

Isotherm, Kinetic and Thermodynamic Studies of Pb (II) and Nickel Ions Removal from Aqueous Solution Using Locally Sourced bio-Adsorbent

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Abstract: A biomaterial adsorbent, locust bean seed coat powder (LBSCP) was prepared from locust bean seed coat for heavy metals removal from aqueous solutions. The LBSCP was characterized using XRF, for its elemental composition, FTIR, for functional groups, and SEM for surface morphology and the potential of LBSCP for the removal of Pb (II) and Ni (II) ions was investigated. The results obtained indicated that the locust bean seed coat powder (LBSCP) possessed excellent adsorption potential to adsorb the selected heavy metals (Pb (II) and Ni (II) ions). The LBSCP was activated using HCl, then the effect of dosage (1.0, 1.5, 2.0, 2.5, 3.0 g), time (15, 20, 25, 30, 35 min), temperature (288, 293, 303, 313, and 323 K) on the adsorption efficiency of the sample was tested using Pb (II) and Ni (II) ions solutions prepared from Pb(NO₃)₂ and Ni(NO₃)₂ salts. The result showed that removal efficiency (99.95%) was the most effective with Pb²⁺ ions when 1.0 g of MLBSCP was used. The result also showed that at 15 min of contact time more of Pb²⁺ ions (99.89 %) were removed by MLBSCP. The equilibrium adsorption data were tested with two different isotherms: Langmuir, and Freundlich. Best fitted was found to be Langmuir isotherm. The positive values of change in Gibb's free energy (ΔG) for the experiment range of temperatures showed that the adsorption process for the adsorption of pb²⁺ and Ni²⁺ is non-spontaneous. The positive values obtained for enthalpy change (ΔH) reveals endothermic nature of the adsorption process. The values obtained for change in entropy were negative suggesting that there was a decrease in the randomness between the adsorbent aqueous solutions interface during the adsorption process.

Key words: LBSCP, Kinetics, Isotherm, Adsorption, Thermodynamic, lead (II) ions, Nickel (II) ions.

1. Introduction

Many industries most especially that are involved in manufacturing and production discharge waste waters containing many hazardous materials such as heavy metals, phenols and dyes. The contamination of water by industrial activities constitutes serious challenges to human health and the environment [1]. All heavy metals are toxic, non-biodegradable and as a result should be removed from waste water before discharging into the water bodies. A number of technologies for the removal of heavy metals from aqueous solutions have been developed which include; chemical separation, filtration, membrane separation, electrochemical treatment, ion- exchange, and adsorption [2]. All these methods with exception of adsorption are not cost effective, have low output and inefficient in removing trace level of heavy metals from wastewater. Adsorption remains the outstanding process due to its simplicity, high efficiency and easy

recovery [3]. Adsorption process has been singled out to be a feasible substitute for removing heavy metals from wastewater however; other natural and synthetic solids have been investigated as adsorbents of heavy metals removal from aqueous solutions. Among these, zeolite, clay, silica gel, resin, activated alumina and activated carbon [4]. activated carbon is the most widely used adsorbent as a result of its well-developed pore structure, large active surface area, excellent mechanical properties and multiple functional groups at their surface [5], [6]. Though efficient but the high cost of activated carbon limits its large scale use for heavy metals removal. Biosorption of heavy metals from aqueous solution is a relatively new technology for the removal of heavy metals from industrial waste water [7]. Heavy metal deposition in body causes oral ulcer, cancer, renal failure [8]. The exposure of nickel (Ni) and lead (Pb) causes damages to both external and internal organs and can lead to death as a result of accumulation in the body system. Many industries, such as painting, petrochemical, newsprint, smelting, metal electroplating, mining, plumbing, and battery industries are the major sources of lead pollution. The permissible level for lead in drinking water according to [9] is 0.05 mg/L. and according to Bureau of Indian Standards (BIS) [10] is 0.1 mg/L. Therefore, the concentrations of lead must be reduced to levels that would meet environmental regulations for various bodies of water and nickel salts are commonly utilized in metal plating and its concentration in industrial wastewater varies between 6 to 12 mg/L, which is exceed the safe limit (0.15 mg/L) [11]. The chronic toxicity of nickel to humans and the environment is well known and when it is high, nickel concentration causes gastrointestinal irritation, lung and bone cancers [12]. The application of bio degradable materials are increasing for the removal of heavy metals from waste water since they are non-hazardous, abundant in nature and readily available at low cost [13]. A number of studies have been investigated on the application of low cost adsorbents from natural sources for heavy metals removal from aqueous solutions. Due to increasing costs and environmental considerations have resulted to the use of inexpensive adsorbents generated from renewable resources. Many researchers have widened the scope of using inexpensive adsorbents from natural materials including agricultural waste and minerals for removal of heavy metals from waste water as a result of industrial activities and environmental pollutants. The need for greener and sustainable alternative adsorbents for removal of heavy metals from aqueous solutions and various pollutants using biomaterials such as starch [14], alginate [15], agarose [16], and chitosan [17], [18]. The objective of this study was to investigate the potential of locust bean seed coat powder (LBSCP) prepared from locust bean seed coat for the removal of lead (Pb^{2+}) and nickel (Ni^{2+}) ions from aqueous solutions.

