Kinetic and Adsorption Isotherm Studies of Ni (II) Using Activated Carbon Prepared from Lapsi Seed Stone by Chemical Carbonization

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Abstract

The present study explored the investigation on adsorption of Ni (II) on the surface of activated carbon prepared from Lapsi Seed Stone by chemical carbonization with the mixture of concentrated sulphuric acid and concentrated nitric acid. The batch adsorption experiments were performed using Atomic Absorption Spectroscopy (AAS) Technique. Two adsorption isotherms such as Langmuir and Freundlich were applied to analyze the results from the experiments. In order to establish best fit adsorption isotherm model the coefficient of correlation (R^2) was determined for each model. The adsorption data was best described by Langmuir with higher value of coefficient of correlation as compared to that of Freundlich isotherm showing a maximum adsorption capacity of 69.5 mg/g. The kinetic of the adsorption of the metal ions is evaluated by the pseudo first order and pseudo second order. The results indicate that pseudo second order provides a more appropriate description of the metal ion adsorption on the activated carbon. It has been concluded that the activated carbon prepared from Lapsi seed stone can be used as an effective adsorbent for the removal of Ni(II) from aqueous solution

Key words: *Nickel,Activated carbon, Lapsi, Adsorption isotherm, Adsorpion kinetics*

Introduction

Nickel is released into water bodies by anthropogenic activities such as manufacturing process of stainless steels, super alloys, metallic alloys, coins, batteries etc.Direct exposure to nickel causes dermatitis.Some nickel compounds as carbonyl are carcinogenic and easilhy absorbed skin. Acute poisoning of Ni (II) causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness [1].The metal ions therefore should be reduced to lower level to the permissible before being discharged to water bodies. The methods used to remove the heavy metal ions include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, electrochemical treatment, membrane filtration, reverse osmosis and adsorption. However, most of these methods have drawbacks such as incomplete removal of heavy metals, high operational cost, problem for disposal of metallic sludge.

Adsorption process, therefore, has been mostly applied for the removal of pollutants from water. Many researches have been carried out work to find the cheaper ad chemico –physically feasible adsorbent [2].

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Many studies have shown the development of low cost activated carbon prepared from locally available and cheaper materials like apricot stone [3], olive stone [4], date stone [5] peanut shell [6] coconut shell[7], palm shell [8], rice husk [9] etc. for the production of activated carbon.

Most of activated carbons are prepared by a two- stage process carbonization followed by activation. The frst step is to enrich the carbon content and to create an initial porosity and activation process helps in enhancing the pore structure. The activation can be carried by two different processes physical and chemical. Chemical activation has two importantadvantages as compared to physical activation. One is lower temperature in which the process is accomplished[10].Present study explored the preparation of activated carbon by treatment with chemicals like concentrated sulphuric acid and nitric acid which have been used to carbonize the precursor.The carbonization thus is termed as chemical carbonization.

In current study, kinetics and adsorption isotherms of Ni (II) adsorption onto AC-SN (Activated carbon prepared by the treatment of concentrated sulphuric acid and nitric acid) has been studied through a pseudo-first-order [11]a pseudo-second-order [12].Adsorption isotherm usually gives an information about the equilibrium state between the amount of adsorbed metal ion onto the adsorbent surface and the concentration of metal ions in solution.There are many types of adsorption isotherms. Among them Langmuir [13] and Freundlich [14] are the most commonly applied adsorption isotherms.

Experimental

Materials

The precursor used in this study is Lapsi seed stone , the waste material of Lapsi fruits left after the production of vitamin –C rich products. The Lapsi seed stones were collected from Paun (vitamin – C rich products) Factory, Godavari, Lalitpur, were washed well with tap water to remove impurities. The seed stones were then washed with deionized water, and dried in a hot box oven a temperature maintained at 105 ^{0}C for 24 hours. The dried stones were grinded by electric grinder and sieved into the fraction of 300 µm. The grinded particles were treated with the mixture of concentrated nitric acd and sulphuric acid and heated at a temperature of 150 ºC for 24 hours. The resulted material was washed several times with distilled water by shaking on magnetic stirrer. The washing was continued till pH of the washing attained a value between 6-7.The washed carbon was dried in an oven at 110°C and then ground and sieved using a 100 µm sieve. The carbon prepared was represented as AC-SN (Activated carbon prepared by treatment with concentrated sulphuric acid and nitric acid)

Chemicals and Instruments

All the chemicals and reagents, used were of analytical grade . Stock solutions of Ni (II) ions required were prepared from its nitrate salt using distilled water. In order to measure the pH value of the solution, Digital pH meter was used. Shaker (Digital VDRL Rotator-RPM-S) was used to carry out the adsorption experiments. The concentration of Ni (II) ions after adsorption was determined by using Atomic absorption spectrophotometer (AAS–VARIAN-AA240FS). To adjust the pH of solutions, 0.1 M NaOH and 0.1 M HCl have been used. All the solutions were prepared by diluting the stock solutions with distilled water.

