

Nickel (II) removal from aqueous solutions by *Lagerstroemia Indica* Seeds activated carbon

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Abstract - The ability of activated carbon prepared from *Lagerstroemia Indica* seeds (LIS) was studied to remove Ni (II) from aqueous solutions. Batch adsorption experiments were performed in order to examine the effects of pH, contact time, adsorbent dose and initial Ni metal ion concentration on the removal process. The kinetic data were fitted by pseudo second order model. Adsorption isotherms were studied and compared with the Langmuir, Freundlich and Temkin isotherms. The thermodynamic parameters ΔG° , ΔH° and ΔS° evaluated showed that the adsorptions on LIS to be exothermic and spontaneous in nature.

Keywords — Activated carbon, Adsorption, contact time, first order kinetics, Langmuir and Freundlich isotherm, pH

I. INTRODUCTION

Pollution by toxic heavy metals is a global environmental problem. Heavy metals are non-biodegradable and can be accumulated in living organisms [1]. Nickel is one of the most important metals often found in effluents discharged from industries involved in galvanization and in the manufacture of alloys [2]. Heavy metals are continuously released into the aquatic environment from natural process like volcanic activity and weathering of rocks. Industrial processes have greatly enhanced the mobilization of heavy metals; Excess heavy metals are introduced into aquatic ecosystems as byproducts of industrial processes. Many industries like electro plating, metal finishing, metallurgical, chemical manufacturing and mining industries. They are highly toxic as ions or in compound forms; they are soluble in water and may be readily absorbed into living organisms [3]. After absorption these metals can bind to vital cellular components such as structural proteins, enzymes and nucleic acid and interfere with their functioning. This problem has received considerable attention in recent years due primarily to concern that those heavy metals in the waste streams can be readily adsorbed by marine animals and directly enter the human food chains, thus presenting a high health risk to consumers [4]. Cadmium for example damages the kidneys. A number of technologies for the removal of metal ions from aqueous solutions have been developed over the years. The most important of these techniques include coagulation, chemical precipitation [5]. Floatation [6], Ion exchange, reverse Osmosis and electro dialysis [7]. Out of these the most used are the reduction and precipitation as well as coagulation techniques. These methods however, are less efficient and create sludge. Ion

exchange and reverse osmosis even though effective and efficient are expensive, hence only few industries think of it, alternate methods like adsorption on agricultural and biological waste have been employed by many workers [8,9,10].

The objective of this study is to prepare activated carbon from *Lagerstroemia indica* seed by chemical activation with Phosphoric acid. Large availability of this material around our city attracted us to utilize it as potential adsorbent for the removal of toxic metals. The adsorption capacity of *Lagerstroemia indica* seed used as the adsorbent for the removal of metals varying with process factors including initial metal ion concentration, contact time, initial pH, adsorbent dose and temperature.

II. METHODS AND MATERIALS

2.1 Adsorbent preparation

The *Lagerstroemia indica* seeds (LIS) used in this study was collected from local fields. The collected seeds were extensively washed with tap water to remove soil and dust, sprayed with distilled water then dried, charred with excess quantity of phosphoric acid for 10h. Then the resultant carbon is washed with excess quantity of distilled water and dried at 110°C for 1 hour and stored in air tight lid container for further studies. It is then screened through a mesh sieve with a particle size range of 180-300 μm .

2.2 Adsorbate solution

A stock solution of (1000mg/L) of Nickel (II) was prepared by dissolving 4.478g of nickel sulphate ($\text{NiSO}_4 \cdot \text{H}_2\text{O}$) in 1000mL double distilled water.

2.3 Batch adsorption experiments

Adsorption isotherm study was carried out with different initial concentrations of Ni (II) ranging from 10 to 40 mg/L while maintaining the adsorbent dosage at 0.1 g. The effect of contact time and pH was studied with Ni (II) concentration of 10-40 mg/L and an adsorbent dosage of 0.1 g. The solution pH was adjusted in the range of 5-11 by using dilute hydrochloric acid and sodium hydroxide solutions. Experiments were carried out by varying the adsorbent amount from 0.1 to 1.0 g with Ni (II) concentration ranging from 10 to 40 mg/L. The concentration of free Ni (II) ions in the effluent was determined spectrophotometrically by developing a rosy red color using di methyl glyoxime and tri-sodium citrate and iodine solution.

2.4 Adsorption studies

The sorption of nickel (II) was performed by batch technique. For this aim a 50 mL of the test solution, which adjusted to desire pH and concentration of these metal ions was contacted with 100mg of *Lagerstroemia indica* seed carbon used for this study. This was stirred at low speed (750rpm) for different contact times at room temperature. After an enough contact time the solution was separated from carbon by centrifugation at 2500rpm. UV spectrophotometer has been used to perform for the determination of amounts of nickel in supernatants; the percentage adsorption of nickel (II) from aqueous solution was computed.