2. Material and Methods

Locust bean seed was sourced locally from Auchi, Edo State, Nigeria. The seed coat was removed by cooking to soften the strongly attracted seed coat for easy dehauling. The resulting wet seeds coats were transferred into a thermostatically controlled electric oven and dried at 105 °C for 6 hr allowed to cool and ground into powder using an electric blender. The locust bean seed coat powder (LBSCP) was sieved into different particle sizes using sieves of 300, 250, 200, 150, and 100 microns. The particle size of 100 microns was stored in a dry air tight plastic container for further use.

2.1. Activation of the Adsorbent

The LBSCP was treated with 2 M HCl by adding 400 mL of the acid to 250 g of the sample and left to stand for 48 hr. the resulting mixture was stirred and washed severally with deionized water until the filtrate became neutral to litmus. The wet residue was analytically transferred into an electrostatically control oven and dried for 3 hr at 105°C. The dried LBSCP was kept in an air-tight container for further use as an adsorbent.

2.2. Characterization of Adsorbents

The adsorbents (modified and unmodified) were characterized using, X-ray fluorescence (XRF) for elemental composition of the sample, Fourier Transform Infrared (FT-IR), for surface functional group, and Scanning Electron Microscopy (SEM) for surface morphology.

2.3. Preparation of Solutions

The reagents used in this study were of analytical grade. All lead (II) ions solutions were prepared using deionized water. A 1000 mg/L Pb (II) ions stock solution was prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ in deionized water. All working solutions were prepared by diluting the stock solutions with deionized water. Ni (II) ions stock solution was prepared following the procedure described above using $\text{Ni}(\text{NO}_3)_2$ salts.

2.4. Adsorption Studies

The adsorption experiment was conducted using the batch method to determine the effects of the different parameters on the sorption process. The adsorption experiments for the removal of lead ions were conducted by mixing 2.0 g of modified and unmodified LBSCP with 50mL of a solution of known concentration in 200 mL flasks at room temperature. The influence of initial lead ion concentration was performed in the range 2.0, 2.5, 3.0, 3.5, 4.0 mg/L, time 15, 20, 25, 30, 35 min, adsorbent dosage 1.0, 1.5, 2.0, 2.5, 3.0 g, and temperature 15, 20, 30, 40, 50 °C, in each case, the parameter to be studied was varied while others were kept constant. At the end of the stirring and agitation time required in each study, the solution was filtered and the filtrate was analyzed for residual lead (II) ions concentration using atomic absorption spectrophotometer (AAS). The data obtained in the batch studies was used to determine the amount of metal ions adsorbed at a time by the difference in their initial and final concentrations. Each experiment was carried out in duplicate. The adsorbent uptake capacity was calculated according to equation 1. The same process was repeated for the removal of nickel ions.

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

The removal percent of the metal ions by LBSCP in solution was calculated using equation 2

$$\% Re = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

2.5. Data Analysis

2.5.1. Adsorption Isotherms

The adsorption isotherm is the relation between the amount adsorbed and the equilibrium pressure or concentrations at constant temperature. From a practical point of view, an isotherm is a graphical representation of how much of a specific contaminant is effectively removed by a given weight of adsorbent, and it is a means to this end. This enables the refiner to judge between adsorbent efficiencies i.e. which clay will be more economically efficient. Theoretically, it is a means to empirically determine the manner by which an adsorbate is removed by the adsorbent and mathematically define the adsorptive nature of an adsorbent [19]. An isotherm is the expression of the relationship between the partial pressure of an adsorbate gas, or solute concentration in solution, and surface coverage of the adsorbent at a constant temperature [20]. In this study two adsorption isotherms have been used to test the favourability of the adsorption process. Langmuir and Freundlich isotherms are used for fitting the experimental data in adsorption studies to understand the extent and degree of applicability of adsorption. The two isotherms depend on temperature and they have two constants each in their general form.

