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Surface Modification of Powdered Maize Husk with Sodium Hydroxide for Enhanced Adsorption of Pb(II) Ions from Aqueous Solution

Chidi E. Duru¹* Margaret C. Enedoh¹, Ijeoma A. Duru²

¹Surface Chemistry and Environmental Technology (SCENT) Research Unit, Department of Chemistry, Imo State University, Owerri, PMB 2000, Imo State, Nigeria.

²Federal University of Technology Owerri, Department of Chemistry, PMB 1526, Imo State Nigeria

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Abstract

The impact of sodium hydroxide pretreatment of maize husk on its lead ion removal efficiency was investigated. Pretreatment of maize husk with this alkali increased its surface area and porosity from $528.74 \text{ m}^2/\text{g}$ and $0.477 \text{ cm}^3/\text{g}$ to $721.54 \text{ m}^2/\text{g}$ and $0.642 \text{ cm}^3/\text{g}$, respectively. Batch adsorption studies were carried out to evaluate the effects of initial pH, adsorbent dose, initial lead ion concentration, initial solution temperature, and contact time on the adsorption process. The maximum removal efficiency of maize husk at pH 5 and adsorbent dose 2 g/L was 62.85 %, which increased to 82.84 % after pretreatment and was attained in 15 min. The adsorption data for the natural and pretreated maize husk were best fitted in the Freundlich isotherm model, with their adsorption intensity (n) having values >1, which indicated that lead ion adsorption onto the adsorbent types was a favorable physical process. The adsorption of lead ions onto the adsorbents followed the pseudo-first-order kinetic model. The experimental adsorption capacities of maize husk (31.43 mg/g) and its modified form (41.22 mg/g) were very close to those obtained from this model (31.03 mg/g and 40.65 mg/g respectively). The ΔH and ΔG values of the adsorption process showed that the adsorption of lead ions by both adsorbents was an endothermic process and occurred spontaneously. Alkali pretreated maize husk can therefore be used as a cheap adsorbent to remove lead ions from aqueous solution.

Keywords: Lead, maize husk, adsorbent, pretreatment, isotherm

1 Introduction

The various industrial activities going on in different parts of the world are the primary sources of soil and water pollution by heavy metals. Toxic metals like mercury, chromium, cadmium, arsenic, nickel, and lead have been reported to be in high concentrations in industrial wastewater due to different manufacturing activities [1]. The presence of lead in both surface and borehole water above regulated concentrations has been observed even though its widespread use was discontinued in many countries of the world [2]. It is still used in many industrial production processes like smelting, refining, car repair, battery manufacturing, and many others. It is highly poisonous and can affect almost every organ in the body, especially the nervous system. Its toxicity in children has a more significant impact than in adults because they have softer tissues, internal and external organs. It has resulted in severe health conditions like behavioral problems, learning deficits,

Coresponding author: Chidi E. Duru, Surface Chemistry and Environmental Technology (SCENT) Research Unit, Department of Chemistry, Imo State University, Owerri, PMB 2000, Imo State, Nigeria. E-mail: chidiedbertduru@gmail.com, Tel: +2348037131739

lowered intelligence quotient, anemia, increased blood pressure, damage to the brain and kidneys, miscarriage, reduction in male fertility, blood disorders, and death [3].

Conventional treatment techniques chemical like precipitation, ion exchange, membrane process, crystallization, and electrochemical treatment have been used to remove toxic metals from polluted water [4]. These processes are expensive and inefficient when the heavy metal ions are contained in the water at concentrations below 100 mg/L [5]. Researchers are currently exploring the potentials of agro-waste materials in the adsorption of metal ions from polluted water [6, 7, 8, 9]. The findings from these studies have been very promising. The merits of using plant wastes in wastewater treatment include availability, low cost, selective adsorption of heavy metal ions, good adsorption capacity, and regeneration potential.

Most adsorption studies have focused on the use of untreated plant wastes in heavy metal removal from water. Recently, the pretreatment of plant waste to extract soluble organic compounds introduced into the treated water and enhance their chelating efficiencies has been applied by many researchers [10,11]. Pretreatment methods involving the use of different modifying agents like mineral and organic acid solutions (hydrochloric acid, nitric acid, sulphuric acid, tartaric acid, citric acid, etc.), base solutions (sodium hydroxide, calcium

hydroxide, sodium carbonate), oxidizing agent (hydrogen peroxide), organic compounds (ethylenediamine, formaldehyde, methanol), to eliminate coloration of the aqueous solution, remove soluble organic compounds and increase metal adsorption efficiency have been applied in many studies [12,13,14]. Chemical modification can sometimes improve the adsorption efficiency of biomass by increasing the number of binding sites, providing better ion-exchange properties, and forms new functional groups that favor metal uptake.

Southeastern Nigeria and many other parts of the world produce millions of tons of maize kernel annually. The enormous amounts of maize husk waste generated after the harvest have posed serious disposal challenges in the towns and cities. Recently, it has been shown that this plant waste is rich in minerals like calcium, sulphur, potassium, and many phytochemicals with medicinal value [15]. Studies on applying this biomass as an adsorbent for zinc, iron, and copper uptake have given very promising results [16, 17, 18, 19]. There has been no attempt to use maize husk in the past or recent times, whether in natural or pretreated forms, to adsorb lead from aqueous solutions. In this study, the effect of initial solution pH, biomass load, initial metal concentration, and contact time on the adsorption of lead onto a natural and sodium hydroxide pretreated maize husk were determined. Isotherm and kinetic models were used to give a better insight into the mechanisms of the adsorption process.

