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Removal of Pb^{2+} and Ni^{2+} ions from aqueous solutions by adsorption onto activated locust bean (*Parkia biglobosa*) husk

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ABSTRACT

Locust bean husk (LBH) activated with H_3PO_4 was used as an adsorbent to remove Pb^{2+} and Ni^{2+} from aqueous solution. The effects of varying initial metal ion concentration and adsorbent dose on the adsorption capacity were identified through laboratory experimental investigations. An equilibrium adsorption experiment at ambient temperature was carried out and the experimental data of adsorption fitted into Langmuir and Freundlich adsorption models. The result showed that the amount of metal ion adsorbed onto activated LBH increases with an increase in the initial metal ion concentration. In the given time duration of 2 hours and at the initial metal ion concentration of 100 ppm, Pb^{2+} and Ni^{2+} showed their highest uptake value of 19.85 mg/g (79.4%) and 11.10 mg/g (57.1%) respectively. For the effect of adsorbent dosage, the maximum adsorbent capacity was at a dosage of 0.8 g, recording adsorption capacity of 4.07 mg/g for Pb^{2+} and 2.94 mg/g for Ni^{2+} . Langmuir model having higher R^2 values of 0.961 and 0.952 for Pb^{2+} and Ni^{2+} respectively fitted the equilibrium adsorption data better than the Freundlich model for the two metals.

Keywords: Activated locust bean husk (LBH), Heavy metals, Wastewater, Isotherm, Sorption

INTRODUCTION

Water pollution may be due to various sources, namely, from sewage, industrial wastes or pesticides runoff from farm land. Such water if supplied directly to consumers without treatment may lead to the spread of waterborne diseases. Some specific pollutants include industrial chemicals such as chlorinated hydrocarbons, heavy metals, including cadmium, lead, chromium, arsenic, mercury and nickel, saline water, bacterial and industrial waste [1]. Among these pollutants, the contribution of heavy metals to environment is of major concern because of its toxicity, bioaccumulation, persistence and non-biodegradable nature.

Some of the techniques which have been used in the removal of heavy metals from effluents include ion exchange, chemical precipitation, electrodialysis, electrolytic extraction, reverse osmosis, and cementation. These methods are expensive and in addition have the inability to remove metals at low concentration [2,3]. Compared with the aforementioned techniques, adsorption has proved to be less expensive alternative for the removal of metals from aqueous solution [4]. Literature has indicated the potential of some agricultural waste products as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without causing environmental degradation [5]. The aim of this research is to study the adsorption of heavy metals (Pb^{2+} and Ni^{2+}) from aqueous solutions by activated locust bean husk. This aim will be achieved by determining some physicochemical properties of the adsorbent and examining the adsorption capacity of activated locust bean husk for

these heavy metals by evaluating equilibrium adsorption isotherms, initial metal ion concentration and adsorbent dose in order to ascertain the optimum conditions as well as nature of the adsorption process of these heavy metals (Pb^{2+} and Ni^{2+}) onto the activated locust bean husk.

MATERIALS AND METHODS

Sample Collection and Treatment.

Locust bean fruit was collected from Kazaure Local Government Area of Jigawa State. After collection, it was taken to Biological Science Department of Ahmadu Bello University where it was identified as *Parkia biglobasa* using method described by Prescott [6]. The locust bean husk was removed and was washed several times with tap water and then with distilled de-ionized water to remove impurities and salts. The LBH was sun-dried and later dried in an oven at 60°C for 24 hours. The dried locust bean husk was cut, ground in a mortar and sieved to $180\ \mu\text{m}$ particle size.

Preparation of Activated Locust Bean Husk

The adsorbent was prepared as described by Hanafiah *et al.* [7]. About 400 g of the sieved material above was mixed with $600\ \text{cm}^3$ 1M phosphoric acid (purity 85% Merck, Germany) in a plastic container. The mixture was transferred into copper crucibles and heated in an oven at 105°C for 30 min with occasional stirring before it was removed and left overnight. After cooling, the activated locust bean husk was repeatedly washed with distilled de-ionized water until the pH of the filtrate fell between 6.3. The adsorbent was then dried in an oven at 105°C for 1 hour and stored in a desiccator.

Preliminary Study

Moisture and Dry Matter Content Determination

Clean silica crucibles were dried in a desiccator and weighed. 1 g of the dry sample was weighed. It was dried in an air-circulated oven at 105°C for 3 hours after which it was cooled in a desiccator and then weighed [8].

Calculation

$$\text{Moisture (\%)} = \frac{\text{Loss in Weight on Drying (g)}}{\text{Initial Sample Weight (g)}} \times 100 \quad (1)$$

$$\text{Dry Matter (\%)} = \frac{\text{Oven Dry Weight (g)}}{\text{Initial Sample Weight (g)}} \times 100 \quad (2)$$

Ash Content Determination

Copper crucible was heated in a furnace at 500°C , cooled in a desiccator and weighed. Oven dried sample from the moisture content determination was used. The crucible containing the dry sample was placed in a muffle furnace and temperature was allowed to rise to 500°C . After 3 hours, it was removed and allowed to cool in a desiccator and weighed [9].

Calculation

$$\text{Ash (\%)} = \frac{\text{Ash Weighed (g)}}{\text{Oven dry weight (g)}} \times 100 \quad (3)$$

pH Measurements

1% (w/v) solution of the sample was made using distilled de-ionized water. pH of the supernatant was measured after 1 hour with an Electric pH Meter.

Bulk density

This was done by measuring the volume of distilled de-ionized water displaced when 2 g of the sample was transferred into a $50\ \text{cm}^3$ of distilled de-ionized water in a $100\ \text{cm}^3$ graduated measuring cylinder [9,10].