2.5.2. Langmuir Isotherm Model

The Langmuir isotherm has been employed to explain the adsorption of oil pigment and other minor oil solutes during oil processing. Though, developed by Irving Langmuir to describe gas adsorption. The model describes a reversible monolayer, chemisorption adsorption onto distinct sites of an idealized adsorbent, at equilibrium. The isotherm expresses the hypothetical relationship between gas pressure and the proportion of adsorption sites occupied by an adsorbate at a fixed temperature. The model assumes that the adsorbate is bound to a fixed number of energetically equal, specific sites, each adsorbing one molecule with no interaction occurring between molecules on adjacent sites [19]. The Langmuir isotherm has been applied in various adsorption processes in the form equation 3.

$$\frac{C_e}{x} = \frac{1}{KLXm} + \frac{C_e}{Xm} \quad (3)$$

where x = amount of solute adsorbed (x/m), C_e = residual amount at equilibrium, m = grams of adsorbent used, K_L is the surface area of the adsorbent ($m^2/100$ g), and X_m is a constant of the intensity of the adsorption. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L and is calculated according to equation 4.

$$R_L = 1 / (1 + K_L C_0) \quad (4)$$

where C_0 is the initial concentration of the ions (Pb^{2+} and Ni^{2+}) in the solution (mg/L), the value of R_L indicates the nature of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) and irreversible ($R_L = 0$).

2.5.3. Freundlich Isotherm Model

Adsorption of substances from a solution or dispersion is predominantly a surface phenomenon and is dependent upon the specific affinity between adsorbent and solute. The solute may be either dissolved or colloiddally dispersed. Freundlich developed an empirical equation that correlates the capacity of the adsorbent with the residual solute concentration according to equation 5

$$\frac{x}{m} = kc^n \quad (5)$$

where x = amount of solute adsorbed (mg), m = amount of adsorbent (g), c = amount of residual solute (concentration) (mg/L) at equilibrium. K is a constant indicating adsorption capacity, and n is a constant of the intensity of adsorption. The constant n is sometimes expressed as $1/n$ to standardize notation so that the constant varies only between 0.1 and 1.0 [21]. Empirical data are evaluated for Freundlich behaviour by using the equation in its logarithmic form, as equation of a straight line, equation 5. [21]

$$\log \frac{x}{m} = \log k + n \log c \quad (6)$$

From a practical perspective, K measures the overall decolourizing power of an adsorbent for the solute adsorbed, while n indicates the range of decolourization wherein the adsorbent has its greatest effect. As the value of k increases for a given value of n , less adsorbent is needed. A high value of k is desired under all circumstances. In general, a high value of n is also desirable as long the value of k remains high [22].

2.5.4. Kinetic Studies

In order to investigate the adsorption mechanism of the metal ions (lead and nickel) onto ULBSCP and MLBSCP, two kinetic models were tested. Pseudo-first order and pseudo-second order models.

2.5.5. Pseudo-First Order Kinetic Model

The applicability of the Pseudo-first order and Pseudo-second order model can be tested for the

adsorption process. The best fit model will give the best correlation coefficient, R^2 values. The Pseudo – first order equation is given as equation 7

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \quad (7)$$

where q_e and q_t refers to the amount of dye adsorbed (mg/g) at equilibrium and at any time t (min) respectively, and K_1 is the equilibrium rate constant of Pseudo– first order adsorption. The integration of equation 6 with the initial condition, $q_t = 0$ at $t = 0$ gives equation 8

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

The slope and intercept of plot of $\log (q_e - q_t)$ against t were used to determine the Pseudo–first order rate constant K_1 for the adsorption process.

2.5.6. Pseudo-second Order Kinetic Model

Pseudo–second order kinetic model is represented by equation 9

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

The slope and intercept of plot of $\frac{t}{q_t}$ against t were used to calculate the pseudo-second order parameters.

2.5.7. Thermodynamic Studies

Thermodynamic study of adsorption process is essential to conclude whether the process is spontaneous or not. The thermodynamic parameters considered in this study are change in Gibb's free energy (ΔG) change in enthalpy (ΔH), change in entropy (ΔS). They have useful role to determine spontaneity and heat change of the adsorption process. The heat of adsorption ΔH_a , may be calculated in a manner similar to that used to calculate the heat of vapourization of a liquid using the following modification of the Clausius-Clapeyron equation 10;

$$\frac{d(\ln P)}{dT} = \frac{\Delta H_a}{RT^2} \quad (10)$$

Integration of this equation gives

$$\ln P = - \frac{\Delta H_a}{RT} + c \quad (11)$$

where c is an integration constant and corresponds to $\frac{\Delta S^o}{R}$

For the adsorption process, Equation 10 can be written as

$$\ln X_e = - \frac{\Delta H_a}{RT} + c \quad (12)$$

$$\text{Therefore; } \ln X_e = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R} \left(\frac{1}{T} \right) \quad (13)$$

The values of ΔH and ΔS can be obtained from the slope and intercept of the graph by plotting $\ln X_e$ against $\frac{1}{T}$.

The Gibb's free energy can be calculated from the relationship presented in equation 14

$$\Delta G = \Delta H - T\Delta S \quad (14)$$

The effect of temperature on the lead and nickel ions adsorption onto the surface of both ULBSCP and MLBSCP at different temperatures (15, 20, 30, 40, and 50 °C) was investigated at pH of 5.0. Thermodynamic functions of adsorption process were calculated using thermodynamic equation 14.