2 Materials and Methods

2.1 Adsorbent collection, preparation, and modification

Maize seeds (genus Oba super II) from the National Agriculture Food Council, Umudike, Abia State Nigeria, were collected and planted by the researchers. At maturity, the husks were collected, thoroughly washed with tap water, and then rewashed with deionized water. They were sun-dried for two days and then oven-dried at 100 °C for 4 h. The dried husks were ground into powder using an electric grinder and sieved to a particle size of 30 mesh using American Society for Testing and Materials (ASTM) standard sieves. Maize husk powder (H) was then pretreated using NaOH solution. This process was carried out by soaking 10 g of H in 500 mL of 1 M solution of the alkali. The mixture was stirred for several minutes and allowed to stand for 24 hours. It was filtered, washed severally with deionized water until the filtrate was neutral to litmus, and then allowed to dry at room temperature for a few days. The dried crumbs of the modified maize husk (HP) were ground to a fine powder (Figure 1) and stored in a desiccator [19].

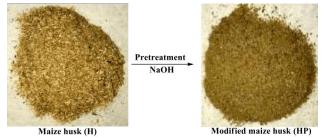


Figure 1: Conversion of maize husk into the pretreated form

2.2 Preparation of Metal Solutions

All the chemicals used were of analytical reagent grade and were prepared with distilled water in all the experiments. The metal stock solution was prepared by dissolving appropriate amounts of lead (II) nitrate, Pb(NO₃)₂ (M.W: 331.21 g/mol; Assay: 99.0 %, Loba Chemie, India) in distilled water. Working standards were prepared by progressive dilution of the stock lead solution with distilled water.

2.3 Experimental Procedure

2.3.1 Analysis of physical and chemical properties of adsorbents

The adsorbents' surface areas and pore sizes were determined at 77 K from nitrogen adsorption isotherms using a High-Speed Surface Area and Pore Size Analyzer, Model: Nova 4200e (Quantachrome Instruments, USA). Before analysis, the adsorbents were dried and degassed at 110 °C until a residual vacuum of less than 0.02 mbar. The multi-point BET plot method was used to determine the specific surface areas, and the t-plot method was used to assess the microporosity of the adsorbent samples. The determination of the mineral element composition of H and HP was carried out using EDX3600B Xray fluorescence spectrophotometer. The samples were pulverized to a fine homogenous size, and the resulting powder pelletized. The fluorescence spectrophotometer was calibrated using pure silver standard and the working curve for the sample selected before the samples' energy dispersive X-ray spectra were obtained. Chemical analysis of the adsorbents was performed using Chesson-Datta gravimetric method [20, 21]. 1 g of the powdered adsorbent (v) was added into 150 mL of deionized water in a beaker, and the mixture was heated in a water bath at 100 °C for 1 h. After this period, the mixture was allowed to cool, and the residue was obtained by filtration and rinsed with 300 mL warm deionized water. This residue was oven-dried to constant weight (w). It was then mixed with 150 mL of 1 M H₂SO₄ and heated in a water bath at 100 °C for 1 h. The mixture was filtered, and the residue was rinsed with 300 mL of deionized water and dried (x). It was immersed in 10 mL of 72 % H₂SO₄ at ambient temperature for 4 h, and then 150 mL I M H₂SO₄ was added into the mixture and refluxed in a water bath for 1 h. The solid obtained after refluxing was rinsed with 400 mL of deionized water and heated in an oven at 105 °C and weighed until a constant weight was achieved (y). The solid was finally heated in a kiln at 600 °C till the attainment of ash. The ash obtained was cooled and weighed (z). The cellulose, hemicelluloses, and lignin content of H and HP were estimated as follows:

$$\% \text{ Cellulose} = \frac{x - y}{v} \times 100 \tag{1}$$

% Hemicellulose =
$$\frac{w-x}{r} \times 100$$
 (2)

$$\% \text{ Lignin} = \frac{y - z}{v} \times 100 \tag{3}$$

2.3.1 Adsorption studies

The batch process was used in all the adsorption experiments in a thermostatic water bath shaker set at 30 °C. 0.2 g of adsorbent was placed in 250 mL Erlenmeyer flasks with 100 mL solution of metal ions of the desired concentration. After agitation on the shaker water bath at 120 rpm over a

predetermined operation time, the liquid phase was taken out and filtered using 0.45 μ m membrane filters (Millipore Corporation, USA). The final concentration of metal ions in the filtrates was analyzed by a fast sequential flame atomic absorption spectrometer (AAS), model 240FS AA (Agilent Technologies, USA). All the instrumental conditions were optimized for maximum sensitivity, and measurements were performed in triplicates. The number of metal ions adsorbed at equilibrium per unit mass of adsorbent was calculated from Eq. 4. The percentage removal of lead ions from aqueous solution (% r) at a given time t, was calculated from Eq. 5.

$$q_e = \frac{(C_o - C_e).V}{m} \tag{4}$$

$$\% \ r = \frac{(c_o - c_t)}{c_o} \tag{5}$$

where q_e is the quantity of metal adsorbed at equilibrium by the adsorbent (mg/g), C_o is the initial concentration of metal (mg/L), C_e is the equilibrium concentration of the adsorptive (mg/L) in solution, C_t is the concentration of the metal at time t, V is the volume of the solution (L) and m is the mass of adsorbent (g).

2.3.2 Effect of pH

To determine the effect of pH on the adsorption of lead by the adsorbent, 100 mL of test solutions containing 100 mg/L of lead ions at different pH levels (2, 3, 4, and 5) were prepared by adjusting the pH to the desired value using 1 M HCl or 1 M NaOH before adding the adsorbent. The pH measurements were done using a Checker plus pH tester by HANNA. 0.2 g of adsorbent was mixed with the test solution at a given pH, and the mixture agitated for 30 min, at 30 °C. The lead ion concentration in the solution after this period was then determined.