Procedure

A $100\ \text{cm}^3$ calibrated measuring cylinder was washed and dried. $50\ \text{cm}^3$ of the water was added to the measuring cylinder and the volume was noted. A 2 g of the sample was transferred into the measuring cylinder and volume of

the increased water level was recorded. Care was taken to ensure there was no air bubbles before taking volume measurements.

Calculation

Volume of water displaced (cm³) = final volume – initial volume.

$$\text{Bulk density (g/cm}^3\text{)} = \frac{M_a}{V_a} \quad (4)$$

where M_a is the mass of the adsorbent (g) and V_a is the volume of water displaced (cm³)

Adsorption experiment

This was carried out by using batch method as described in the literature [11]. The investigation was carried out at ambient temperature (27°C) with a basic reciprocating shaker using 120ml polythene bottle as the reactor. A 1000mg/l stock solution of each of the metals was prepared, from where the working solutions were prepared by serial dilution method. The metals of interest are lead from $\text{Pb}(\text{NO}_3)_2$ and nickel from $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$; the working concentrations in mg/l for all the metals are 10, 20, 30, 40, 60 and 100 mg/l.

All the solutions were prepared in 0.01M NaNO_3 solution. This was used to maintain constant ionic strength of the solution throughout the experiment. The pH of the solution was adjusted to the required value throughout the experiment with 0.1M NaOH and 0.1M HCl.

In order to investigate the effect of concentration on the adsorption of metal ions, 0.2 g of the adsorbent was added to 50 ml each of varying concentrations (between 10- 100mg/l) of the metal ion solutions. The mixture was shaken with basic reciprocating shaker at 150rpm and filtered through whatman filter paper. The concentration of the residual metal ion remaining in the filtrates was determined using atomic absorption spectrometry (AAS).

The effect of adsorbent dose was studied by varying the adsorbent dose used for the adsorption at specific pH, constant concentration (20 mg/l) and agitation time of 2 hours at ambient temperature. The dosages administered were 0.4, 0.6, 0.8, 1.0, and 1.2 g. The concentration of the residual metal ion remaining in the filtrates was also determined using atomic absorption spectrometry (AAS).

The amount of the metal adsorbed was calculated using the equation:

$$q_e = \frac{V(C_o - C_e)}{100M} \quad (5)$$

where q_e is the amount of adsorbate ion adsorbed in milligram per gram of the adsorbent, C_o is the initial concentration of the metal ion before adsorption process, C_e is the equilibrium concentration of the metal ion in the filtrate after adsorption process and M is the mass in gram of the adsorbent and V is the volume of the solution in ml. The percentage metal ion removal (% Rem) was calculated using the equation:

$$\% \text{ Rem} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (6)$$

RESULTS AND DISCUSSION

Effect of Initial Metal ion Concentration on Pb^{2+} and Ni^{2+} Adsorption

Adsorptions of Pb^{2+} and Ni^{2+} at constant adsorbent dose and pH were studied at room temperature by varying the initial metal ion concentration (10, 20, 30, 40, 60, 100 mg/l) of each of the metals.

Figure 1 shows the effect of initial metal ion concentration on Pb^{2+} and Ni^{2+} adsorption. The amount of metal ion adsorbed onto the activated LBH increases with an increase in the initial metal ion concentration. In the given time duration of 2 hours, both metals showed highest metal uptake at initial metal concentration of 100 mg/l. The metal uptake values for lead and nickel are in the range of 1.99 - 19.85 mg/g and 1.47 – 14.28 mg/g respectively. Figure 1 indicates that Pb^{2+} has a higher uptake value than Ni^{2+} . Previous reports have shown that with increasing metal ion concentration, the specific sites are saturated and vacant sites are filled and at low concentrations adsorption sites take up the available metal more rapidly while at higher concentrations metal ions need to diffuse to the adsorbent

surface by intra particle diffusion and greatly hydrolyzed ions will diffuse at a slower rate [12,13,14]. The estimation of the adsorption capacity of the activated LBH was further carried out by analyzing the isotherm data using Freundlich and Langmuir adsorption isotherm models.

Adsorption Modeling

The Langmuir and Freundlich models are the most commonly used for solid – liquid phase isotherms. These isotherms relate the amount of metal ion adsorbed at equilibrium per unit weight of the adsorbent, q_e (mg/g) to the adsorbate concentration at equilibrium, C_e (mg/l). According to the Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, and once an adsorbate occupies a site, no further adsorption can take place at that site and this is defined as:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (7)$$

The linearized form is expressed as

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{b q_{\max} C_e} \quad (8)$$

where q_{\max} is the amount of adsorbate adsorbed per gram of dried adsorbent at equilibrium (mg adsorbate/g of dried adsorbent), q_{\max} is the constant relating to the maximum amount of adsorbate ion bound per g of adsorbent for a monolayer (mg/g), b is Langmuir constant or adsorption coefficient or the adsorption affinity (l/mg) for binding of adsorbate on the adsorbent sites and C_e is equilibrium (residual) adsorbate concentration in solution after sorption (mg/l).

The values of q_{\max} and b can be calculated from the intercept $\frac{1}{q_{\max}}$ and slope $\frac{1}{b q_{\max} C_e}$ of the plot $\frac{1}{q_e}$ against

$\frac{1}{C_e}$ as illustrated in Figures 2 and 3 [15]. The isotherm constant and their coefficients of determination, R^2 are

listed in Table 3.

The Freundlich isotherm model describe non – ideal adsorption onto heterogeneous surfaces involving multilayer adsorption and is defined as

$$q_e = K_F C_e^{1/n} \quad (9)$$

Its linearized form is given as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (10)$$

where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent, K_F is Freundlich constant measuring adsorption capacity (l/mg), C_e is equilibrium concentration of the adsorbent in solution (mg/l), n is constant related to adsorption efficiency and energy of adsorption or adsorption intensity of the adsorbent.