2.5.8. Activation Energy of the Adsorption Process

The activation energy is a purely empirical relationship and is temperature dependent [23]. The activation energy E_a may be calculated using the following modification of the Arrhenius according to equation 15.

$$\ln K = \ln A - \frac{E_a}{RT} \quad (15)$$

where K is the pseudo-second order rate constant (g/mol. min), A is the frequency factor, T is the absolute temperature in Kelvin (K), R is the gas constant (8.314 J/mol K) and E_a is the activation energy (kJ/mol).

For the adsorption process, equation 14 can be written as;

$$\ln X_e = \ln A - \frac{E_a}{RT} \quad (16)$$

where X_e is the residual amount at equilibrium. The linear form of equation 15 was used to determine the activation energy of the adsorption process by plotting $\ln X_e$ against $\frac{1}{T}$

The values of change in enthalpy and change in entropy are calculated from the slope and intercept of the thermodynamic equation.

3. Results and Discussion

3.1. Fourier Transforms Infrared Analysis (FT-IR)

FT-IR Analysis of powered Unmodified and Modified Locust Bean Seed Coat.

The analytical technique for the characterization of both modified and unmodified locus bean seed coat was achieved using FT-IR spectroscopy (Perkine-Elmer 1000 spectrophotometer). The quality features of infrared spectroscopy have been so useful and one of the most effective tools for characterization [24] especially for functional groups. For the elucidation of the interactions and structural modification of LBSCP were obtained over a range of 400-650 cm^{-1} .

Presented in Fig. 1 and Fig. 2 are the spectra of unmodified locust bean seed coat powder (ULBSCP) and modified locust bean seed coat powder (MLBSCP). The results clearly revealed some modifications in the LBSCP modified with 2 M HCl, this was evident in shifting and disappearing of some absorption bands as compared with UMLBSCP. For instance, the absence of absorption bands at 2922.2, 2105.9, 1738.9, and 1237.5 cm^{-1} and shifting of band from 1013.8 cm^{-1} in ULSBSCP to 1028.7 cm^{-1} in MLBSCP showed the effect of modification in the properties of the sample.

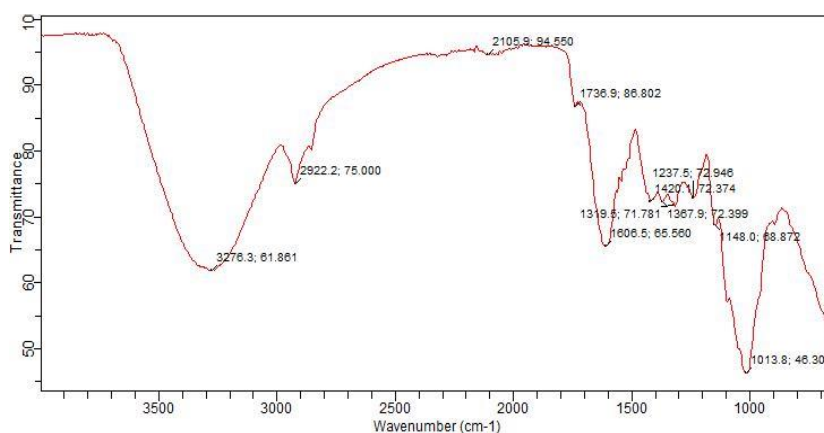


Fig. 1. FTIR spectrum of ULBSCP.

The absorption bands (strong intensity and very broad) at 3276.3 and 3291.2 cm^{-1} in both ULBSCP and MLBSCP were due to the presence of O-H group. The absorption peak at 2922.2 cm^{-1} in ULBSCP was as a

result of C-H stretch from alkane, while the weak intensity band at 2105.9 cm^{-1} was due to C=C group. However, the absorption peaks at 1608.5 and 1738.9 cm^{-1} were due to C=O from carboxylic group. The peaks at 1319.6 cm^{-1} and 1367.9 cm^{-1} were CH_2 scissoring probably from alkyl group. The absorption bands at 1237.5 and 1013.8 cm^{-1} were as a result of C-O from carbonyl group while the band at 1148.0 cm^{-1} was due to O-C-O group. The MLBSCP in Fig. 2 also showed strong intensity and very broad absorption band at 3291.2 cm^{-1} and indication of the presence of OH stretching from carboxylic group. The absorption peaks at 1617.7, 1148.0, 1099.6 and 1028.7 cm^{-1} were due to the presence of C-O probably from carboxylate group. However, the appearance of peak at 1408.0 cm^{-1} showed the presence of N-H bending and the band at 1319.6 cm^{-1} was due to CH_2 scissoring. The absence of peaks in the spectra range of 900 – 650 cm^{-1} regions indicate the absence of aromatic ring.