Adsorption Experiments

Batch mode of adsorption experiments were carried out by suspending 0.05 g of adsorbent mixed with 25ml of adsorbate solution taken in 50 ml stoppered conical flasks. The flasks were then stirred well on Digital VDRL Rotator –RPM –S to find out the optimum condition for the experiments. Solution of NaOH and HCl have been utilized to adjust the pH of the solution. The concentration of Pb (II) ions after adsorption was determined by atomic absorption spectrophotometer (AAS –VARIAN-AA240FS).The amount of metal ions uptake can be calculated by the following equation [15].

$$q_e = \frac{(C_o - C_e) \times V}{W} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1)$$

Where C_o = initial concentration of metal ion

C_e = equilibrium concentration of metal ions

W= mass of adsorbent in gram (g)

V = volume of the solution in liter (L)

The percentage of removed metal ions (Rem %) in solution is calculated by using following the formula

$$\mathrm{Rem}(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2)$$

Results and Discussion

Effect of pH

The pH of the aqueous solution plays an important role on the adsorption of metal ions on the adsorbent. Hence the adsorption of of Ni (II) ions on AC-NS has been carried out over pH range of 2-7 at laboratory temperature. The effect of pH on removal of the metal ions is shown in Fig.1.The Figure shows that percentage removal of metal ions increases with increase in pH and attains almost constant value at pH range of 6-7. The adsorption study on higher pH was not studied since the precipitation of metal ions occurs above the pH. At low pH the percentage of removal of Ni (II) was found to be low. This may be due to the fact that higher concentration of hydrogen ions competes with metal ions.at lower.

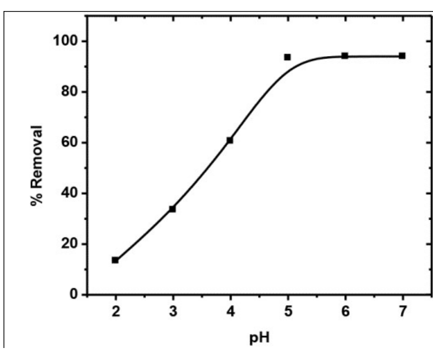

Figure 1: *Effect of pH for the adsorption of Ni(II) on AC-NS*

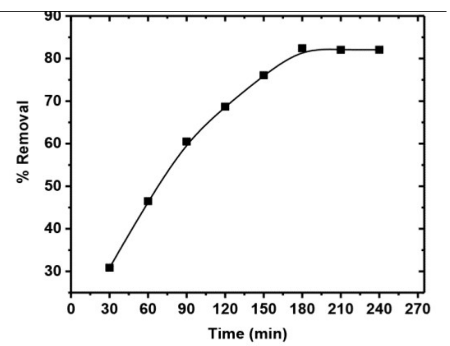

Figure2*: Effect of contact time for adsorption of Ni (II) on AC-NS*

Effect of Contact time

The amount of Ni(II) ions adsorbed by activated carbon is affected by contact time. Effect of contact time on the metal ions adsorbed is shown in Fig.2. The figure shows that the rate of adsorption has been observed very fast at initial state The fast adsorption may be caused by the fact that at initial state higher driving force make fast transfer of metal ions to the surface of adsorbent particles and availability of the uncovered surface area on the adsorbent. On further increasing time it has taken a long time to attain equilibrium for the adsorption of metal ions diffusing slowly into the pores of activated carbon due to the decrease in availability of the uncovered surface area, the active sites and less driving force. Thus the adsorption rate becomes slower. It has taken 180 minutes to reach equilibrium for AC-SN.

Adsorption isotherms

Adsorption isotherm gives an information about the distribution of the adsorbed molecules between liquid and solid phase. Langmuir and Freundlich adsorption isotherms are the most commonly used adsorption isotherms. Present work explored the application of two the adsorption isotherms to describe the relation between the amount of the adsorbate and its equilibrium concentration in solution at laboratory temperature.