Figures 4 and 5 shows Freundlich isotherm model for the different heavy metal ions adsorption. The isotherm constants and correlation coefficients, R^2 , are also listed in Table 2. A plot of $\log q_e$ against $\log C_e$ gives a straight line with a slope, $1/n$ and an intercept of. $\log K_F$. The K_F value increases with the total adsorption capacity of the adsorbent to bind the adsorbate. The numerical value of n is a useful index to determine favorability of the adsorption.

Figures 2 – 5 represents Langmuir and Freundlich fitting of adsorption isotherms of Pb^{2+} and Ni^{2+} respectively on activated LBH. Table 2 indicates the Langmuir and Freundlich isotherm parameters for the adsorption of these metal ions on activated LBH at 27°C.

The values of the maximum metal uptake (q_{\max}) for Pb^{2+} and Ni^{2+} are 55.5 mg/g and 47.6 mg/g respectively. Therefore, the order of adsorption can be deduced from Table 2 as follows: $Pb^{2+} > Ni^{2+}$ and this is in agreement with the trend in Figure 1. This can be attributed to many factors ranging from types of adsorbent and binding sites

affinity to the metal to be adsorbed etc. The maximum metal uptake (55.5 mg/g) obtained for lead was an improvement upon 29.7mg/g reported by Kalyani *et al.* [16] for lead adsorption using eggshell powder.

It was observed that the linearized forms of the isotherms (Langmuir and Freundlich isotherm) were linear over the concentration range studied and the result fitted better in the Langmuir model in terms of R^2 value, recording 0.961 for lead and 0.952 for nickel. In other words, the equilibrium data were well represented by Langmuir isotherm equation when compared to Freundlich isotherm because Langmuir isotherm averagely possesses higher correlation coefficient than Freundlich isotherm. The high degree of correlation for the linearized Langmuir relationship suggests monolayer adsorption on specific sites or single surface reaction [16].

All the values of $\frac{1}{n}$ in Table 3 falls within 0 – 1 range which strongly suggest favorable adsorption. The essential features of the Langmuir isotherm was expressed in terms of a dimensionless constant called the equilibrium parameter, R_L .

Separation Factor, R_L

The shape of Langmuir isotherm can be used to predict whether the adsorption system is favorable or unfavorable in batch process. Separation factor is a dimensionless constant used in expressing the essential characteristics of Langmuir isotherm. Separation constant, R_L , is defined as

$$R_L = \frac{1}{1 + bC_o} \quad (11)$$

Where b is the Langmuir constant (l/mg), C_o is the initial metal ion concentration of the selected metal (mg/l), It is known that R_L values between 0 and 1 indicate favorable adsorption [17,18].

Figure 6 shows the separation factor for adsorption of these metal ions onto activated LBH over the whole concentration range studied. It was observed that as the concentrations of the metals increased, the separation factor decreased for each metal. The lower the separation factor the more effective the adsorption [19]. The separation factor values were all found to fall between 0 – 1 which indicate favorable adsorption. Hence, the most effective adsorption was achieved at 100 mg/l for both metals and the sorption of Pb^{2+} was the more effective since it has the smaller separation factor. From Figure 6, the order of effective separation can be deduced as $Pb^{2+} > Ni^{2+}$.

Effect of Adsorbent Dose on Pb^{2+} and Ni^{2+} Adsorption

The efficiency of metal removal is significantly influenced by the amount of adsorbent used [15]. Figure 7 shows a graphical representation of effect of adsorbent dose on Pb^{2+} and Ni^{2+} uptake respectively. A trend of increment in adsorption capacity with increment in adsorbent dose was observed from 0.4 to 0.8g. Adsorbent recorded a maximum capacity of 4.07 mg/g (81.4%) for Pb^{2+} and 2.94 mg/g (58.7%) for Ni^{2+} at 0.8 g dosage. Further increment of adsorbent above 0.8g resulted in a decline in adsorption capacity. The initial increment in adsorption capacity with increase in adsorbent dosage was expected, since the number of adsorbent particles increased and thus more surface area was available for metal attachment. Same trend was reported by earlier researchers [20,21].

It is plausible to suggest that with higher dosage of adsorbent there would be greater availability of exchangeable sites for metal ions as noted by Babel and Kurniawan [22] and Najua *et al.* [23]. Further increment in adsorbent dosage beyond maximum adsorption capacity at 0.8g however resulted in a decline in capacity as shown in Figure 7. This reduction in capacity had been explained as due to overlapping of the adsorption sites as a result of overcrowding of adsorbent particles beyond the optimum dose [23,24]. Moreover, the highest dosage could impose a screening effect on the dense outer layer of the cells, thereby shielding the binding site from metals [25]. From Fig. 7, it was observed that all the heavy metals showed a unique adsorption behaviour at the various adsorbent dosage as different uptake value was recorded for each of the metal ion at various adsorbent dosage.

Table 1: Physicochemical parameters of the Locust Bean Husk

Parameters	LBH
Dry matter content (%)	91.8
Moisture content (%)	8.2
pH of 1% Solution	6.21
Bulk Density (g/cm ³)	0.49
Ash Content (%)	3.5

