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Adsorption of nickel from aqueous solutions using clean adsorbent as applications of green chemistry

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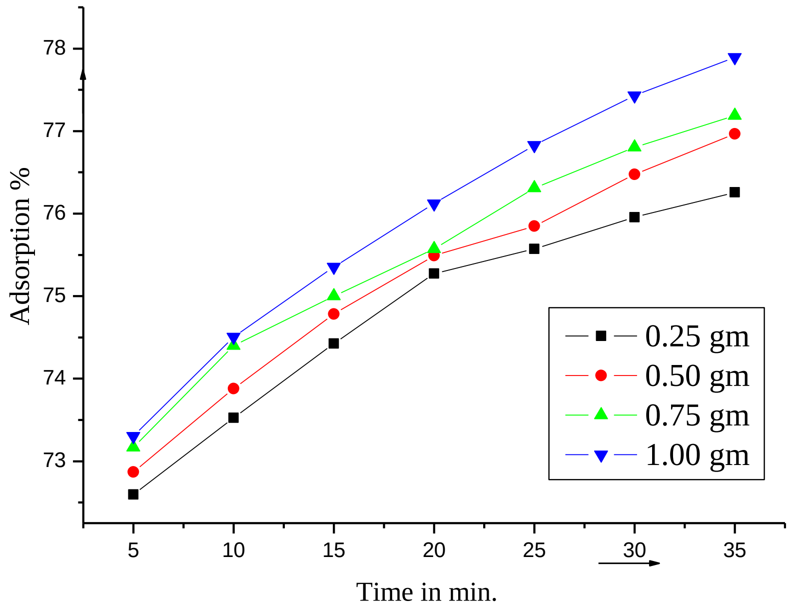
- **Novelty and Highlights:**

  Agricultural waste of Red gram seed husk is used as an adsorbent for the adsorption of nickel (II) metal ion. It is a cheap, readily available and eco-friendly adsorbent.

- **Graphical Abstract:**



Nickel (II) metal ion adsorption at Red gram seed husk depends on initial concentration of metal ion, adsorption dose, temperature etc.

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Abstract Cajanuscajan (Red Gram) seed husk has been used as adsorbent for the removal of Ni (II) ion from aqueous solutions. Adsorption experiments were performed by studying parameters like contact time, initial concentration of Ni (II) ion, amount of adsorbent, initial pH and temperature. The optimum conditions were obtained at initial pH 5, temperature 33^0 C, contact time 35 min, and 100mg/L initial concentration of Ni (II) ion. Adsorption kinetic models include Lagergren pseudo-first order; pseudo-second order and intraparticle diffusion were applied in order to investigate the adsorption. Langmuir and Frendlich isotherm models were used to investigate the adsorption techniques. Thermodynamic parameters such asΔG^0, ΔH^0 and ΔS^0 were evaluated

Key words: Adsorption, Red gram seed husk powder, Ni (II) ions, Langmuir and Frendlich isotherm models, pseudo-first order and pseudo-second order kinetics

Introduction

The increasing contamination of urban and industrial wastewater by toxic metal ions is a alarming environmental problem. The problem of eliminating pollutants from water is an important process and is becoming more important with the increasing of industrial activities. About 97 % of water contamination is generated by chemicals, paper, petroleum and primarily metal sectors [1].

Various technologies employed to remove toxic heavy metal ions includes ion-exchange, electro-deposition , solve removal of extraction, reverse osmosis, electro-dialysis, precipitation, flocculation, sorption, ultrasound oxidation process, Biological process, and adsorption[2-9], etc., but the selection of the wastewater treatment method is based on the concentration of waste and the cost of treatment.