III. RESULT AND DISCUSSION

3.1 Effect of adsorbent dose

The effect of adsorbent dose on Ni (II) removal was studied by keeping all other experimental conditions constant except that of adsorption dose. The results showed that with increase in adsorbent concentration there is a decrease in the amount adsorbed per unit mass of the adsorbent. The adsorption of metal ions as a function of adsorbent dose depicted in Fig.1 revealed that with the adsorbent the percentage of adsorption increased while sorption capacity diminished with increase in adsorbent dose in the case of nickel metal ions used in this study.

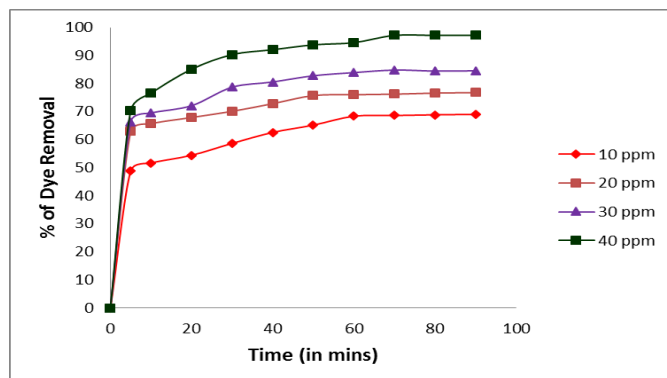


Fig.1. Effect of adsorbent dose

3.2 Effect of contact time and initial metal concentration

The experimental results of adsorptions at various initial metal concentrations (10, 20, 30 and 40 mg/L) on clay was shown in Fig.2. It was observed that the percentage removal at equilibrium increases from 69.01% to 97.32% as the initial metal concentration was increased from 10 mg/L to 40 mg/L. At lower concentrations, the ratio of the initial number of metal ions to the available surface area is low. Subsequently, the fractional adsorption becomes independent of initial concentration. However, at higher concentrations the available sites of adsorption become fewer and hence the percentage removal of metal becomes dependent upon initial concentration [11,12]. The equilibrium was found to get established at 40, 50, and 60 min for nickel with the adsorbent as the initial metal concentration was increased from 10 mg/L to 40 mg/L. The curves are single, smooth and continuous, leading to saturation, suggesting the possible monolayer coverage of the metal on the adsorbent surfaces [13].

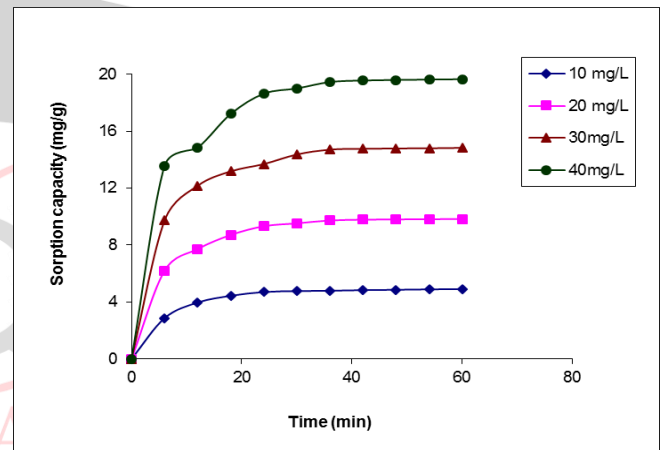


Fig.2. Effect of initial dye concentration

3.3 Effect of pH

Adsorption experiments were carried out at various pH values ranging from 5 to 11, maintaining the pH by adding required amount of dilute hydrochloric acid and sodium hydroxide solutions. The sorption capacity increased with increase in pH. Fig. 3 indicates that maximum metal removal had occurred in basic medium.

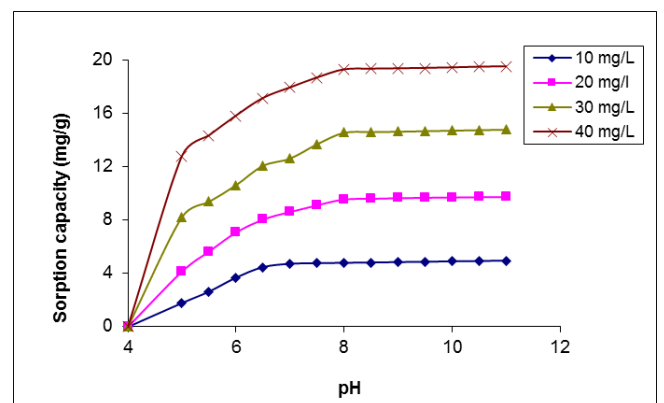


Fig.3. Effect of pH

3.4 Effect of temperature

The effect of temperature on the removal of Ni (II) by LIS was shown in Fig.4. The amount of metal adsorbed decreased with increasing temperature from 303 K to 315 K indicating the adsorption process to be exothermic. This may be due to the decrease in the rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of adsorbent with increase in temperature.