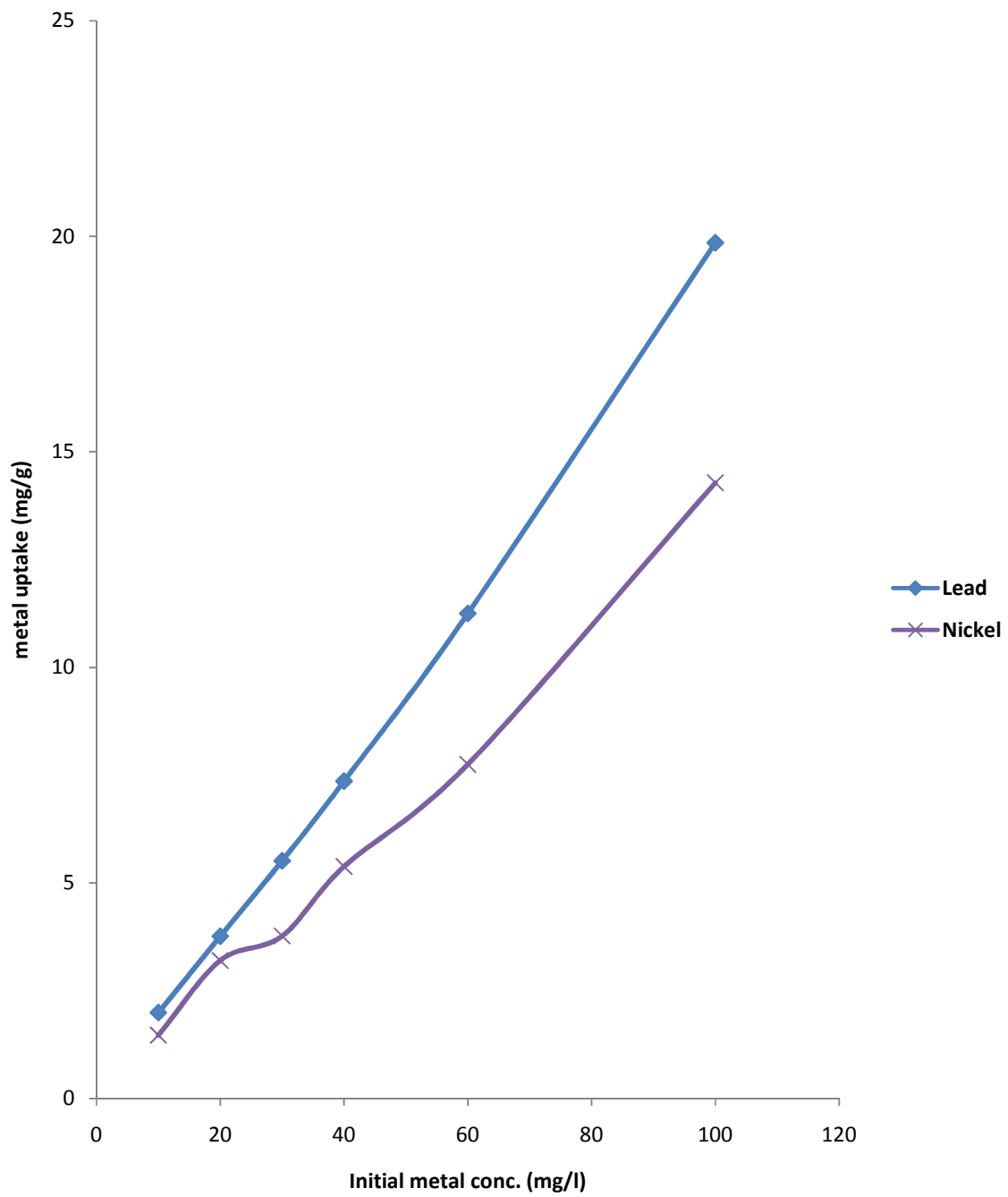


Figure 1: Effect of Initial Metal Ion Concentration on Pb²⁺ and Ni²⁺ Adsorption.

