for adsorption onto PMSAC.

ISOTHERM MODELS	Pb(II)	Cd(II)	Cu(II)	Ni(II)
Langmuir model				
q_L (mg/g)	0.607	0.6468	0.3128	0.3939
K_L (L/mg)	-3.876	1.1739	3.3026	-5.2889
R^2	0.991	0.949	0.985	0.987
Freundlich model				
K_f (mg/g) (mg/L) ^{1/n}	1.663	0.731	0.299	0.195
N	2.382	1.923	2.412	1.417
R^2	0.992	0.992	0.998	0.986
Dubinin-Radushkevich model				
q_m (mg/g)	1.4202	1.786	2.983	0.779
β (mol ² /kJ ²)	-6.0x10 ⁻⁸	-2.0x10 ⁻⁷	-8.0x10 ⁻⁸	-1.0x10 ⁻⁷
R^2	0.654	0.921	0.981	0.751

Table 5. Langmuir equilibrium parameter (R_L) ranges for adsorption of Pb(II), Cd (II), Cu(II) and Ni(II) unto PMSAC.

METAL IONS	R_L VALUES
Pb(II)	0.839 – 0.160
Cd(II)	0.616 – 0.120
Cu(II)	0.953 – 0.207
Ni(II)	0.781 – 0.398

The R_L values in Table 5 at different initial adsorbate concentrations for all the metal ions used in this study indicate a favourable adsorption process.

Adsorption kinetics

Applications of adsorption kinetic models to the experimental data were used to analyze the adsorption rate and the possible adsorption mechanism of the metal ions onto PMSAC. The pseudo first order, pseudo second order and the intraparticle diffusion equation kinetic models were applied and the results as shown in Table 5. The pseudo-first order kinetic model (Lagergren equation) is expressed as:

$$\log q_e - q_t = \log q_e - \left(\frac{K_1 t}{2.303} \right) \quad (8)$$

where q_t and q_e represent the amounts of metal ions adsorbed at time t and at equilibrium in (mg/g) respectively. K_1 is the pseudo-first order adsorption rate constant (min^{-1}). A slope and intercept of the plots of $\log(q_e - q_t)$ versus t were used to estimate the rate constant (K_1) and q_e . The pseudo-first order equation was unfit to describe the kinetics of the adsorption. The Pseudo second-order kinetic model assumes that chemisorption is the rate determining step. The model equation is:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e} \right) t \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e} \right) t \quad (10)$$

t = contact time (min), q_t and q_e are the amounts of metal ions adsorbed at time and at equilibrium in (mg/g), K_2 = equilibrium rate constant of pseudo-second order adsorption (g/mg min). The values of q_e and K_2 were estimated from the slope and intercept of the linear plot of $\frac{t}{q_t}$ against t . The initial sorption rate, h (mg/gmin), was got from the equation:

$$h = K_2 q_e^2 \quad (11)$$

The pseudo-second order equation provided the best fit to the experimental result.

The kinetic data were subjected to the Weber and Morris intraparticle diffusion model equation analysis thus:

$$q_t = K_{id} t^{1/2} + I \quad (12)$$

K_{id} is the intraparticle diffusion rate constant ($\text{mg/gmin}^{1/2}$) and I is the intercept. The intercept of the plot indicated the boundary layer effect. Intraparticle diffusion is assumed to be the sole rate-determining step if the plot is linear and passes through the origin [38].

In tables 5, high regression coefficient (R^2) values for all the metal ions and the presence of the intercept (I) pointed to the presence of

intraparticle diffusion as possible but not the sole mechanism.

Adsorption thermodynamics

An increase in the metals ions adsorption with increase in solution temperature from 305 to 325 K was recorded indicating an endothermic process. Such increase could be as a result of a more kinetic energy acquired by the metal ions which makes the diffusion easier to the surface of the adsorbent [19].

