

Use of Agricultural Waste for the Removal of Nickel Ions from Aqueous Solutions: Equilibrium and Kinetics Studies

Manjeet Bansal, Diwan Singh, V.K.Garg and Pawan Rose

Abstract—The potential of economically cheaper cellulose containing natural materials like rice husk was assessed for nickel adsorption from aqueous solutions. The effects of pH, contact time, sorbent dose, initial metal ion concentration and temperature on the uptake of nickel were studied in batch process. The removal of nickel was dependent on the physico-chemical characteristics of the adsorbent, adsorbate concentration and other studied process parameters. The sorption data has been correlated with Langmuir, Freundlich and Dubinin-Radushkevich (D-R) adsorption models. It was found that Freundlich and Langmuir isotherms fitted well to the data. Maximum nickel removal was observed at pH 6.0. The efficiency of rice husk for nickel removal was 51.8% for dilute solutions at 20 g L⁻¹ adsorbent dose. FTIR, SEM and EDAX were recorded before and after adsorption to explore the number and position of the functional groups available for nickel binding on to the studied adsorbent and changes in surface morphology and elemental constitution of the adsorbent. Pseudo-second order model explains the nickel kinetics more effectively. Reusability of the adsorbent was examined by desorption in which HCl eluted 78.93% nickel. The results revealed that nickel is considerably adsorbed on rice husk and it could be an economic method for the removal of nickel from aqueous solutions.

Keywords—Adsorption, nickel, SEM, EDAX.

I. INTRODUCTION

HEAVY metals are continuously released into the aquatic environment from natural processes like volcanic activity and weathering of rocks. Industrial processes have greatly enhanced the mobilization of heavy metals. The presence of heavy metals in the environment is of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relatively low concentrations [1], [2]. They are highly toxic as ions or in compound forms; they are soluble in water and may be readily absorbed into living organisms. Nickel(II) containing wastewaters are common as it is used in a number of industries including electroplating, batteries manufacturing, mining, metal finishing and forging. Higher concentrations of nickel cause cancer of lungs, nose and bone. Dermatitis (Ni itch) is the most frequent effect of exposure to Ni, such as coins and jewellery. The higher concentration of Ni(II) in ingested water may cause severe damage to lungs, kidneys, gastrointestinal distress, e.g.,

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nausea, vomiting, diarrhoea, pulmonary fibrosis, renal edema, and skin dermatitis [3]. A number of methods are available for the removal of metal ions from aqueous solutions. These are ion exchange, solvent extraction, reverse osmosis, electro dialysis, precipitation, flocculation and membrane separation processes [4]-[8]. However, these techniques have certain disadvantages, such as high capital and operational costs or the treatment and disposal of the residual metal sludge. Adsorption compared with other methods appears to be an attractive process due to its efficiency and the ease with which it can be applied in the treatment of heavy metal containing wastewater [9]. In recent years, a number of adsorptive materials, such as aquatic plants [10], agricultural by-products [11], industry by-product [4], sawdust [12], clay [13], zeolite [14], and microorganisms [15] were used in heavy metal removal from wastewaters. Agricultural waste materials being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewability, low cost and more efficiency seem to be a viable option for heavy metal remediation. Present investigation is devoted to study the removal of Ni(II) from synthetic aqueous wastewater by using rice husk. This agricultural byproduct is available in large amount in India and other countries. It is both used as fuel in brick kilns or packing material and available at negligible price. The effect of various process parameter, namely pH, adsorbent dose, initial metal ion concentration, contact time and temperature on the removal of Ni(II) have been investigated. The data may be used full for environmental engineer in designing of heavy metal containing waste water containing treatment systems.

II. MATERIALS AND METHODS

Rice husk was collected from a pre-consumer agricultural product process industry located at Kurukshetra (Haryana). The collected rice husk was dried under sun and impurities were separated manually. It was boiled with distilled water for 5 h to make it free from colored compounds and filtered. The residual material so obtained was dried at 80°C in hot air oven for 24 h, and then the material was grinded and sieved through the sieves of 300 μ size. The material was stored in airtight plastic container for further use. The surface morphology and elemental constitutions of the adsorbents was studied by SEM and EDAX (model Quanta 200 EFG, FEI, Netherlands).