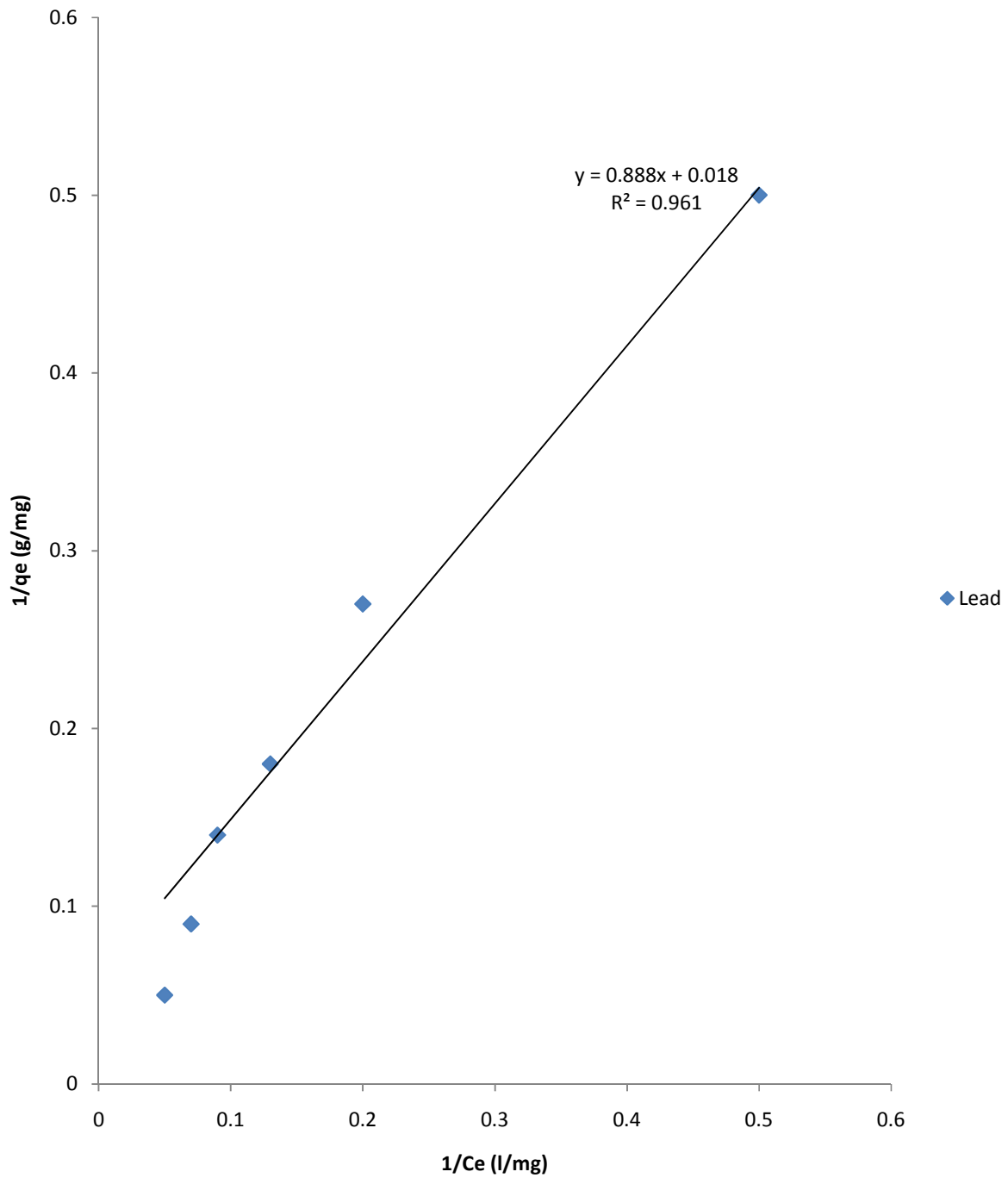


Figure 2: Langmuir Adsorption Isotherm for Pb^{2+} Adsorption

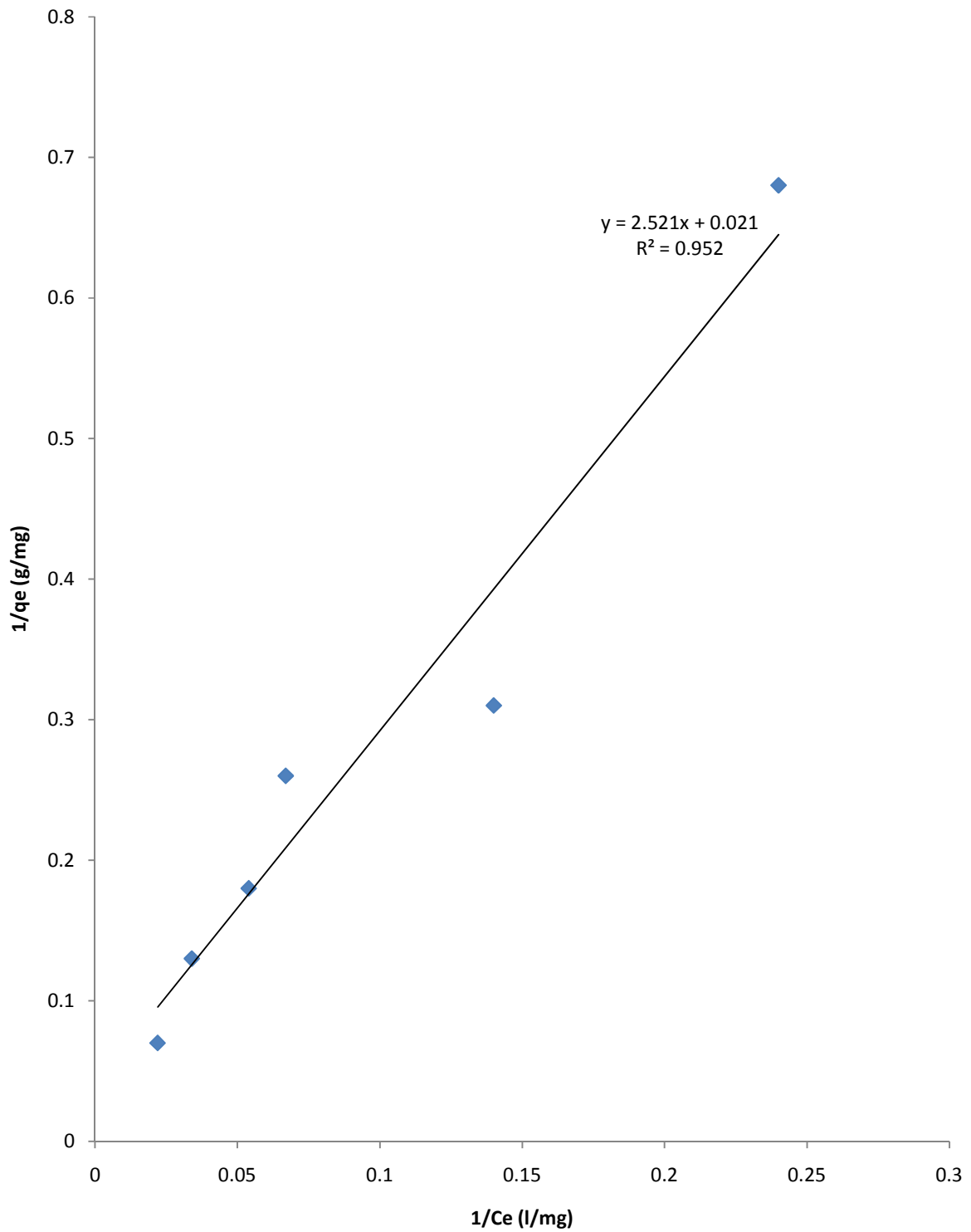


Figure 3: Langmuir Adsorption Isotherm for Ni^{2+} Adsorption.