2.3.3 Effect of adsorbent dose

The effect of the dose of adsorbent on the adsorption of lead ions was studied using different biomass concentrations (0.1, 0.2, 0.4, 0.8, 1.2, and 1.4 g) in 100 mL of 100 mg/L of metal ions at initial pH of 5 [22]. After mixing a given weight of adsorbent with the metal solution, the mixture was agitated for 30 min, at 30 °C and the concentration of lead ions in the solution determined.

2.3.4 Adsorption kinetics

Adsorption kinetic experiments were conducted to assess the rate of Pb(II) ion uptake onto H and HP. The effect of contact time on the adsorption of lead ions by the adsorbent was determined at 3 min intervals for 30 min, with an initial lead ion concentration of 100 mg/L and solution initial pH of 5 at 30 °C. 0.2 g of adsorbent was mixed with 100 mL of the metal solution in each flask and agitated. The flasks were withdrawn at the specified time intervals and the lead ion's concentration at a given time determined.

2.3.5 Equilibrium and isotherm studies

The impact of the initial concentration of lead ions (100, 50, 25, and 12.5 mg/L) at initial solution pH of 5, on the adsorption of this metal by the adsorbents, were studied. 0.2 g of a given adsorbent was mixed with 100 mL solution of the metal ion at a

given concentration and agitated for 30 min, at 30 °C. An aliquot was collected from the flask after this time, filtered, and the concentration of lead ions in the filtrate determined.

2.3.6 Thermodynamic studies

The effect of temperature on the uptake of lead ions was conducted by contacting 0.2 g of each adsorbent with 100 mL of lead ion solution at pH 5, and an initial concentration of 100 mg/L. the mixtures were agitated for 30 min in a water bath at different temperatures (30, 35, 40, 45, and 50 °C). The data were used to compute and compare the adsorption process's thermodynamics by the two adsorbent systems.

2.3.7 Mechanistic and surface morphology studies

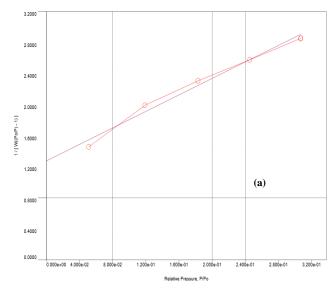
The functional groups on the adsorbent surfaces were detected using Agilent Cary 630 Fourier transform infrared (FTIR) spectrophotometer. The adsorbent sample was mixed with a spatula full of KBr in an agate mortar and ground to a fine powder using a pestle. The powder was pressed to form thin transparent pellets before the infrared spectrum of the adsorbent was taken. Equal loads of H and HP (0.2 g) were stirred in 50 mL of equimolar solutions of lead ions (50 mg/L) for 30 min. They were filtered, washed with deionized water, and dried in a desiccator. The surface morphology of the adsorbents was examined with a scanning electron microscopy (SEM) model Phenom ProX by phenomWorld Eindhoven, The Netherlands. The samples were placed on a double adhesive in a sample stub and then coated with a sputter coater by Quorum Technologies Model Q150R, with 5 nm of gold. After that, they were taken to the chamber of the SEM machine, where they were viewed via Navcam. The brightness contrasting was automatically adjusted, and afterward, the morphologies of different magnification were store in a USB 2.0 flash drive (USB stick).

3 Results and Discussion

The multi-point BET plots for H and HP are shown in Figure 2. The data from these plots showed that H possessed a very large surface area ($528.74~\text{m}^2/\text{g}$), which increased to $721.54~\text{m}^2/\text{g}$ after modification. This is about 36 % increase in the surface area of this biomass after it was modified with alkali. The t-plots for H and HP are shown in Figure 3. The data from these plots showed that both H and HP were highly microporous.

Table 1: Physical and chemical characteristics of H and HP

Adsorbent			HP
BET surface area (m²/g)		528.74	721.54
Pore volume (cm³/g)		0.325	0.368
Micropore volume (cm³/g)	0.477	0.642	
Pore diameter (Å)	2.80	3.00	
	P	0.62	0.55
	S	3.80	2.25
Mineral element analysis (wt %)	K	3.11	0.26
	Са	6.17	6.11
	Fe	0.94	0.93
	Zn	0.21	0.20
	Cellulose	74.22	96.83
Lignocellulose composition (%)	Hemicellulose	20.17	3.41
	Lignin	5.61	0.24



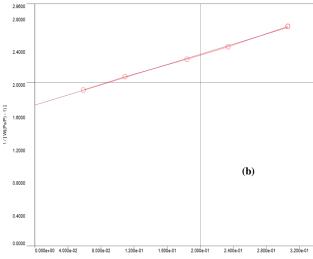
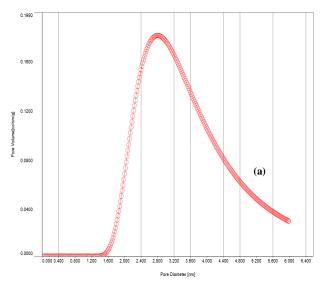


Figure 2: Multi-point BET plots for (a) H (b) HP at 77 K

The micropore volume of H (0.447 cm³/g) increased to 0.642 cm³/g, which is about a 44 % increase in porosity due to modification. The X-ray fluorescence scans of H and HP are shown in Figure 4. The main mineral elements in the biomass were calcium, sulphur, potassium, iron, phosphorus, and zinc. Pretreatment had minimal effect on the mineral composition of the biomass (Table 1). The gravimetric analysis of maize husk showed that it contained 74.22 % cellulose, 20.17 % hemicelluloses, and 5.61 % lignin. After alkali pretreatment, the cellulose yield increased to 96.83 %, with a drop in the hemicelluloses and lignin content to 3.41 % and 0.24 %, respectively. A large amount of hemicellulose and lignin in the maize husk lignocellulose dissolved in the alkali pretreatment solution and washed off with deionized water during the rinsing of the biomass. These observations are in agreement with findings from previous studies [23].