Langmuir isotherm

The Langmuir isotherm assumes that a continuous monolayer of adsorbate molecules surround a homogenous solid surface[16]. The linear form of the Langmuir isotherm equation is indicated by following equation.

$$\frac{Ce}{qe} = \frac{1}{bqm} + \frac{Ce}{qm} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where C_e = concentration of the adsorbate in equilibrium (mg/L)

q_e = the amount of the adsorbate adsorbed under equilibrium

q_m=the monolayer adsorption capacity (mg/ g) and

b = the Langmuir constant [17, 18]

The slope and intercept of the plot Ce/q_e versus Ce as shown in Fig. 3 have been used to determine Langmuir constant and adsorption capacity respectively.

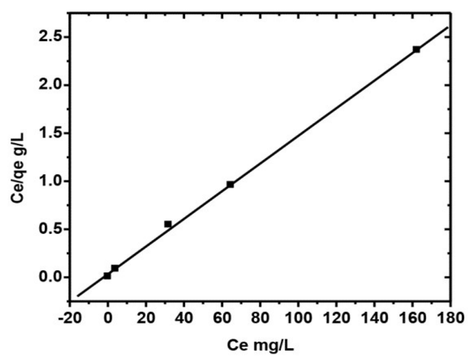

Figure 3: *Langmuir isotherm of Ni (II) adsorption onto AC-SN*

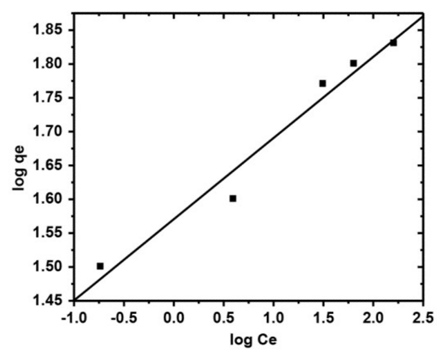

Figure 3: : *Freundllich isotherm of Ni (II) adsorption onto AC-SN*

Langmuir constant and adsorption capacity are determined from the slope and intercept of the plot Ce/q_e versus Ce as shown in Fig 3.

Freundlich isotherm

Freundlich isotherm is applicable to adsorption processes that occur on heterogonous surfaces[19]. This isotherm gives an expression which defines the surface heterogeneity and the exponential distribution of active sites and their energies.

Linear form of Freundlich isotherm may be represented as follows

$$\log qe = \log K_f + \frac{1}{n}\log Ce \qquad (4)$$

Where K_f and n = Freundlich constants related to adsorption capacity and adsorption intensity respectively.

From the slope and intercept of the straight portion of the linear plot obtained by plotting log versus log qe versus logCe, the values of Freundlich parameters can be calculated as shown in Fig 4. Langmuir and Freundlich constants are given in Table-2. Figures-3 and 4 reveal that the isotherm data better fit the Langmuir equation than Freundlich equation since the values of the coefficient of correlation (R^2 = 0.997) are higher than that of Freundlich isotherms (R^2 =0.811). This supports the theory that the number of active sites on the carbon surface is limited and uptake of nickel ions forms a monolayer on the surface. Langmuir and Freundllich parameters are shown in Table 1.

Table 1: Lanmguir and Freundlich parameters for adsorption of Ni(II) ions onto AC-NS

Heavy metal-ions	Langmuir parameters		R^2	Freundlich parameters		R^2
	q_{max} mg/g	b		K_f (mg/g)	(n)	
Ni(II)	69.5	0.438	0.998	37.2	8.33	0.966

Adsorption of the capacity of Ni (II) on PAALSSC is higher than that of activated carbons prepared from other adsorbents such as Tea factory waste, Rice hull but lower than that of Cotton stalk as shown in Table 2. From the table it is concluded that PAALSSC is better in the adsorption of Ni (II) than other adsorbents except AC prepared from Cotton stalk

Table 2: Adsorption capacity of Ni (II) ions by various adsorbents for comparison with that of AC-NS

S.N.	Adsorbents	Adsorption capacity q_{max} mg g^{-1}	References
1	Tea factory waste	15.30	Malkoc and Yasar, 2005[19]
2	AC from cotton stalk by H_3PO_4	31.45	Huang et al., 2011[20]
3	NaOH treated rice hull	12.30	Mashall et al., 1995[21]
5	AC-NS	69.49	This study

Adsorption kinetics

The adsorption kinetic study plays an important role to determine the efficiency of adsorption. To analyze rate of adsorption pseudo first order and second order kinetic models have been applied to the adsorption kinetic data

Pseudo First Order

Legergren in 1898 [22] has given pseudo first order model. According to Lagergren the pseudo first order equation is represented as follows:

$$\frac{dqt}{dt} = k_1(q_e - q_t) \quad \text{..........(5)}$$

Where q_e and q_t = the amount of the metal ions adsorbed at equilibrium and time t, respectively (mg/g)

k_1 = the pseudo –first order rate constant (Lmin^{-1}).