The standard free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were evaluated to assess the feasibility of the adsorption process. The ΔG° is related to the thermodynamic equilibrium constant (K_c) thus:

$$\Delta G^\circ = RT \ln K_c \quad (13)$$

T = temperature (K)
R = ideal gas constant (8.314 J/mol K) and
 K_c is defined by the equation:

$$K_c = \frac{C_a}{C_e} \quad (14)$$

and C_a is the metal ion concentration adsorbed from solution at equilibrium (mg/L) and C_e is the equilibrium metal ion concentration in solution (mg/L).

The Gibb's free energy ΔG° is related to the enthalpy change (ΔH°) and entropy change (ΔS°) at a constant temperature by the Van't Hoff equation as shown below:

$$\ln K_c = -\left(\frac{\Delta G^\circ}{RT}\right) = -\left(\frac{\Delta H^\circ}{RT}\right) + \left(\frac{\Delta S^\circ}{R}\right) \quad 15$$

The values of enthalpy change (ΔH°) and entropy change (ΔS°) were estimated from the slope and intercept of the plot ($\ln K_c$ versus $1/T$). The thermodynamic parameter values are presented in Table 5. Values of enthalpy change (ΔH°) for all the metal ions are positive, indicating the endothermic process. The positive entropy change (ΔS°) indicated an increase of sorption at the solid/liquid interface during the adsorption

process [39]. An observed increase in the change of ΔG° with increase in temperature indicates an increased spontaneity of the process. The magnitude of ΔH° gives an idea of the sorption type. Hence, for physisorption ΔH° lies between 2.1–20.9 kJ/mol, while that of chemisorption is in the range of 80–200 kJ/mol [40]. Table 5 shows the values of ΔH° for studied metals could be ascribe to a physical adsorption process.

Conclusion

The present investigation showed that *Pentaclethra Macrophylla* stem activated carbon (PMSAC) can be successfully utilized as a low-cost adsorbent for the simultaneous removal of Pb(II), Cd(II), Cu(II) and Ni(II) ions from aqueous solution by batch adsorption method. The results indicated that adsorption capacity of the adsorbent was influenced by solution pH, initial metal ion concentration, contact time, adsorbent dosage, particle sizes, carbonization temperature and solution temperatures. The result indicated that Cd(II) and Pb(II) ions shows higher percentage removal by PMSAC. The uptake of all the metal ions decreased with increased in initial metal ions concentration by PMSAC. The uptake of metal ions increased with increase in the agitation time till the equilibrium time (90 minutes) was reached. Percentage of metal ions removal increased with increase in adsorbent dosage due to increased adsorption surface area and more active site. The percentage adsorption of the metal ions onto the adsorbent decreased with increased in particle size of adsorbent due to a decrease in the adsorption sites of the adsorbent. There was a sharp increase in the percentage removal of metal ions onto PMSAC at carbonization temperature ranges (300 - 400 °C) with a slight decrease at 450 °C due to damaged cells of the adsorption site which enhance the adsorption capacity.

The influence of solution temperature on the adsorption shows a slight increase in the adsorption of the metal ions with increase in solution temperature from 305 to 325 K, indicating that the process is endothermic.

Equilibrium data fitted into the Langmuir isotherm model for adsorption process having R_L

values less than 1. Dubinin-Radushkevich isotherm model reveal that the adsorption process is physisorption having the energy E value less than 8 KJ/mol [33].

The kinetic models tested indicated that pseudo-second order as the best fit and the presence of intraparticle diffusion during the sorption of the metal ions. Furthermore, due to high percentage removal of the metal ions from aqueous solution suggest that *Pentaclethra Macrophylla* stem activated carbon (PMSAC) has potentials to be used as a cheap adsorbent.