3.1 Effect of pH

The pH of an aqueous solution is an essential factor in the adsorption of metal ions. The effect of pH on the adsorption of Pb ions onto H and HP was studied at pH 2–5 because precipitation of Pb ions from the solution started at pH 5.5 [24, 25]. The adsorbents' Pb ion removal efficiency directly correlated with initial solution pH (Figure 5). The removal efficiency of H at pH 2 was 13.4 %, which increased to 27.1 % after modification. This increase continued from 25.1 % to 37.7 % at pH 3, 33.9 % to 61.7 % at pH 4, and 52.9 % to 73.9 % at pH 5. At lower pH values, H and HP's surface potential were largely positively charged due to their protonation by the high concentration of H⁺ and H₃O⁺ ions in the solution [26].



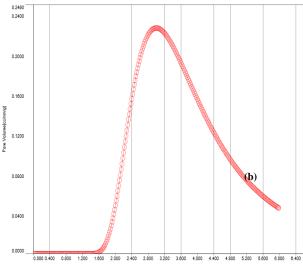


Figure 3: t-plots for (a) H (b) HP at 77 K

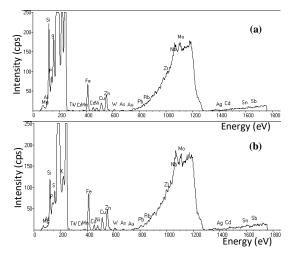


Figure 4: X-ray fluorescence scan of (a) H (b) HP

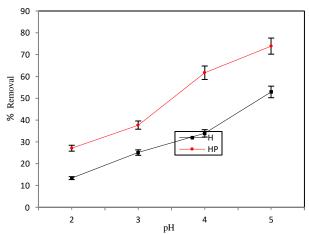


Figure 5: Effect of pH on Pb ion adsorption by H and HP (C_o = 100 mg/L; m = 2 g/L; T = 30 °C)

These charges reduce the attraction of Pb ions in the solution by the surfaces of H and HP. In contrast, an increase in pH created more negatively charged surfaces on H and HP, which facilitated Pb ions' uptake from the solution. These results are in agreement with findings from previous studies [27].

3.2 Effect of adsorbent dose

The effect of different amounts of H and HP on the removal of Pb ions from aqueous solution is shown in Figure 6. The results demonstrated higher removal efficiencies for Pb ions with an increase in the two adsorbents' doses. HP showed a marked increase in its removal efficiency as its load increased in the solution due to the enhanced surface area of this adsorbent [28,29]. The removal efficiencies of H and HP were almost the same at 0.2 g and 0.1 g, 0.4 and 0.2 g, and 0.8 g and 0.4 g doses respectively, indication a 50 % enhancement in efficiency for HP over H. These results showed that pretreatment of H with NaOH could have increased the microporous structure of the biomass thereby creating more adsorption sites for Pb ion uptake. The solubilization of lignin in the alkali pretreatment solution can bring about this adsorption site exposure on the biomass [13].

3.3 Adsorption kinetics

Adsorption kinetic experiments were conducted to determine the adsorption rate of Pb ions onto H and HP, and the results are shown in Figure 7.

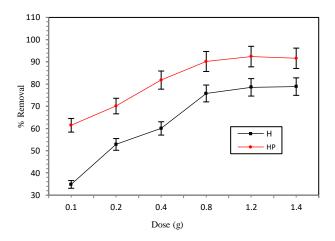


Figure 6: Effect of adsorbent dose on Pb ion adsorption by H and HP (initial pH = 5; C_0 = 100 mg/L; T = 30 °C)

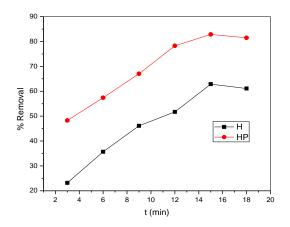


Figure 7: Rate of adsorption of Pb ions by H and HP (initial pH = 5; C_o = 100 mg/L; m = 2 g/L; T = 30 °C)

The plots of In $(q_e - q_t)$ vs t and t/q_t vs t for pseudo-first-order and pseudo-second-order kinetic models are shown in Figure 8. The mathematical and kinetic parameters from the models are summarized in Table 4. These results showed that the data were well fitted in the two kinetic models with the pseudo-first-order model, giving a better fitting as observed in the linear regression correlation coefficient values (R^2) for H and HP. Also, the experimental adsorption capacity (q_e) of the two biomass materials were very similar to those obtained from the models $(q_{e(cal)})$. In other words, the adsorption of lead ions onto H and HP is a pseudo-first-order kinetic process. Also, the pseudo-first-order rate constant for HP was 1.6 times the value obtained for H, suggesting a faster uptake of lead ions by HP.