After integration the equation (5) becomes as follows

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}\, t \quad \text{..........(6)}$$

The validity of kinetic model has been tested by plotting the value of log (q_e - q_t) against ' t 'as shown in Fig -5

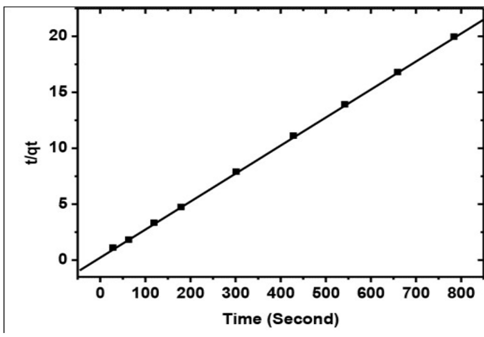

Figure 5: *Pseudo first order plot for Ni (II) adsorption onto AC-NS*

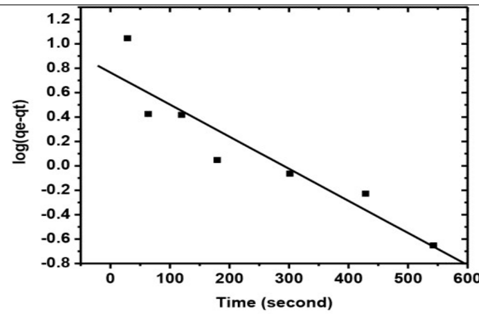

Figure 6: *Pseudo second order plot for Ni II) adsorption onto AC-NS*

The values of kinetics parameters such as k_1 and equilibrium adsorption capacity have been determined from the slopes and intercepts of the curves. The pseudo first order and pseudo second order constants are presented in Table 3.

Table 3: Pseudo first and second order parameter for Ni (II) adsorption on AC-NS

	Pseudo first order model			**Pseudo second order model**			
Heavy metal ions	**q_e(mg/g)**	**K_1(1/min)**	**R^2**	**Experimental value , q_e (mg/g)**	**q_e(mg/g)**	**K_2(g/mg min)**	**R^2**
Ni(II)	5.82	6.056×10^{-3}	0.868	39.4	39.9	0.165	0.999

Pseudo Second order

Ho second order model is often called pseudo second order model. The rate equation of pseudo second order is represented by the following equation.

$$\frac{dqt}{dt} = k_2\,(q_e - q_t)^2 \quad \text{..........(7)}$$

Where k_2 is the second order rate constant of adsorption (g mg $^{-1}$ min $^{-1}$). Integrating the above equation (7) it takes the form as follows [23].

$$\frac{1}{(qe-qt)} = \frac{1}{qe} + k_2\ t \qquad (8)$$

The equation (8) can be rearranged to obtain

$$\frac{t}{qt} = \frac{1}{qe^2}\frac{1}{k_2} + \frac{t}{qe} \qquad (9)$$

The validity of the kinetic mode was tested by plotting the value of 't/qt' against 't ' is plotted as shown in Fig. 6

Conclusion

Adsorption isotherms and kinetic studies for the adsorption of Ni(II) have been investigated by activated carbon from Lapsi seed stone by Chemical carbonization with the mixture of concentrated sulphuric acid and concentrated nitric acid. The adsorption of Ni (II) has been found to be dependent on pH and the maximum adsorption has been observed at pH 5.Optimal contact time for removal of the metal ions has been observed as 180 minutes. The equilibrium data is best described by Langmuir adsorption isotherm with high correlation coefficient (R^2=0.997) as compared to that (R^2=0.966 of Freundlich isotherm showing a maximum adsorption capacity of 69.5 mg/g. Analysis of adsorption kinetic data has shown that the data is found to be the best fit to pseudo second order kinetics (R^2= 0.999) to describe the adsorption process. The results of this study shows that the activated carbon prepared from Lapsi seed stone by chemical carbonization can be used as an effective adsorbent for the removal of Ni (II) ions from aqueous solution.

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