Aqueous solution of nickel (1000 mg L⁻¹) was prepared by dissolving nickel nitrate (AR grade) in double distilled water. The aqueous solution was diluted with distilled water to obtain the working solutions of desired concentration. pH of the

solutions was adjusted using 0.01M NaOH/0.01M HCl. The nickel concentration was determined by Atomic Absorption spectrophotometer (Shimadzu 6300, Japan).

For each adsorption experiment, 50 ml nickel solution of 100 mg L^{-1} concentration was used. After adding desired amount of adsorbent ($4\text{--}20 \text{ g L}^{-1}$) pH was adjusted in the range of 2.0 – 6.0 and the mixture was agitated on orbital shaker (Scigenics Biotech Orbitek) at 180 rpm for 180 min. After that the mixture was filtered to separate the exhausted adsorbent from solution. The residual nickel concentration in solution was determined by Atomic Absorption spectrophotometer. All experiments were replicated thrice and results were averaged. The removal percentage and adsorbent capacity of adsorbent were calculated as reported by [16].

III. RESULTS AND DISCUSSION

A. Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray analysis (EDX)

Fig. 1(a, b) shows the changes in the functional groups and surface properties of the adsorbent after adsorption by FTIR spectra. The spectra of the native and nickel loaded adsorbent were measured in the range of $4000\text{--}400 \text{ cm}^{-1}$ wave number. The FTIR spectrum reveals complex nature of the adsorbents as evidenced by the presence of a large number of peaks. Table I presents infrared adsorption wavelength of each peak and corresponding functional groups of the adsorbent before and after use. The adsorption peak around 3660.64 cm^{-1} indicates the existence of free and intermolecular bonded hydroxyl groups which was not present after nickel exposure indicating participation of these functionalities in metal binding. Peak around 1664.45 cm^{-1} corresponds to the C=O stretching that may be attributed to the lignin aromatic groups (Fig 1a) was shifted to 1595.02 cm^{-1} thus pointing to changes in lignin aromatic groups after nickel loading. Peak around 1332.72 cm^{-1} corresponds to the C-H bending ($-\text{CH}_3$) was shifted to 1352.01 cm^{-1} thus pointing to changes in C-H bending ($-\text{CH}_3$) after nickel exposure. Additional peaks at 401.17 cm^{-1} and 736.76 cm^{-1} can be assigned to bending modes of aromatic compounds was shifted to 418.52 cm^{-1} and 763.76 cm^{-1} , respectively confirms the participation of this group in nickel binding.

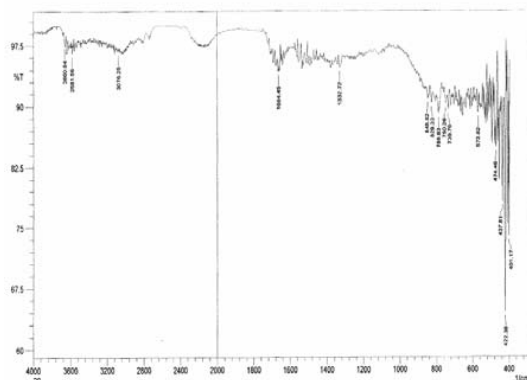


Fig. 1a FT-IR spectra of native adsorbent

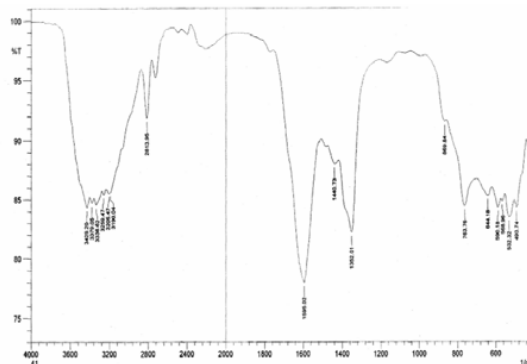


Fig.1b FT-IR spectra of nickel loaded adsorbent

Adsorbent	O-H	C=O	-CH ₃	Bending vibrations
Native	3660.64	1664.45	1332.72	401.17, 736.76
Nickel-loaded	-	1595.02	1352.01	418.52, 763.76

The scanning electron micrographs enable the direct observation of the surface microstructures of different adsorbents. Fig. 2a illustrates the SEM of native adsorbent at 1000X which shows irregular groove and ridges in fibrous network that is considered helpful for the accessibility of nickel to the adsorbent surface. Fig. 2b shows SEM of exhausted adsorbent clearly indicates the presence of new shiny bulky particles and layer over the surface of metal loaded adsorbent which are absent from the native adsorbent before metal loading.