Table 2: Literature reports on biomass based adsorbents for Pb ion

uptake	from ac	queous	solution
		Initial	

Biomass	Modifier	pН	Initial solution concentration (mg/L)	q _e (mg/g)	References
Sawdust (Pinus sylvestris)	Formaldehyde in Sulfuric acid	5.1	1 – 10	9.78	[30]
Walnut sawdust	Formaldehyde in sulfuric acid	Not stated	10 – 200	4.48	[31]
Cucumber peel	-	5	20 – 100	133.60	[32]
Imperata cylindrica leaf powder	Sodium hydroxide	5	5 – 20	13.50	[33]
Bean husk	-	7	10 - 100	12.66	[34]
Cashew nut shell	Sulfuric acid	Not stated	10 – 50	8.3	[35]
Maize husk	-	2	50 - 300	7.38	[36]
Maize husk	Oxalic acid	2	50 - 300	9.33	[36]
Maize husk	-	5	12.5 - 100	31.43	This study
Maize husk	Sodium hydroxide	5	12.5 – 100	41.22	This study

Table 3. Adsorption kinetic models used in this study

Kinetic model	Linearized forms of equations	Parameters	
Pseudo-first-order model	$ln(q_e - q_t)$ $= lnq_e - k_1 t$	t (min): the contact time k ₁ (min ⁻¹): the pseudo-first order rate constant. q _t (mg/g): adsorption capacity at time t. q _e (mg/g): adsorption capacity at equilibrium.	
Pseudo-second- order model	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	k ₂ (g/mg.min): the pseudo- second order rate constant.	

Table 4: Kinetic parameters obtained from the models

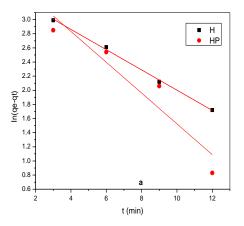
Biomass	q e	Pseudo-first order			Pseudo-second order		
		\mathbb{R}^2	\mathbf{k}_{1}	q _{e(cal)}	\mathbb{R}^2	k_2	$q_{e(cal)}$
Н	31.43	0.9966	0.14	31.03	0.9894	3.11 E-3	40.08
HP	41.22	0.8553	0.23	40.65	0.8539	6.30 E-3	47.62

3.4 Equilibrium and isotherm studies

The adsorption equilibrium data obtained in this study were evaluated using the Langmuir, Freundlich, Elovich, and Dubinin-Radushkevich (D-R) isotherm models [37] (Table 5). A comparison of the R² values from these models indicated that the equilibrium data for H and HP best fitted the Freundlich isotherm model (Figures 9 and 10). The Freundlich isotherm parameters for H and HP are shown in Table 6. The value of n in this model indicates the degree of non-linearity between solution concentration and adsorption as follows: if n = 1, the adsorption is linear; if n > 1, the adsorption is a favorable physical process, and if n < 1, the adsorption is by a chemical process [38]. Therefore, the uptake of lead ions by H and HP occurred on a heterogeneous surface by multilayer adsorption, and the number of ions adsorbed increased infinitely with an increase in concentration [39].

Table 5: Adsorption isotherm models used in this study

Isotherm model	Linearized forms of equations	Parameters
Langmuir Isotherm	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	C_e (mg/L): equilibrium concentration of Pb ions q_m (mg/g): maximum adsorption capacity of the adsorbent K (L/mg): Langmuir constant q_e (mg/g): adsorption capacity at equilibrium C_o (mg/L): initial concentration of Pb ions
Freundlich Isotherm	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	K_F (mg ^{1-$\frac{1}{n}$L$\frac{1}{n}$g⁻¹): relative adsorption capacity of the adsorbent n: adsorption intensity}
Elovich Isotherm	$\ln \frac{q_e}{c_e} = \text{In } K_E q_m - \frac{q_e}{q_m}$	K_{E} (L/mg): Elovich equilibrium constant q_{m} : Elovich maximum adsorption capacity
D–R Isotherm	$\ln q_e = \ln q_s - \beta \epsilon^2$ $\epsilon = RT \ln(1 + \frac{1}{C_e})$	q_s (mg/g): sorption capacity β : activity coefficient related to mean sorption energy ε (J/mol): Polanyi potential R (Jmol- 1 K- 1): 8.314 Γ (K): 303



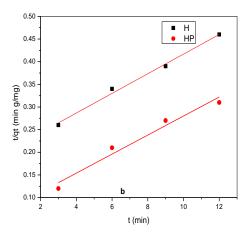


Figure 8: (a) Pseudo first-order (b) Pseudo second-order kinetic plots for H and HP (initial pH = 5; $C_o = 100$ mg/L; m = 2 g/L; T = 30 °C)

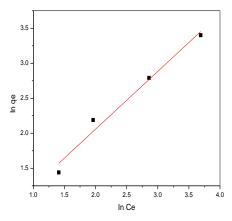


Figure 9: Freundlich isotherm plot for H (initial pH = 5; C_o = 12.5-100 mg/L; m = 2 g/L; T = 30 °C)

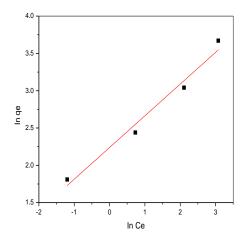


Figure 10: Freundlich isotherm plot for HP (initial pH = 5; C_o = 12.5-100 mg/L; m = 2 g/L; T = 30 °C)

Table 6: Freundlich isotherm parameters for H and HP

Adsorbent	\mathbb{R}^2	n	\mathbf{K}_{F}
Н	0.9866	1.19	1.51
HP	0.9666	3.57	9.38

The n values for H and HP were 1.19 and 3.57, respectively, indicating that lead adsorption on these adsorbents was by a favorable physical process, with the surface of HP favoring this process more than that of H.