Adsorption is one of the most popular methods for the removal of metal ions from the aqueous solutions. Adsorption is a surface phenomenon, in which molecules of adsorbate are attached and held to the surface of an adsorbent until equilibrium is reached between adsorbate and adsorbent. The adsorption phenomenon depends on the interaction between the surface of the adsorbent and the adsorbed species. The interaction may be due to: i) chemical bonding, ii) hydrogen bonding, iii) hydrophobic and iv) Van der Waals forces [10].

The present study focuses on the removal of Nickel (Ni) from aqueous solution; Nickel is a naturally occurring hard, silvery-white metal. It's wide spread industrial applications such as Nickel plating and making of steel, coins, jewellery, batteries and heat exchangers have resulted in its presence in many industrial effluents. Nickel is an essential micronutrient, but with prolonged contact and at high doses it can cause skin allergic reactions, asthma, bronchitis, lung and heart disorders and adverse effects on stomach and blood. Some Nickel compounds are carcinogenic and metallic Nickel may possibly be carcinogenic to humans. Hence it is necessary to reduce Nickel from wastewater to acceptable levels. In continuation of our earlier work[11-14] we decided to use low cost agricultural material i.e. red gram seed husk powder, as adsorbent for the adsorption of Ni ion from aqueous solutions.

Materials and methods

Preparation of adsorbent the mature and fresh *Cajanuscajan*crop seeds were purchased from local market and washed thoroughly by using distilled water to clean them from dirt and impurities. After that, the red gram crop seeds are soaked into distilled water up to 24 hours. Then their skin was removed from their pulses and washed with distilled water. It is dried in shadow. After drying the husk was ground by grinder to constant size of 60 μm fine powders of red gram seed husk (RGSH). The dried fine powder adsorbent was kept in an air tight glass bottle ready for further experiments.

Preparation of adsorbate all the chemicals used were of analytical grade. Ammonium Nickel sulphate [$NiSO_4$

$(NH_4)_2SO_4.6H_2O$] was purchased from Sd. Fine Chemicals Pvt. Ltd. Mumbai (India). All solutions were prepared in double distilled water. The concentration of nickel (II) metal ion solutions was determined by using UV-Visible single beam Spectrophotometer, (BioEra: Cal No.BI/CI/SP/SB-S-03). Stock solution of Nickel ion (100 ppm) was prepared by weighing and dissolving 0.675 gms. of ammonium nickel sulphate [$NiSO_4$ $(NH_4)_2$ $SO_4.6H_2O$] in one litre of double distilled water in graduated volumetric flask and used to prepare solutions in different concentrations. The concentration of solution was determined from calibration curve spectrophotometrically. The absorbance was determined at 366 nm against blank was determined Nickel (II) ion.

Batch Experiments Batch equilibrium adsorption experiments were conducted by adding known quantity of RGSH powder to Erlenmeyer flasks containing 50 ml of different concentration of Ni (II) ion solution at pH 5.2. The mixture was shaken for different intervals of time. The solutions were then filtered through filter paper and the concentration of Ni (II) ion was measured by spectrophotometer. The amount of Ni (II) ions (mg/g) was calculated using the formulae reported by Vanderborght and Van Griekenm [16], and then the kinetic adsorption parameters were calculated.

$$q = \frac{V(Co-Ct)}{M} \quad (1)$$

Where, q is the amount of Ni (II) ions adsorbed from the solution *(mg/g)*, *Co* is the concentration before adsorption *(mg/L)*, and *Ct* is concentration after adsorption. *V* is the volume of adsorbate*(L)* and *M* is the weight of the adsorbent *(gm)*.

The percentage adsorption of Ni (II) ions was calculated by following equation;

$$\textbf{Adsorption\%} = \frac{(C_0 - C_e)}{C_0} * 100 \quad \textbf{(2)}$$

Where, C_0 and C_e are the initial and equilibrium concentrations respectively.

Results and discussion

Effect of contact time and initial concentration the effect of contact time was studied at different initial Ni (II) ion concentrations and RGSH dosage.