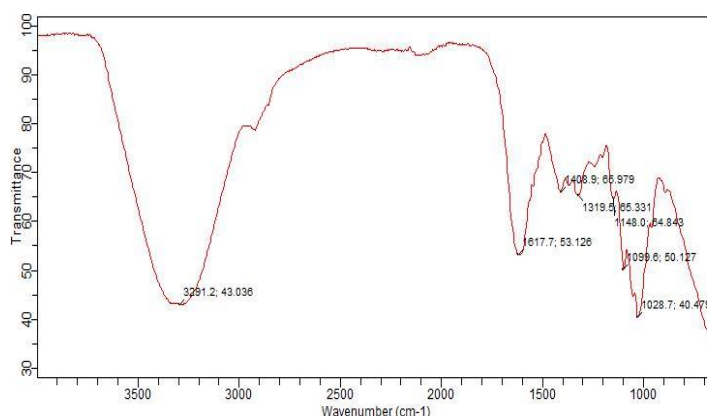


Fig. 2. FTIR spectrum of MLBSCP.

3.2. Scanning Electron Microscopy (SEM) Analysis

Presented in Fig. 3 and Fig. 4 were the scanning electron micrographs of ULBSCP and MLBSCP. The SEM (Phenom Prox by phenomworld Eindhoven Netherlands) micrographs were studied for the surface and morphological characteristics in the adsorbent materials. The photographs showed that the surface morphology of the ULBSCP appears in form of flake-like, shaft, rough, rigid and with tiny particles closely packed together, however, the MLBSCP sample appears to be more porous with gravity within the surface and this could be as a result of the treatment of the sample with 2M HCl whereby some of the impurities and other minerals have been leached from the sample.

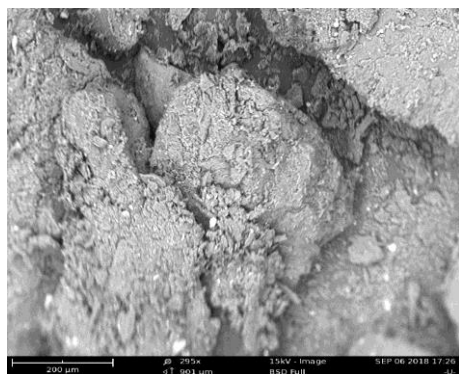


Fig. 3. SEM Spectrum of ULBSCP.

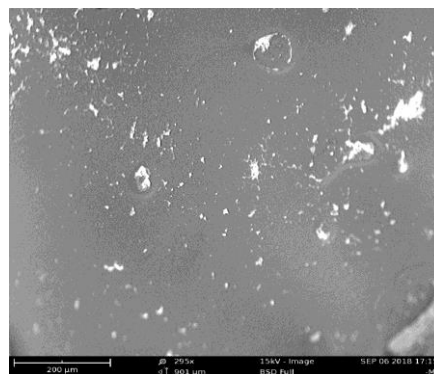


Fig. 4. SEM Spectrum of MLBSCP.

3.3. Elemental Composition of ULBSCP and MLBSCP

The mineral oxides composition in the locust bean seed coat was determined using the XRF analysis

(Philip pW 1390). The result of the ULBSCP and MLBSCP was presented in Table 1. The result showed elemental compositions of MLBSCP and ULBSCP were leached from the sample. This was evident in the overall reduction in the concentration of elements present after modification with the acid (2 M HCl). Other oxides with high concentrations were oxides of aluminum, calcium potassium. However, oxide of sodium (Na_2O) was absent in both ULBSCP and MLBSCP

Table 1. Elemental Composition of ULBSCP and MLBSCP

Compound	ULBSCP (Wt %)	MLBSCP (Wt %)
Na_2O	0.000	0.000
MgO	3.884	0.672
Al_2O_3	5.221	5.682
SiO_2	26.634	2.938
K_2O	15.440	3.242
CaO	16.760	6.873
TiO_2	0.721	0.570
Mn_2O_3	0.654	0.287
Fe_2O_3	1.818	1.274
ZnO	0.108	0.043
SrO	0.090	0.036

3.4. Effects of Adsorbent Dosage

Both the ULBSCP and MLBSCP were varied from 1.0 to 3.0 g of 50 mg/L of aqueous solution containing the metal ions. Figure 5 revealed the percentage metal ions adsorbed by both the ULBSCP and MLBSCP. It was observed that MLBSCP has the higher percentage removal from aqueous solutions with reference to nickel ions removed from aqueous solutions. However, removal efficiency was most effective with lead ions when 1.0 g of MLBSCP was used. The percentage removal efficiency decreased when the MLBSCP dosage was increased to 1.5 g, this trend continued with adsorbent dosage of 2.0 g while the percentage removal efficiency increased at 2.5 g (99.95 %) and remain constant when the dosage was increased to 3.0 g (99.95 %) indicating that adsorption equilibrium has been reached and no further removal of lead ions from the aqueous solutions. The same trend was observed in the percentage removal efficiency of nickel ions by MLBSCP only that after the initial decrease, and with further increase in MLBSCP dosage from 1.5 to 2.5 g, the removal efficiency was increased at 3.0 g of adsorbent dosage. The effective removal of lead ions by both ULBSCP and MLBSCP could be as a result of the high volatility and low solubility of lead ions in the aqueous solutions which probably leads to an increase in the kinetic energy of lead ions to quickly adsorb at the surface of the adsorbent. As shown in figure 5, a dose of 1.0 g is sufficient to remove more than 99 % lead ions from 50 mg/L initial concentration of lead ions within 30 min since further increase of the adsorbent dosage to 2.0 g resulted in decrease of percentage removal of lead ions from aqueous solutions. The same trend was observed with nickel ions. The decrease in percentage removal experience might due to the saturation of available exchangeable active sites during the adsorption process.