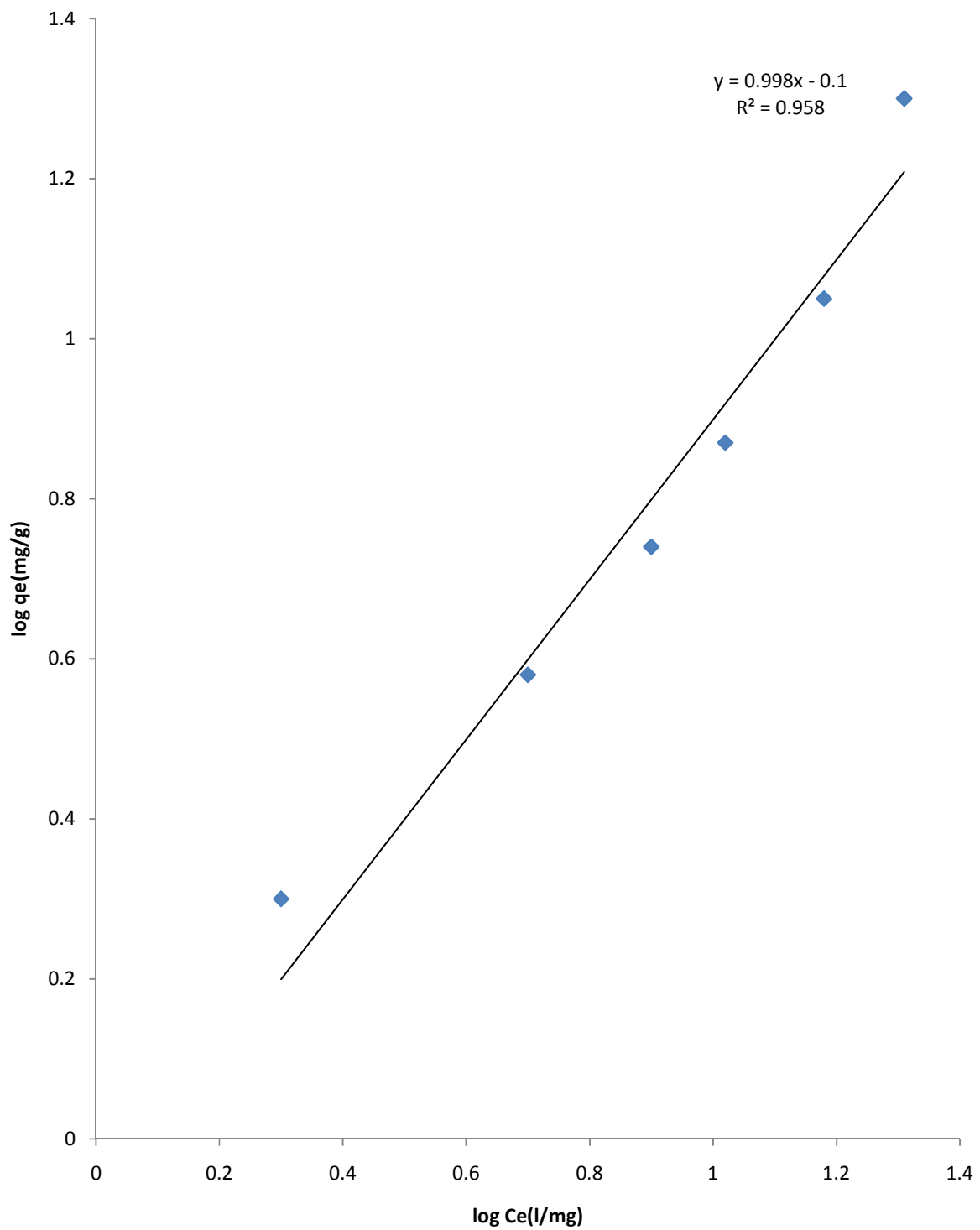


Figure 4: Freundlich Adsorption Isotherm for Pb²⁺ Adsorption.