A graph of percentage adsorption against time is plotted (Fig 1) for a fixed RGSH dose of 0.5 gm/50 ml, and varied Ni (II) metal ion concentration. It can be clearly observed that the percentage adsorption increased rapidly until time reached 35 min. After this time, there was drop in percentage adsorption. The highest percentage adsorption was found to be 39.78, 56.88, 74.72, and 77.16 for concentration of 5 mg/L, 10 mg/L, 15 mg/L, and 20 mg/L respectively. One of the reasons for high adsorption is due to higher probabilities of collision between Ni ion and RGSH adsorbent.

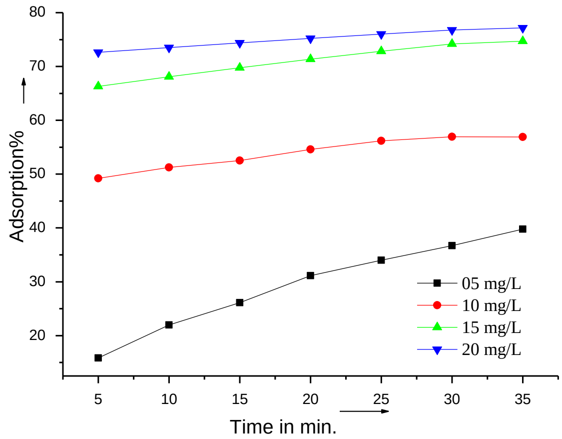

Fig. 1 effect of contact time on percentage adsorption of Ni(II) [Adsorbent dose = 0.5 gm, Temp = 304.5k, pH = 5.9]

Effect of adsorbent dose Adsorbent dose is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of adsorbate. The effect of adsorbent dose was studied with on Ni (II) ion removal keeping all the experimental conditions constant. The adsorption of Ni (II) ion by RGSH at different adsorbent doses from 0.25 gm. to 1.0.gm. for 20 mg/L of Ni (II) ion concentration at pH 5.9 was studied.

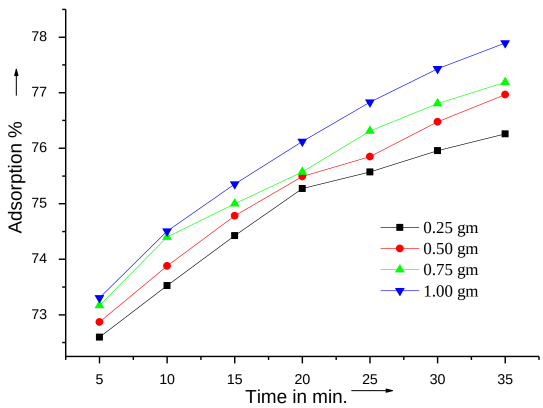

Fig. 2 effect of adsorbent dose on percentage adsorption of Ni (II), [Initial conc.= 20 mg/L,Temp=304.5k,pH=5.9]

The result (Fig.2.) shows that as the adsorbent mass increases from 0.25 to 1.0 gm., the percent Ni (II) ion adsorption increase from 76.26 to 77.90 %. This is because of the availability of more and more binding sites for complexation of Ni (II).

Effect of pH the pH of the adsorbate solution is considered one of the most important factors affecting the adsorption process. The effect pH of solution was studied between 2.0 to 11.0 shown in **Fig. 3**. At higher pH, Ni(II) may get precipitated as hydroxide.

The result reveals that the pH increases from 2 to 6 the percentage adsorption of Ni (II) ion increases up to 78.80 %. The increase in percentage adsorption may be attributed to higher degree of ionization of metal ion at higher pH and the reduced competition of H^+ ions with the Ni metal ions for adsorption sites. The maximum adsorption of Ni (II) ion occurred at pH 6.After pH 6 to 9 percentage adsorption of Ni (II) ion decreases up to 71.94 %.