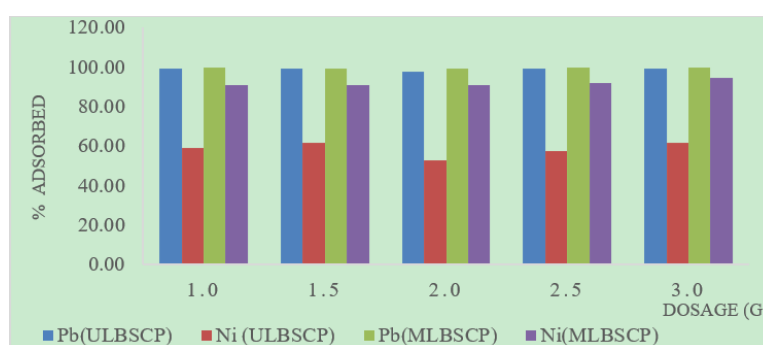


Fig. 5. Percentage of Pb^{2+} and Ni^{2+} ions adsorbed at various dosages.

3.5. Effect of Contact Time

The effect of contact time as it affects the degree of metal ions removal by both ULBSCP and MLBSCP from aqueous solutions was shown in figure 6, the results showed the percentage removal efficiencies of the adsorbents. It was observed that the highest percentage removal of lead ions and nickel ions occurred at 15 min contact time with 99.89 and 96.62 % respectively at 50 mg/L using 2.0 g of MLBSCP.

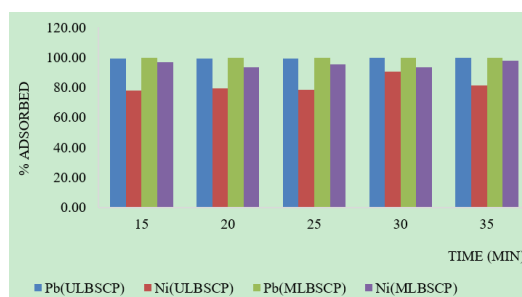


Fig. 6. Percentage of Pb^{2+} and Ni^{2+} ions adsorbed at various contact time.

Decrease in percentage removal of both ions (lead and nickel) was observed when the contact time was increased from 20 to 25 min, however, an increase in percentage removal of lead ions was observed at contact time of 30 min and further increase at 35 min. The percentage removal of nickel also decreases at 20 min and further experience increase at 25 min of contact time. The increase noticed in the percentage removal of the ions from aqueous solutions could be as a result of desolvation of the adsorbent with time, so that the mass transfer resistance to the adsorbate in the boundary layer decreases.

3.6. Effect of Temperature

The study was carried out at various temperatures ranging from 15-50 °C at 50 mg/L and 2 g adsorbent of adsorbent dosage. The result of the study was presented in Fig. 7, the result showed that removal efficiency was most effective with lead ions at 15 °C and nickel at 20 °C and this could be as a result of high surface area, surface acidity, and greater availability of exchangeable sites, increase pore volume and size.

The percentage removal efficiency decrease with lead ions at 20 °C while percentage removal of nickel ions decrease at 30 °C. The decrease in percentage removal efficiencies in lead and nickel ions could be as a result of the saturation of available adsorption exchangeable active sites during the adsorption process. However, the increase in percentage removal of lead (II) ions when the temperature was increased above 20 °C and nickel ions above 30 °C could be due to the desolvation of the adsorbent with temperature causing the mass transfer resistance of the adsorbate in the boundary layer to decrease.

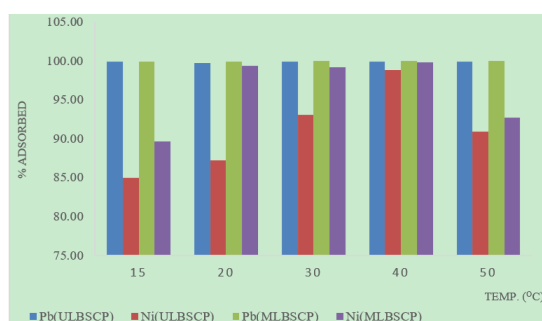


Fig. 7. Percentage of Pb^{2+} and Ni^{2+} ions adsorbed at various temperature.