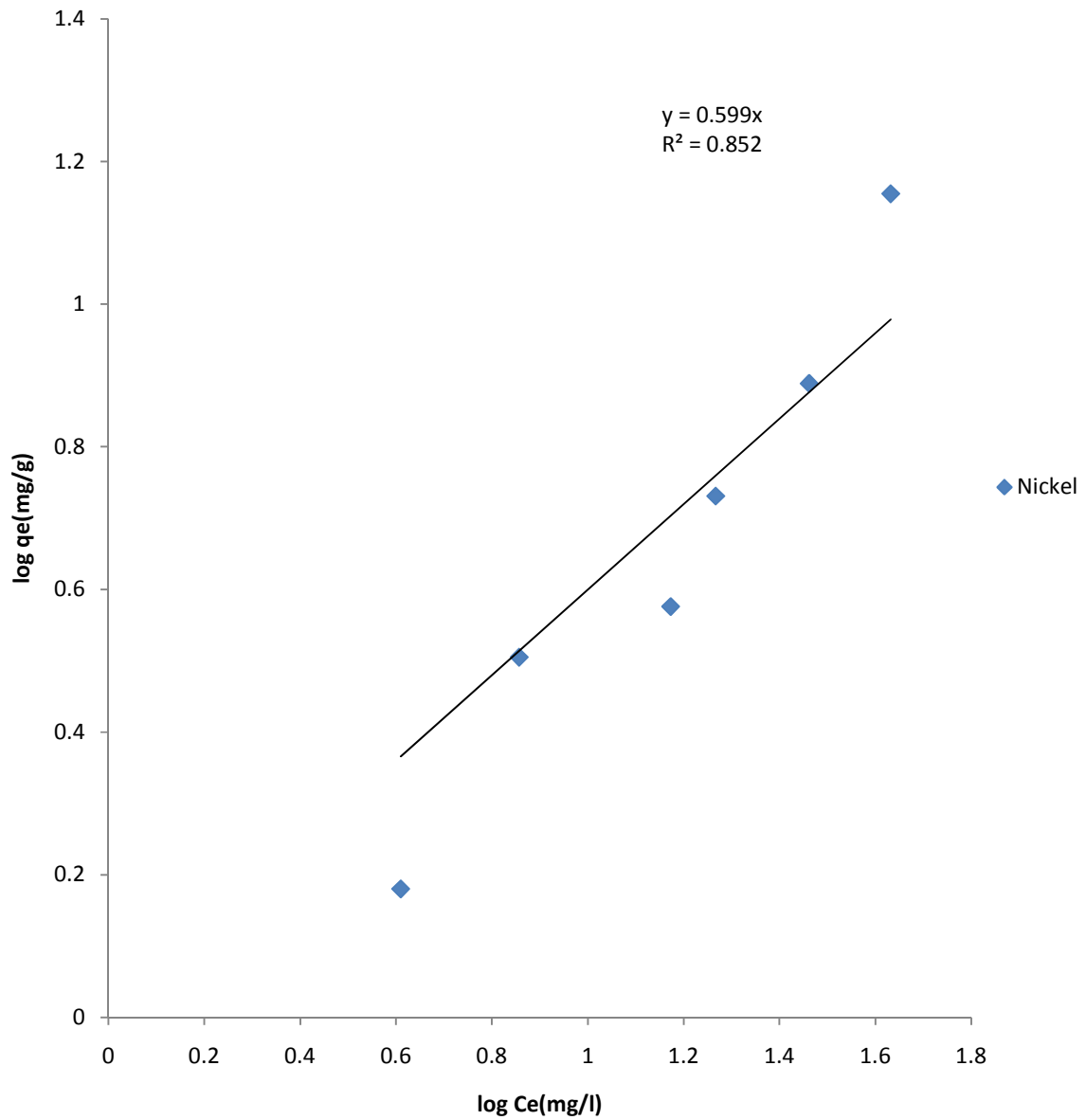


Figure 5: Freundlich Adsorption Isotherm for Ni²⁺ Adsorption.

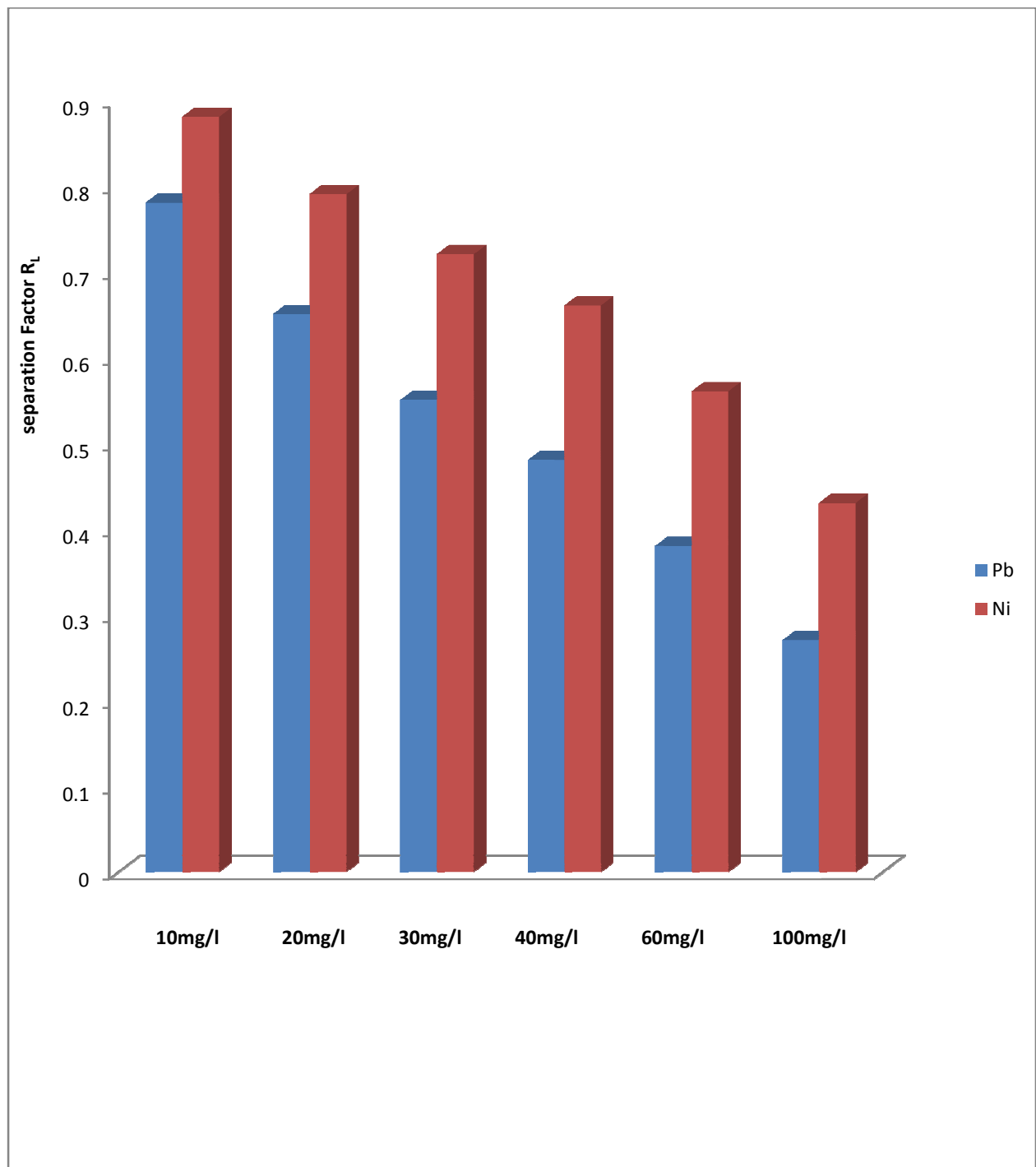


Figure 6: Separation Factor, R_L Variation with Concentration(mg/l) on Adsorption of Pb^{2+} and Ni^{2+}