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References

1. P. Satish, R. Sameer and P. Naseema, *Int. J. Environ. Sci.*, 3 (2012) 322.
[DOI: 10.6088/ijes.2012030131031](https://doi.org/10.6088/ijes.2012030131031).
2. O. A. Ekpete, M. Horsfall Jnr. and T. Tarawou. *ARPN J. Eng. Appl. Sci.*, 5 (2010) 26.
http://www.arpnjournals.com/jeas/research_papers/rp_2010/jeas_0910_384.pdf
3. H. Serencam, A. Gundogdu, Y. Uygur, B. Kemar, V. N. Bulut, C. Duran, M. Soylek and M. Tufekci, *Bioresource Technol.*, 99 (2008) 1992.
<https://doi.org/10.1016/j.biortech.2007.03.021>
4. G. Issabayeva, M. K. Aroua and N. M. Sulaiman, *Desalination*, 262 (2010) 94.
<https://doi.org/10.1016/j.desal.2010.05.051>
5. F. Fu and Q. Wang, *J. Environ. Manage.*, 92 (2010) 407.
<https://doi.org/10.1016/j.jenvman.2010.11.011>
6. B. H. Hameed, A. T. M Din and A. L. Ahmad, *J. Hazard Mater.*, 14 (2007) 819.
<https://doi.org/10.1016/j.jhazmat.2006.07.049>
7. S. S. Ahluwalia and D. Goyal, *Bioresource Technol.*, 98 (2005) 2243.
<https://doi.org/10.1016/j.biortech.2005.12.006>
8. R. Abdul, Z. Yacob. M. Abdul. S. Ratna, D. Dewi and I. Vincinisvarri., *The Malay J. Anal. Sci.*, 1 (2008) 264.
9. B. S. Grigis and M. F. Ishak, *Mate Letters* 39 (1999) 107.
[https://doi.org/10.1016/S0167-577X\(98\)00225-0](https://doi.org/10.1016/S0167-577X(98)00225-0)
10. Z. Y. Yao, J. H. Qi and L. H. Wang, *J. Hazard Mater.*, 174 (2010) 137.
<https://doi.org/10.1016/j.jhazmat.2009.09.027>
11. WHO. Cadmium in Drinking-water, *WHO Guidelines for Drinking-water Quality*, 3rd Edition, Geneva, Switzerland (2008)
https://www.who.int/water_sanitation_health/dwq/fulltext.pdf
12. A. R. Iftikhar, H. N. Bhatti, V. Hanif and R. Nadeem, *J. Hazard. Mater.* 16 (2009) 941.
<https://doi.org/10.1016/j.jhazmat.2008.04.040>
13. R. Wang, Q. Li, D. Xie, H. Xiao and H. Lu, *Appl. Surf. Sci.*, 279 (2013) 129.
<https://doi.org/10.1016/j.apsusc.2013.04.049>
14. R. Yavuz, H. Akyildiz, N. Karatepe and E. C. Etinkaya, *Fuel Process Technol.* 91 (2010) 80.
<https://doi.org/10.1016/j.fuproc.2009.08.018>
15. B. Singha and S. K. Das, *Colloids Surfaces B: Biointerfaces*, 107 (2013) 97.
<https://doi.org/10.1016/j.colsurfb.2013.01.060>
16. W. Choi, S. G. Chung, S. W. Hong, D. J. Kim and S. H. Lee, *Water Air Soil Pollut.* 223 (2011) 1837.
<https://doi.org/10.1007/s11270-011-0988-1>
17. C. Duan, N. Zhao, X. Yu, X. Zhang and J. Xu, *Cellulose*, 20 (2013) 849.
<https://doi.org/10.1007/s10570-013-9875-9>
18. S. M. Andrabi, *Eur. J. Wood Wood Products*, 69 (2010) 75.
<https://doi.org/10.1007/s00107-009-0398-x>
19. N. R. Ekere, B. A. Agwogie and J. N. Ihedioha, *Int. J. Phytoremediat.* 18 (2015) 116.
<https://doi.org/10.1080/15226514.2015.1058329>
20. M. Makeswari and T. Santhi, *Res. Chem. Intermediat.*, (2013) 1.
<https://dx.doi.org/10.1016/j.arabjc.2013.10.005>