3.7. Isothermal Studies

The adsorption isotherms for lead and nickel ions were obtained for ULBSCP and MLBSCP. The

corresponding adsorption parameters for Langmuir and Freundlich constants were summarized in Table 2 and Table 3, the results showed that the values of $1/n$ calculated were below one (1) for ULBSCP and MLBSCP indicating that the adsorption of the metal ions on ULBSCP and MLBSCP was favourable.

Table 2. Langmuir Isotherm Constants

Metal ions	ULBSCP				MLBSCP			
	$Q_{max}(\text{mg/g})$	$b(\text{L/mg})$	R_L	R^2	$Q_{max}(\text{mg/g})$	$b(\text{L/mg})$	R_L	R^2
Pb ²⁺	1.111	-2250.8	1.71×10^{-5}	0.917	47.36	-1.029	3.76×10^{-3}	0.948
Ni ²⁺	2.187	0.703	0.069	0.812	9.709	0.22	0.193	0.589

Table 3. Freundlich Isotherm Constants

Metal ions	ULBSCP			MLBSCP		
	$K_f(\text{mg/g})$	n	R^2	$K_f(\text{mg/g})$	n	R^2
Pb ²⁺	-0.899	-8.518	0.972	-0.916	-8.525	0.974
Ni ²⁺	-1.424	-8.576	0.928	-1.08	-8.787	0.966

However, the experimental data from Table 3 did not fit to the Freundlich model, giving negative slopes and intercepts leading to the conclusion that the adsorption behaviour of the tested system did not follow the assumption on which the Freundlich approach is based in both ULBSCP and MLBSCP. The essential characteristics of the Langmuir isotherm, the dimensionless constant separation factor R_L values obtained showed that the Langmuir model was more favourable. Therefore, Langmuir isotherm model conformed better in the adsorption process based on positive values of its Q_{max} .

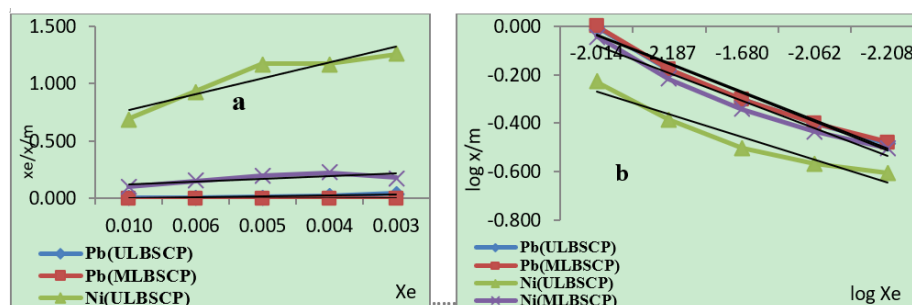


Fig. 8. (a) Langmuir isotherms for the adsorption of lead and nickel ions and (b) Freundlich isotherm for the adsorption of lead and nickel ions from aqueous solutions.

3.8. Kinetic studies

The correlation coefficient (R^2) values obtained for the adsorption of lead and nickel ions onto ULBSCP and MLBSCP were presented in Table 4 and Table 5 for pseudo-first order and pseudo-second order kinetics respectively.

Table 4. Pseudo First Order Kinetics

Metal ions	ULBSCP			MLBSCP		
	K_1/min	$q_e(\text{mg/g})$	R^2	K_1/min	$q_e(\text{mg/g})$	R^2
Pb ²⁺	0.233	0.004	0.865	-0.231	-1.574	0.942
Ni ²⁺	1.441	0.156	0.951	0.284	2.661	0.683

The results showed that the R^2 of ULBSCP and MLBSCP in pseudo-first-order kinetics for the removal of lead ions were 0.865 and 0.942 respectively and nickel ions are 0.951 for ULBSCP and 0.683 for MLBSCP. However, the values of R^2 obtained in pseudo-second-order kinetic for the adsorption of lead ions onto ULBSCP and MLBSCP were 0.957 and 0.966 respectively while the correlation coefficients for the adsorption of nickel ions onto ULBSCP and MLBSCP were 0.522 and 0.913 respectively. Based on the values of correlation coefficient obtained, pseudo-second-order kinetic model for the adsorption of lead ions onto

both ULBSCP and MLBSCP was more suitable to describe the adsorption process better than pseudo-first-order model but conform better in MLBSCP (R^2 , 0.966).