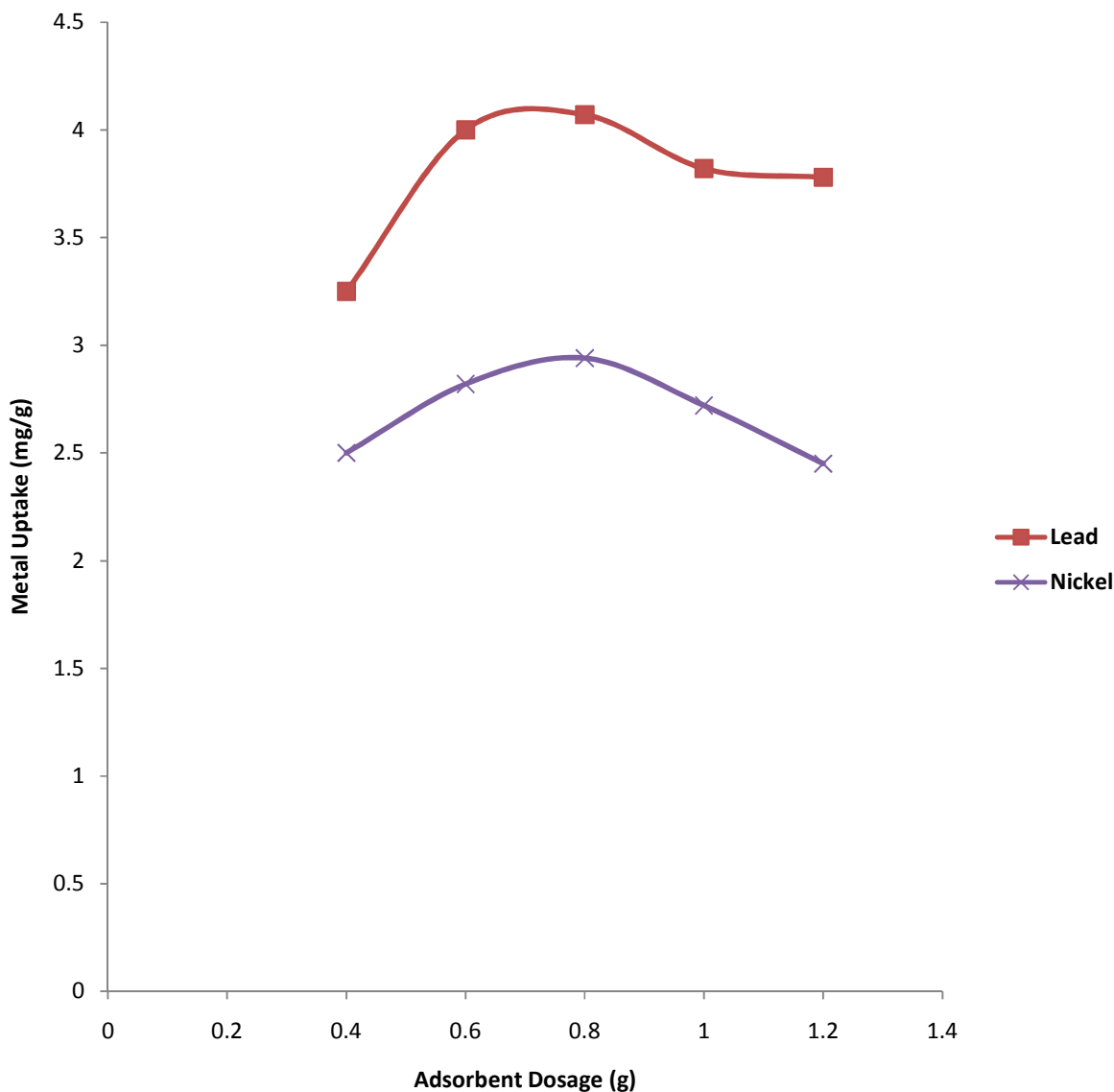


Figure 7: Effect of Adsorbent Dose on Pb²⁺ and Ni²⁺ Adsorption

Table 2: Langmuir and Freundlich isotherm constants for the adsorption of all the Selected Metal ions on activated Locust Bean Husk

Metals	Langmuir Constant				Freundlich Constant		
	q _{max} (mg/g)	b(lmg ⁻¹)	b(lmol ⁻¹)	R ²	1/n	K _F (l/g)	R ²
Lead	55.55	0.020	4144.0	0.961	0.998	0.7900	0.958
Nickel	47.60	0.008	463.65	0.952	0.599	1.0000	0.852

(q_{max}, is the maximum metal uptake (mg/g), b, is Langmuir constant (l/mg) K_F, is Freundlich Constant measuring adsorption capacity(L/mg), and n, is constant related to adsorption efficiency and energy of adsorption or adsorption intensity of the adsorbent.)

CONCLUSION

This research showed that activated locust bean husk is an effective adsorbent for Pb²⁺ and Ni²⁺ removal from aqueous solution. It was observed that the uptake of the selected heavy metal ions by activated LBH increases with

increasing initial metal ion concentration. The optimum dosage for the removal of Pb^{2+} and Ni^{2+} by activated LBH was found to be 0.8g, recording adsorption capacity of 4.07 mg/g for Pb^{2+} and 2.94 mg/g for Ni^{2+} . Hence, the batch studies conducted in this present work provides vital information, that Adsorption of Pb^{2+} and Ni^{2+} by activated LBH is dependent on initial metal ion concentration and adsorbent dosage.

Langmuir and Freundlich isotherm models were used for the mathematical description of adsorption of the selected heavy metal ions by activated LBH and it was found that Langmuir model having higher R^2 values of 0.961 and 0.952 for Pb^{2+} and Ni^{2+} respectively fitted the equilibrium adsorption data more than the Freundlich model for the two metals. The maximum metal uptake (q_{max}) for Pb^{2+} and Ni^{2+} are 55.5 mg/g and 47.6 mg/g of the dry weight of the activated LBH respectively at adsorbent dose of 0.2 g and initial metal ion concentration of 20mg/l. From the isotherm constants, it was also observed that the trend of metal affinity for activated LBH surface was $Pb^{2+} > Ni^{2+}$. Hence, adsorption of these heavy metals by the activated LBH is a monolayer sorption process.

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