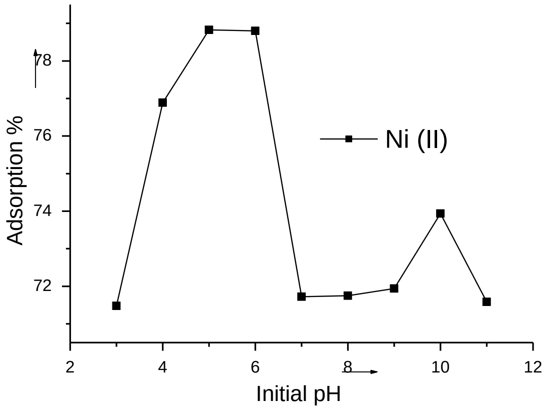

Fig. 3: Effect of initial pH on percentage adsorption of Ni (II) [Initial conc. = 2.0mg/L, Volume – 2.5ml, Temp. = 304.5K]

Effect of temperature has a pronounced effect on the adsorption capacity of various adsorbents. The temperature effect was investigated for temperatures ranging from 306.2 to 326.2 K. The results are shown in Fig.4.

The percentage Ni(II) ion adsorption decreases with increase in temperature. Since adsorption is an exothermic process. Thus the removal of Ni(II) ion is leading to a decrease in the residual forces on the surface of the RGSH adsorbent and hence causing a decrease in the surface energy of the adsorbent [17].

Thermodynamic study was performed to find the nature of adsorption process. Thermodynamic parameters such as Gibb's free energy changeΔG^0, enthalpy change ΔH^0 and entropy change ΔS^0 were calculated by using Van't Hoff's equation.

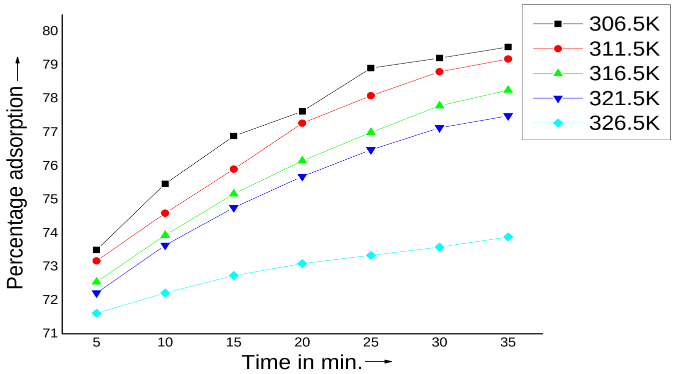

Fig. 4: Effect of temperature on percentage adsorption of Ni(II) [Initial conc. = 20mg/L, Adsorbent dose = 0.5gm, pH = 5.9]

Table: 1. Thermodynamic parameter values of RGSH adsorbent with Ni (II) metal ion solution at different temperatures.

Temp (K)	−(ΔG°) KJ/mole	−(ΔH°) KJ/mole	−(ΔS°) J/mole
306.5	3.620	7.656	13.223
311.5	3.555		
316.5	3.491		
321.5	3.426		
326.5	3.362		

TheΔG^0 values obtained in this study for the Ni (II) ion are < -10 KJ /mole, it indicates that physical adsorption was the predominant mechanism in the adsorption process. The Gibb's free energy indicates the degree of spontaneity of the adsorption process, where more negative value reflects a more energetically favourable adsorption process. The negative value of ΔG^0 (Table:1.) indicates that the adsorption is favorable and spontaneous [18,19].The negative value ofΔS^0 andΔH^0 suggests that the decreased disorder and randomness at the solid solution interface with exothermic adsorption.

Adsorption isotherm adsorption isotherms are important for the description of how molecules of adsorbate interact with adsorbent surface. Hence Langmuir and Freundlich isotherms were selected in the present study.