3.5 Thermodynamic studies

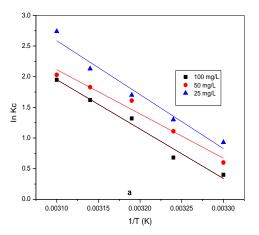
The thermodynamic parameters, including enthalpy change (ΔH), entropy change (ΔS), and free energy change (ΔG), were considered to determine if the adsorptive process occurred spontaneously. The values of ΔH and ΔS were obtained from the Van't Hoff equation:

$$\ln K_c = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{6}$$

where R is the gas constant (8.3145 J/mol K), T is the absolute temperature (K), and ΔH and ΔS were calculated from the slope and intercept of the linear plots of In K_c and $\frac{1}{T}$ (Figure 11). The equilibrium constant (K_c) was calculated from the equation:

$$K_{c} = \frac{c_{Ae}}{c_{e}} \tag{7}$$

where C_{Ae} and C_{e} are the equilibrium concentrations of lead ions (mg/L) on the adsorbent and in the solution, respectively.



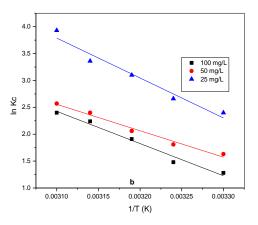


Figure 11: Van't Hoff plot for (a) H (b) HP (initial pH = 5; C_o = 25-100 mg/L; m = 2 g/L; T = 30-50 °C)

The ΔG at 303 K was obtained from the relationship:

$$\Delta G^{o} = \Delta H^{o} - T \Delta S^{o} \tag{8}$$

The positive values of ΔH at the studied initial metal ion concentrations (Table 7) indicated that the adsorption process was endothermic. Lead ions were adsorbed more efficiently onto H and HP at higher temperatures. Similar results have been reported in other studies [40]. The adsorption of lead ions by H

was more favored by an increase in temperature than HP. The free energy of adsorption (ΔG) of lead ions onto H and HP were negative and indicated that the process was spontaneous, and spontaneity increased with an increase in temperature. The positive values of entropy change showed an increase in randomness at the solid/solution interface on H and HP during lead ion adsorption.

Table 7: Thermodynamic parameters for the adsorption of lead ions onto

H and HP						
Adsorbent	Co (mg/L)	\mathbb{R}^2	ΔG	ΔH	ΔS (kJ/mol K)	
			(kJ/mol)	(kJ/mol)		
	100	0.9735	-0.58	66.99	0.223	
H	50	0.9670	-1.47	60.04	0.203	
	25	0.9620	-2.00	73.14	0.248	
	100	0.9734	-3.24	49.79	0.175	
HP	50	0.9755	-4.00	40.84	0.148	
	25	0.9491	-5.54	61.73	0.222	

3.6 Mechanistic studies

The superimposed infrared spectra of H and HP in their natural forms and after lead ion adsorption are shown in Figure 12.

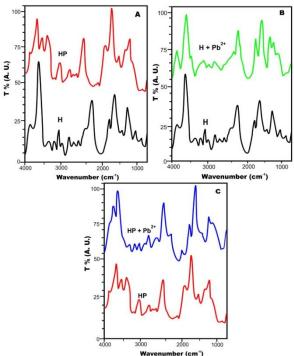


Figure 12: FTIR spectra of (A) H and HP (B) H before and after adsorption (C) HP before and after adsorption

The major bands observed on H were a strong band at 1396.56 cm⁻¹ corresponding to an aromatic –OH, a strong band at 1624.55 cm⁻¹ corresponding to a C=O stretch, a strong and broadband at 3495.59 cm⁻¹ corresponding to an –OH from a polymer and a weak band at 2883.62 cm⁻¹ corresponding to a C-H stretch from alkanes [41]. The absorption peaks initially observed on H became stronger and more prominent on HP, with better separation of peaks at the multiplet bands. After adsorption of lead ions, the absorption band of the –OH in the

polymer shifted to 3488.43 cm⁻¹ in H and disappeared completely in HP. This indicated that the complexation mechanism was involved in the adsorption of lead ions by H and HP. The modification exposed the –OH functional groups on HP for better interaction with lead ions. The disappearance of the –OH band on HP pointed to a greater metal ion adsorption intensity by this adsorbent, which resulted in the shielding of the hydroxyl functional group on it by the adsorbed lead.

3.7 Surface morphology analysis

To predict the change in the adsorbents' surface morphology after modification, the SEM images (Figure 13) of H and HP were taken at ×8000 magnification. The image obtained for H showed a smooth and continuous crystalline surface, which can be attributed to a high presence of lignin on the biomass. After modification, numerous hollow cylindrical shaped pores appeared on HP, which increased its heterogeneity substantially. The highly porous nature of HP would result in an increased surface area, which would create more potential sites for the adsorption of lead ions when compared to H. This indicated that the treatment of H with sodium hydroxide was highly effective in the delignification of the biomass.

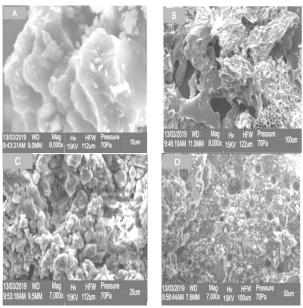


Figure 13: Surface morphology of (A) H (B) HP (C) H after Pb adsorption (D) HP after Pb adsorption

The images of H and HP after the adsorption of lead ions were observed at ×7000 magnification. The surface of H became slightly rough due to the deposition of metal ions on it. The heterogeneity of the surface of HP reduced due to the occupation of the smaller pore spaces by the metal ions. The larger pores remained significant because they had more room for the uptake of metal ions. These observations were clear indications that pretreatment of maize husk's surface using sodium hydroxide was very efficient in increasing its capacity for the uptake of lead ions from aqueous solution.