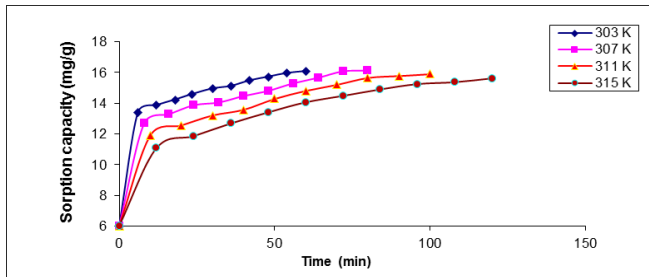


Fig.4. Effect of temperature

3.5 Kinetics of adsorption

In order to investigate the mechanism of adsorption of Ni (II) by the clay the following kinetic models were considered.

3.5.1 Pseudo second order kinetics

In the linearised form pseudo second order kinetic model can be represented as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \dots (1)$$

Where k_2 is the second order rate constant ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}$). A plot of t/q_t and t should give a linear relationship if the adsorption follows second order q_e and k_2 can be calculated from the slope and intercept of the plot. The linear plots (Fig. 5) obtained from experimental data clearly show that the adsorption process follow pseudo second order kinetics.

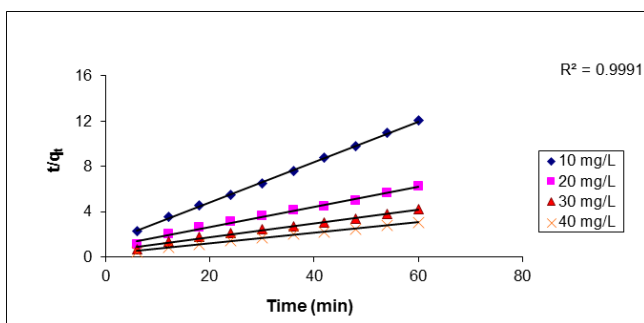


Fig.5. Pseudo second order model for adsorption of Nickel

3.5.2 Elovich kinetic model

The Elovich equation mainly applied for chemisorptions and valid for systems with heterogeneous adsorbing surfaces [14] is generally expressed in its integrated form as

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t \quad \dots (2)$$

Where 'a' is the initial adsorption rate ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}$) and 'b' is related to the extent of surface coverage and the activation energy for chemisorptions ($\text{g} \cdot \text{mg}^{-1}$). A plot of q_t vs. $\ln t$ gives a straight line with a slope of $1/b$ and an intercept $\log 1/b \ln(ab)$ with good correlation coefficients (0.9862, 0.9808, 0.9749 and 0.9765). Fig.6 strongly supports the validity of the Elovich equation suggesting chemisorptions.

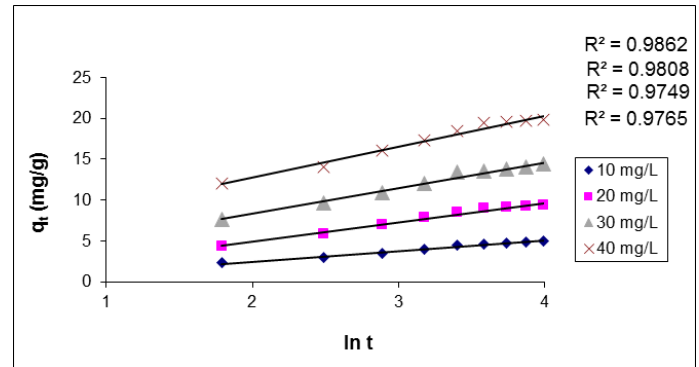


Fig.6. Elovich kinetic model

3.6 Adsorption isotherms

The experimental data were fit into Langmuir and Freundlich isotherms

3.6.1 Langmuir isotherm

In linear form the Langmuir model [15] is usually expressed as,

$$C_e / q_e = i / b Q_0 + C_e / Q_0 \quad \dots (3)$$

Where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/L) and Q_0 and 'b' are Langmuir constants related to adsorption capacity and rate of adsorption respectively. A linear plot of C_e/q_e vs. C_e is shown in Fig. 7.