21. C. Orwa, A. Mutua, R. Kindt, R. Jamnadass and S. Anthony, *Agroforest tree Database: a tree reference and selection guide version 4.0* (2009) (available at: <http://www.worldagroforestry.org/sites/treedatabases/treedatabases.asp> accessed on 4 November 2015).
22. D. O. Ladipo, B. T. Kang and M. J. Swift, *Nitrogen Fixing Tree Research Reports* 11 (1993) 104. <https://www.winrock.org/factnet-a-lasting-impact/fact-net-research-reports/nitrogen-fixing-tree-research-reports-volume-11-1993/>
23. ASTM, *Standard test methods for moisture in activated carbon*. Philadelphia, PA: ASTM Committee on Standards. (1999). <http://archive.wcponline.com/pdf/0802astm.pdf>
24. O. A. Ekpete, M. Horsfall, Jnr, E. N. Verla and A. W. Verla, *Res. J. Chem. Sci.*, 3 (2011) 39. <http://www.isca.in/rjcs/Archives/v1/i3/02.pdf>
25. D. I. Mall, V. C. Srivastava and N. K. Agarwal, *Dyes and Pigments*, 69 (2006) 210. <https://doi.org/10.1016/j.dyepig.2005.03.013>
26. Shrivastava and V. B. Gupta. *Chron Young Sci.*, 2 (2011) 21. DOI:10.4103/2229-5186.79345
27. V. K. Gupta and I. Ali, *J. Colloid Interface Sci.*, 271 (2004) 321. <https://doi.org/10.1016/j.jcis.2003.11.007>
28. American Water Works Association, (AWWA), *Standards for granular activated carbons*. USA. (1991) <https://store.awwa.org/store/productdetail.aspx?productid=18525>
29. F. E. Okieimen, C. O. Okieimen and R. A. Wuana, *J. Chem. Sci.*, 32 (2007) 126. <http://www.sciepub.com/reference/152370>
30. M. Rafatullah, O. Sulaiman, R. Hashim and A. Ahmad, *J. Disper. Sci. Technol.*, 3 (2010) 918. [doi/abs/10.1080/01932690903224003](https://doi.org/10.1080/01932690903224003)
31. G. A. Mahmoud, *Monatshefte for Chemie-Chem. Monthly*, (2013) 1. <https://link.springer.com/article/10.1007/s00706-013-0957-z>
32. G. Chen, J. Fan, R. Liu, G. Zeng, A. Chen, and Z. Zou, *Environ. Technol.*, 33 (2012) 2653. <https://doi.org/10.1080/09593330.2012.673015>
33. J. S. Al-Jariri and F. Khalili, *Desalination Water Treatment*, 21 (2012) 308. <https://doi.org/10.5004/dwt.2010.1623>
34. A. D. Folasegun and G. A. Kovo, *J. Mater. Res. Technol.*, 3 (2014) 129. <https://doi.org/10.1016/j.jmrt.2014.03.002>
35. M. Ahmedna, W. E. Marshall and R.M. Rao, *Bulletin of Louisiana State University Agricultural Center*, 54 (2000) 45. <https://digitalcommons.lsu.edu/cgi/viewcontent.cgi?referer=https://www.google.com/&httpsredir=1&article=1455&context=agexp>
36. I. Langmuir, *J. Ame. Chem. Soc.*, 38 (1916). 2221. <https://doi.org/10.1021/ja02268a002>
37. H. M. F. Freundlich, *J. Phys. Chem.*, 57, (1906) 385. <https://doi.org/10.1515/zpch-1907-5723>
38. K. R. Hall, L. C. Eagleton, A. Acrivos and T. Vermeulen, *Industr. Engr. Chem. Fundament*, 5 (1966) 212. <https://doi.org/10.1021/i160018a011>
39. H. Uzun, Y. K. Bayhan and Y. Kaya, *J. Hazard. Mater.*, 153 (2008) 52. <https://doi.org/10.1016/j.jhazmat.2007.08.018>
40. T. Fan, Y. Liu, B. Feng, G. Zeng, C. Yan, M. Zhou, H. Zhou, Z. Tan and X. Wang, *J. Hazard Mater*, 160 (2008) 655. <https://doi.org/10.1016/j.jhazmat.2008.03.038>