4 Conclusion

The effect of pretreatment of maize husk on its lead ion adsorption potentials was studied. The data from the multi-point BET plots and t-plots for natural maize husk (H) and its pretreated form (HP) showed that pretreatment significantly increased the surface area of the biomass from 528.74 m²/g to $721.54 \text{ m}^2/\text{g}$, and its porosity from $0.447 \text{ cm}^3/\text{g}$ to $0.642 \text{ cm}^3/\text{g}$. The lead ion removal efficiency of H and HP increased with an increase in pH (2-5) and adsorbent dose (1 g/L - 12 g/L). The maximum lead ion removal efficiency of H and HP was 62.85 % and 82.84 %, respectively, which was attained in 15 min at 30 °C. The experimental equilibrium adsorption capacity of the biomass was 31.43 mg/g, which increased to 41.22 mg/g after modification. The pseudo-first-order kinetic model better explained the rate of lead ion removal from aqueous solution by both adsorbent types. The Freundlich isotherm model was followed in the uptake of lead ions onto the modified and unmodified adsorbent forms, indicating that adsorption of lead occurred on a heterogeneous surface by multilayer adsorption. The positive ΔH values and negative ΔG values for the adsorption process at different initial lead ion concentrations (25 - 100 mg/L) and 2 g/L adsorbent dose showed that lead adsorption onto the biomass types was an endothermic process and occurred spontaneously. Complexation was the observed mechanism followed during the uptake of lead ions onto maize husk and its pretreated form.

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Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors' contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing.

References

- M.S. Abdel-Raouf and A.R.M. Abdul-Raheim, Removal of heavy metals from industrial waste water by biomass-based materials: a review, J. Pollu. Eff. Cont., 5(1) (2017) 180.
- C.E. Duru, M.C. Enedoh and I.A. Duru, Physicochemical assessment of borehole water in a reclaimed section of Nekede mechanic village, Imo State, Nigeria, Chemistry Africa, 2(4) (2019) 689-698
- 3. A.L. Wani, A. Ara and A.J. Usmani, Lead toxicity: a review, Interdiscip. Toxicol., 8(2) (2015) 55-64.

- S. Babel and T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater., 97 (2003) 219-243.
- J. Wang and C. Chen, Biosorption of heavy metals by Saccharomyces cerevisiae: a review, Biotechnol Adv., 24(5) (2006) 427-51.
- R. Foroutan, R. Mohammadi, S. Farjadfard, H. Esmaeili, M. Saberi, S. Sahebi, S. Dobaradaran and B. Ramavandi, Characteristics and performance of Cd, Ni and Pb bio-adsorption using *Callinectes* sapidus biomass: real wastewater treatment, Environ. Sci. Pollut. Res., 26(7) (2019) 6336-6347.
- N.K. Mondal, A. Samanta, P. Roy and B. Das, Optimization study of adsorption parameters for removal of Cr(VI) using *Magnolia* leaf biomass by response surface methodology, Sustain. Water Resour. Manag., 5 (2019) 1627-1639.
- F. de Freitas, L.D. Battirola, R. Arruda and L.R.T. de Andrade, Assessment of the Cu(II) and Pb(II) removal efficiency of aqueous solutions by dry biomass Aguape: kinetic of adsorption, Environ. Monit. Assess., 191(12) (2019) 751.
- V.O. Njoku, A.A. Ayuk, E.N. Ejike, E.E. Oguzie, C.E. Duru and O.S. Bello, Cocoa pod husk as a low cost biosorbent for the removal of Pb(II) and Cu(II) from aqueous solutions, Aust. J. Basic Appl. Sci., 5(8) (2011) 101-110.
- Y. Ozudogru and M.J. Merdivan, Adsorption of U(VI) and Th(IV) ions from aqueous solutions by pretreatment with *Cystoseira barbata*, J. Radioanal. Nucl. Chem., (2019). doi.org/10.1007/s10967-019-06943-6
- W. Qu, D. He, Y. Guo, T. Yining and S. Ren-Jie, Characterization of modified *Alternanthera philoxeroides* by diethylenetriamine and its application in the adsorption of copper(II) ions in aqueous solution, Environ. Sci. Pollut. Res., 26(21) (2019) 21189-21200.
- C.E. Duru, I.A. Duru, C.E. Ogbonna, M.C. Enedoh and P. Emele, Adsorption of copper ions from aqueous solution onto natural and pretreated maize husk: adsorption efficiency and kinetic studies, J. Chem. Soc. Nigeria, 44 (5) (2019) 798-803.
- G.T. Asere, V.C. Stevens and D.G. Laing, Use of (modified) natural adsorbents for arsenic remediation: a review, Sci. Total Environ., 676 (2019) 706-720.
- W.S. Wan Ngah and M.A.K.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review, Bioresour. Technol., 99 (2008) 3935-3948.
- C.E. Duru, Mineral and phytochemical evaluation of Zea mays husk, Scientific African, 7 (2020) e00224.
- C.E. Duru and I.A. Duru, Studies of sorbent efficiencies of maize parts in Fe(II) removal from aqueous solutions, Int. Lett. Chem. Phys. Astron., 72 (2017) 1-8.
- C.E. Duru and I.A. Duru, Adsorption capacity of maize biomass parts in the remediation of Cu²⁺ ion polluted water, WNOFNS, 12 (2017) 51-62.
- C.E. Duru, I.A. Duru, F.C. Ibe and M.C. Enedoh, Profiling of Zn²⁺ ion sorption in modeled aqueous solutions by different parts of maize biomass, IOSR JAC, 10(3–1) (2017) 70-75.
- C.E. Duru, M.A. Nnabuchi and I.A. Duru, Adsorption of Cu onto maize husk lignocelluloses in single and binary Cu-Zn solution systems: equilibrium, isotherm, kinetic, thermodynamic and mechanistic studies, Egypt. J. Chem., 62(7) (2019) 1695-1705.
- R. Datta, Acitogenic fermentation of lignocelluloses acid yield and conversion of components, Biotechnol. Bioeng., 23(9) (1981) 2167-2170.
- P. Mahyati, A.R. Patong, M.N. Djide and D.P. Taba, Biodegradation of lignin from corn cob by using a mixture of Phanerochaete Chrysosporium, Lentinus Edodes and Pleurotus Ostreatus, Int. J. Sci. Technol. Res., 2(11) (2013) 79-82.
- S. Rajoriya, A. Haquiqi, B. Chauhan, G. Tyagi, A.S. Pundir and A.K. Jain, Influence of adsorption process parameters on the removal of hexavalent chromium (Cr(VI)) from wastewater: a review, J. Environ. Treat. Tech., 8(2) (2020) 597-603.