Langmuir isotherm Langmuir adsorption isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. The Langmuir isotherm is valid for monolayer adsorption onto the surface containing a finite number of identical sites. The linear form of the equation is given by,

$$\frac{1}{q_e} = \left(\frac{1}{Q_0}\right) + \frac{1}{bQ_0C_e} \qquad (3)$$

Where, C_e (*mg/L*) is the equilibrium concentration of the adsorbate, q_e(*mg/gm*) is the amount of adsorbate adsorbed per unit mass of adsorbent, at equilibrium, Q_0 (*mg/gm*) and *b* (*L/mg*) are Langmuir constants related to maximum monolayer adsorption capacity and energy of adsorption respectively. The values of Q_0 and *b* are calculated from the slope and intercept of plot of $\frac{1}{q_e}$ against $\frac{1}{C_e}$ respectively. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameterR_L. Which is a dimensionless constant referred to as separation factor or equilibrium parameter [20].

$$R_L = \frac{1}{1+bC_0} \qquad (4)$$

Where, C_0 is initial concentration in ppm and *b* is Langmuir constant related to the energy of adsorption. R_LValue indicates the adsorption nature to be either unfavorable if R_L> 1, linear if R_L= 1, favorable if 0 <R_L< 1 and irreversible if, R_L= 0 [21].

Freundlich isotherm Freundlich presented an empirical adsorption isotherm for non-ideal sorption on heterogeneous surfaces as well as multilayer sorption and is also expressed as:

$$\frac{x}{m} = K_f {C_e}^{1/n} \qquad (5)$$

Where *x* is the quantity adsorbed, *m* is the mass of the adsorbent,C_e is the equilibrium concentration of adsorbate (*mg/L*), The constants K_f and *n* can be obtained by taking *log* on both sides of equation (3) as follows,

$$\log\frac{x}{m} = \frac{1}{n}\log C_e + \log K_f \qquad (6)$$

The constant K_f is an approximate indicator of adsorption capacity, while $\frac{1}{n}$ is a function of the strength of adsorption in the adsorption process [22]. If $n = 1$ then the partition between the two phases are independent of the concentration. If value of $\frac{1}{n}$ is below one, it indicates a normal adsorption, on the other hand $\frac{1}{n}$ being above one indicates co-operative adsorption [23]. A plot of $\log\frac{x}{m}$ against $\log C_e$ gives a straight line with an intercept on the ordinate axis. The value of *n* and K_f can be obtained from the slope and the intercept of the linear plot.
The R_L value was found to be between 0 and 1 for Ni(II) ion studies, it is confirmed that the ongoing adsorption of Ni (II) ion is favourable. The data reveal that the Langmuir model yields better fit than the Freundlich model.

Table 2 isotherm parameter values of RGSH with Ni (II) ion solution.

	Langmuir constants				Freundlich constants		
Ni (II) ion *(mg/L)*	Q0 (mg/gm.)	b*10-5 (L/gm.)	R_L	R^2	n	K_f (mg/gm.(L/gm.))1/n	R^2
20	326.428	0.023	0.997	0.998	1.243	17.9362	0.997

The value of *n* suggests that deviation from linearity, if *n* = 1 the adsorption is homogenous and there is no interaction between adsorbed species. The value of *n*is greater than unity, (1< n <10), that means favourable adsorption [24]. If value of $\frac{1}{n}$> *1* indicates the adsorption is favoured and new adsorption sites are generated [25-28]. The value of *n* presented in table 2. The value of *n* was found to be between 1 and 10, this indicates favourable adsorption.
Morris-Weber relationship According to this model, the plot of amount of substance adsorbed per unit mass of adsorbent against square root of time gives a curve, which can be divided in to three segments, (i) The initial portion representing rapid internal diffusion or boundary layer diffusion and surface adsorption. (ii) The linear portion including a gradual adsorption state due to intra particle diffusion, and (iii) A plateau to equilibrium where the intra particle diffusion starts to decrease due to the low concentration in solution as well as fewer available adsorption sites.

$$q_t = K_{id}t^{1/2} + C \qquad (7)$$

Where,q_t is amount of substance adsorbed per unit mass of adsorbent; K_{id} is the intra particle diffusion coefficients *mg/(gm.min*^{½}*)*.The plot of q_t against $t^{1/2}$does not pass through origin. This indicates that intra particle diffusion is not the rate limiting step. straight line with slope K_{id} an intercept of zero, if the adsorption is limited by the internal diffusion process.