Table 5. Pseudo Second Order Kinetics

Metal ions	ULBSCP			MLBSCP		
	$K_2g/(mgmin)$	q_2mg/g	R^2	$K_2g/(mg\ in)$	q_2mg/g	R^2
Pb ²⁺	4.068	0.626	0.957	0.124	2.008	0.966
Ni ²⁺	0.111	2.081	0.522	1.263	0.925	0.913

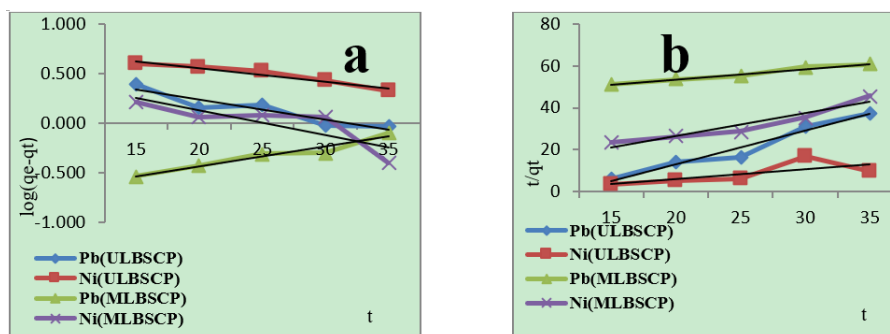


Fig. 9. Pseudo-first-order for the adsorption of lead and nickel ions using (a) ULBSCP and (b) MLBSCP.

3.9. Thermodynamics Studies

The results of the thermodynamics parameters were presented in Table 6. The positive values obtained for enthalpy change (ΔH) revealed endothermic nature of the adsorption process. The values obtained for change in entropy were negative suggesting that there was a decrease in the randomness between the adsorbent aqueous solutions interface during the adsorption process.

Table 6. thermodynamic Parameters of the Adsorption Process

Metal ions	ULBSCP				MLBSCP			
	$\Delta H(kj/mol)$	$\Delta S(kj/mol)$	$E_a(kj/mol)$	$A(g/mol\ min)$	$\Delta H(kj/mol)$	$\Delta S(kj/mol)$	$E_a(kj/mol)$	$A(g/mol\ min)$
Pb ²⁺	42.82	-0.192	-15.46	0.391	63.49	-0.278	-17.77	0.374
Ni ²⁺	90.61	-0.341	-92.61	0.268	40.43	-0.161	-41.33	0.335

Table 7. Values of Free Energy (ΔG) for the Adsorption of Lead and Nickel Ions from Aqueous Solutions

ULBSCP	Values of ΔG (kj/mol)				
	Temp(K)	ULBSCP		MLBSCP	
		Pb ²⁺	Ni ²⁺	Pb ²⁺	Ni ²⁺
288	98.21	7.468	143.61	86.67	
293	99.17	9.171	145.01	87.48	
303	101.09	12.576	147.79	89.08	
313	103.02	15.981	150.57	90.69	
323	104.94	19.37	153.35	92.29	

It also showed that the degree of freedom of translational, rotational and vibrational at the transition state compared to the bulk became negligible and ineffective which is characteristic of physico-sorption and usually favoured at low temperature indicating less affinity of the adsorbent materials and less ordered adsorbed species on the surface. The values of activation energy obtained were reported in Table 6. The result showed that activation energy of the adsorption process was negative. This could be attributed to the nature of some chemical reactions rate that proceed more slowly at higher reaction temperatures and therefore effectively comply with negative activation energy [25]. The negative values of E_a was an indication that lower temperature favoured ions removal by adsorption onto LBSCP [26].

The positive values of change in Gibb's free energy (ΔG) for the experiment range of temperatures

showed that the adsorption process for the adsorption of Pb^{2+} and Ni^{2+} was non-spontaneous indicating that equilibrium occurred quickly and the reaction was not feasible which suggested that the reaction would not proceed on its own at the working temperatures. It was observed from Table 7 that as the temperature increases the values of Gibb's free energy obtained increased suggesting that the adsorption process would be more favourable at low temperature.

4. Conclusion

The outcome of the study showed that activated locust bean seed coat powder (LBSCP) was found to be an efficient adsorbent for the removal of Pb (II) and Ni (II) ions from aqueous solutions. The acid activation resulted in modification of the sample. The reduction in the elemental composition of the sample after activation is an indication of structural distortion of the sample which makes it effective for the adsorption of heavy metal ions from aqueous solutions. The adsorption of Pb (II) and Ni (II) ions from aqueous solutions followed pseudo second order kinetics. The adsorption isotherm fitted well the Langmuir isotherm model due to positive values of its adsorption capacity (Q_{max}) though with lower R^2 values. The thermodynamics data confirmed the non-spontaneous nature of adsorption of both Pb (II) and Ni (II) ions from aqueous solutions. The negative values of E_a were indications that lower temperature favoured ions removal by adsorption onto LBSCP. The study revealed that activated locust bean seed coat powder from locust bean seed coat could be used as an adsorbent for heavy metals removal from aqueous solutions and also resulted to cheaper and most effective method of waste water purification by removing poisonous heavy metal ions from waste water before discharging into body surface body waters.

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