- H. Shuhaida and K.G. Soh, Effect of sodium hydroxide pretreatment on rice straw composition, Ind. J. Sci. Technol., 9(21) (2016) 1-9.
- G. Blazque, M. Carlero, F. Hernainz, G. Tenorio and M.A. Martin-Lara, Equilibrium biosorption of lead(II) from aqueous solutions by solid waste from olive-oil production, Chem. Eng. J., 160 (2010) 615-622.
- A. Mlayah and S. Jellali, Study of continuous lead removal from aqueous solutions by marble wastes: efficiencies and mechanisms, Int. J. Environ. Sci. Technol., 12 (2015) 2965-1978.
- K.M. Nguyen, B.Q. Nguyen, H.T. Nguyen and H.T.H. Nguyen, Adsorption of arsenic and heavy metals from solutions by unmodified iron-ore sludge, Appl. Sci., 9 (2019) 619-633.
- B.S. Zadeh, H. Esmaeili, R. Foroutan, S.M. Mousavi and S.A. Hashemi, Removal of Cd²⁺ from aqueous solution using Eucalyptus sawdust as a bio-adsorbent: kinetic and equilibrium studies, J. Environ. Treat. Tech., 8(1) (2020) 112-118.
- 27. S. Rajoriya, A. Haquiqi, B. Chauhan, G. Tyagi, A.S. Pundir, A.K. Jain and D. Agarwal, Adsorption Studies on the removal of hexavalent chromium (Cr (VI)) from aqueous solution using black gram husk, J. Environ. Treat. Tech., 2020 8(3) (2020) 1144-1150.
- N. Arumugam, S. Chelliapan, S.T. Thirugnana and A.B. Jasni, Optimisation of heavy metals uptake from leachate using red seaweed *Gracilaria changii*, J. Environ. Treat. Tech., 8(3) (2020) 1089-1092.
- V.C. Taty-Costodes, H. Fauduet, C. Porte and A. Delacroix, Removal of Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of *Pinus sylvestris*, J. Hazard. Mater., 105 (2003) 121-142.
- Y. Bulut and Z. Tez, Removal of heavy metal ions by modified sawdust of walnut, Fresenius Environ. Bull., 12 (2003) 1499-1504.
- M. Basu, A.K. Guha and L. Ray, Adsorption of lead on cucumber peel, J. Clean. Prod., 151 (2017) 603-615.
- M.A.K. Hanafiah, S.C. Ibrahim and M.Z.A. Yahya, Equilibrium adsorption study of lead ions onto sodium hydroxide modified Lalang (*Imperata cylindrica*) leaf powder, J. Appl. Sci. Res., 2 (2006) 1169-1174.
- C.T. Onwordi, C.C. Uche, A.E. Ameh and L.F. Petrik, Comparative study of the adsorption capacity of lead (II) ions onto bean husk and fish scale from aqueous solution, J. Water Reuse Desal., 9(3) (2019) 249-262.
- K. Nuithitikul, R. Phromrak and W. Saengngoen, Utilization of chemically treated cashew-nut shell as potential adsorbent for removal of Pb(II) ions from aqueous solution, Sci. Rep., 10(1) (2020) 3343.
- A.I. Adeogun, M.A. Idowu, A.E. Ofudje, S.O. Kareem and S.A. Ahmed, Comparative biosorption of Mn(II) and Pb(II) ions on raw and oxalic acid modified maize husk: kinetic, thermodynamic and isothermal studies, Appl. Water Sci., 3 (2013) 167-179.
- H.N. Tran, S. You and H.A. Hosseini-Bandegharaei Chao, Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: a critical review, Water Res., 120 (2017) 88-116.
- 37. A.N.A. El-henday, Surface and adsorptive properties of carbons prepared from biomass, Appl. Surf. Sci., 252 (2005) 287-295.
- H. Freundlich, About adsorption in solutions, Z. Phys. Chem., 57U(1) (1907) 385-470.
- F. Gorzin and M.M.B.R. Abadi, Adsorption of Cr(VI) from aqueous solution by adsorbent prepared from paper mill sludge: Kinetics and thermodynamics studies, Adsorp. Sci. Technol., 36(1-2) (2017) 149-169.
- B.D. Mistry, Handbook of spectroscopic data Chemistry, Oxford Book Company, 2009.