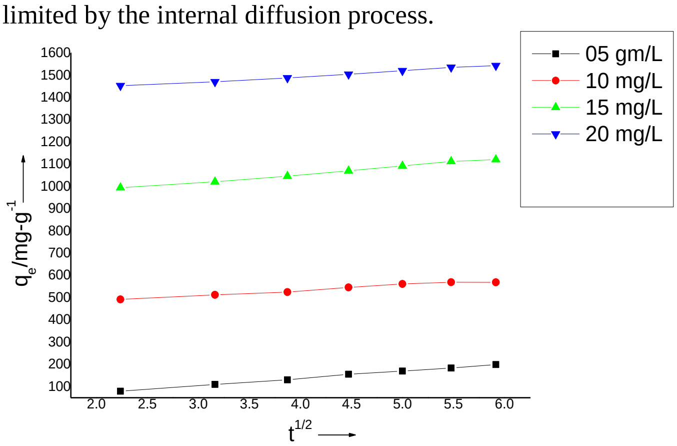

Fig 4. : Plot of q_t against $t^{1/2}$ in internal diffusion model with Initial concentration of Ni (II) metal ion

Kinetic model of adsorption kinetic studies are significant for any kind of adsorption process. Lagergren pseudo-first and pseudo-second order kinetic models can be suggested for an adsorption. Pseudo-first order kinetics is present to describe the rate of adsorption process in liquid-solid phase. The Lagergren pseudo-first order rate equation is given as,

$$\frac{dq}{dt} = K_1(q_e - q_t) \qquad (8)$$

After definite integration by applications of the conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$ Equation (8) becomes,

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \qquad (9)$$

Where, q_e (*mg/gm*) is the amount of adsorption at equilibrium, q_t (*mg/gm*) denotes the amount of adsorption at time *t* (*min.*) and K_1 (*min^{-1}*) is the rate constant of the pseudo-first order model. Based on experimental results, linear graphs were plotted between $\log(q_e - q_t)$ versus t, to calculate K_1, q_e and R^2.

The pseudo-second order equation is developed by Ho can be written as

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \qquad (10)$$

Where, K_2 (*gm.mg^{-1}min^{-1}*) is the rate constant of the pseudo-second order.

The linear form of equation is

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \qquad (11)$$

K_2 and q_e can be obtained from the intercept and slope of plotting t/q_t against t .

Table: 3. Kinetic parameter values of RGSH adsorbent with Ni (II) ion.

Ni (II) ion (mg/L)	Pseudo-First order			Second order		
	K_1 (min^{-1})	q_e (mg/gm)	R^2	K_2 (gm./mg.min)	q_e (mg/gm)	R^2
20	$41.753*10^{-3}$	121.459	0.991	$1.556*10^{-3}$	1544.609	0.999

The value of R^2 with first order kinetics was 0.991, while for second order is 0.999 for RGSH adsorbent. It is clear that the adsorption of Ni (II) metal ion on RGSH adsorbent was better represented by pseudo second order kinetics. This indicates that the adsorption system belongs to the second order kinetic model.

Conclusion

The percentage adsorption of Ni (II) on RGSH increase with increasing RGSH adsorption dose. initial concentration of Ni (II) ion solution and with decrease in temperature. The negative value of ΔG^0 confirms that the adsorption is feasible and spontaneous. The negative value of ΔS^0 and ΔH^0 suggests decrease in disorder and randomness at the solid solution interface with exothermic adsorption.

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