The values of Q_0 and b were calculated from the slope and intercept of the plots and the values are given in Table 1. These values indicate that the maximum monolayer adsorption capacity of LIS for Ni (II) was 7.26 mg/g . The crucial features of the Langmuir isotherm was examined by the dimensionless constant separation term (R_L) which was calculated using

$$R_L = \frac{1}{(1+b C_0)} \quad \dots (4)$$

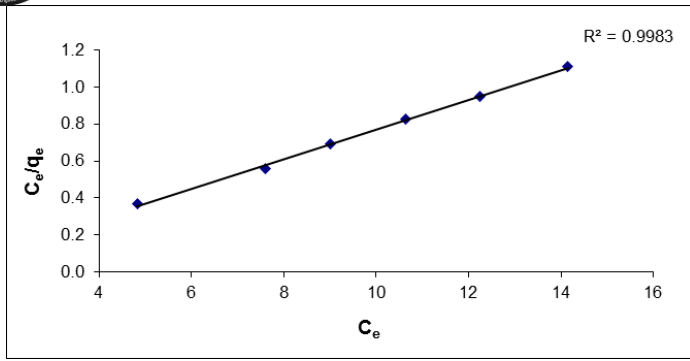


Fig.7. Langmuir isotherm

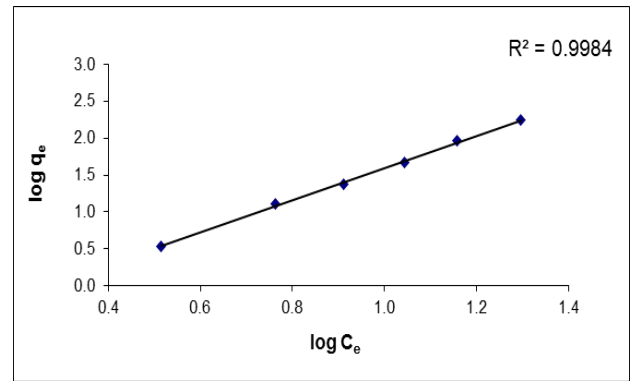


Fig.8. Freundlich isotherm

Where C_0 is initial metal concentration (mg /L). The nature of adsorption is if, $R_L > 1$ Unfavourable, $R_L = 1$ Linear, $R_L = 0$ Irreversible, $0 < R_L < 1$ Favourable. In the present study, the R_L values were all less than unity in the concentration range studied, showing that the adsorption process was favourable.

Table 1. Data for Langmuir adsorption isotherm for Nickel

Conc. of Metal mg/L	Nickel (LIS)			
	R_L	Q^0	b	R^2
20	0.8812			
40	0.7961			
60	0.7225			
80	0.6613	7.26	0.033	0.9967
100	0.6097			
120	0.5656			

3.6.2 Freundlich isotherm [16]

The Freundlich isotherm can be represented in its logarithmic form as,

$$\log q_e = \log K_f + 1/n \log C_e \dots\dots\dots (5)$$

Where K_f and n are Freundlich constants representing adsorption capacity and intensity of the adsorbent respectively. The plot of $\log q_e$ vs. $\log C_e$ shown in Fig 8. The linear plot with a regression coefficient of 0.9851 shows that the data for the adsorption of Ni (II) fit well with Freundlich isotherm. The value of n , evaluated as 1.96 indicates that the process was favorable [17]. The value of K_f was found to be $6.301 [mg^{1-1/n} L^{1/n} g^{-1}]$ respectively.

3.7 Thermodynamic parameters

The thermodynamic parameters for the adsorption process such as free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were evaluated using the following equations:

$$\ln K_C = \Delta S^0 / R - \Delta H^0 / RT \dots\dots\dots(5)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \dots\dots\dots(6)$$

Where K_C is the Langmuir constant related to the energy of adsorption, R is the gas constant and T is the absolute temperature (K). Negative free energy changes (18.4, 19.1, 19.7, 20.3, kJ/mol at 303 K - 315 K) and positive entropy change (27.2 kJ/mol) of adsorption indicate that the adsorption is favorable and spontaneous process. The exothermic nature of adsorption is confirmed by the negative value of ΔH^0 (43.2 kJ/mol).

IV. CONCLUSION

This study shows that the *Lagerstroemia indica* seed (LIS) activated carbon can be used effectively in the removal of Nickel through adsorption. Adsorption isotherms very well fitted with both Langmuir and Freundlich model. Pseudo second order kinetic model was followed. The sorption suggested that the adsorption is high at basic medium. Elkovich kinetic model suggested that adsorption process is chemisorptive nature. The calculated values of different thermodynamic parameters clearly indicated that the adsorption process of LIS is feasible, spontaneous and exothermic nature.

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