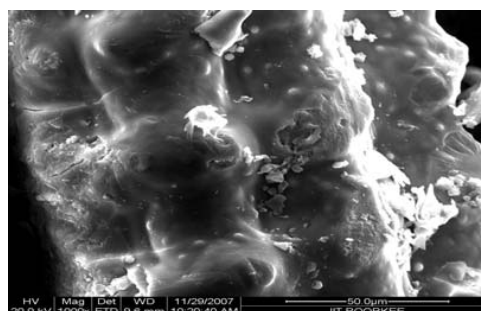


Fig. 2a SEM of native adsorbent

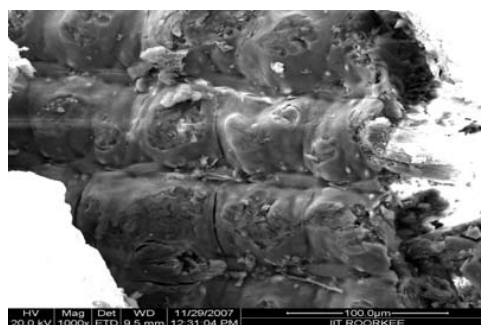


Fig. 2b SEM of nickel loaded adsorbent

EDAX measurements of the samples (with and without metal ion) were recorded for qualitative analysis of the elemental constitution of the adsorbents. Fig. 3 (a, b) shows the EDAX spectra for native as well as metal ion loaded adsorbent. The samples equilibrated with metal ion solution showed distinct peaks for nickel confirming that nickel ions have sorbed onto the adsorbent. EDAX analysis provided direct evidence for the adsorption of nickel onto adsorbent.

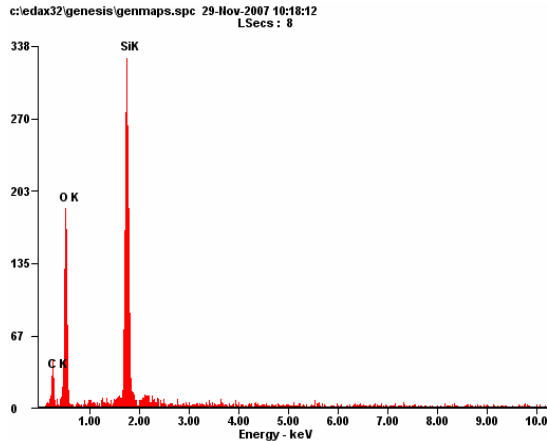


Fig. 3a EDAX of native adsorbent

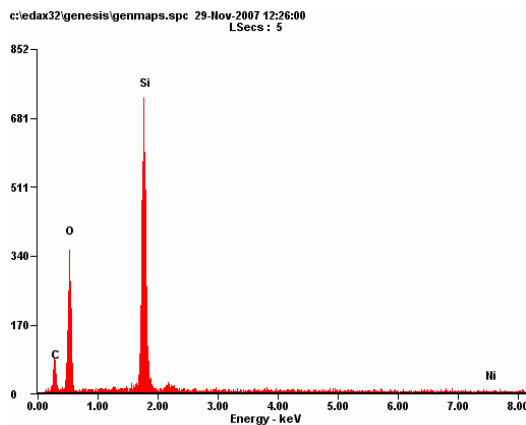


Fig. 3b EDAX of nickel loaded adsorbent

B. Effect of pH

Metal biosorption is critically linked with pH. In order to establish the effect of pH on the adsorption of Ni(II) onto adsorbent, the batch adsorption studies at different pH values were carried out in the range of 2.0-6.0. No studies were done beyond pH 6.0 because of the precipitation of the Ni(II) as its hydroxide (Fig. 4). From results it is evident that maximum adsorption of Ni(II) was 51.4% at pH 6.0. pH of the solution plays a very important role in the metal uptake. Both adsorbent surface metal binding sites as well as metal chemistry in solution are influenced by solution pH. At low pH values, metal cations and protons compete for binding sites on adsorbent surface which results in lower uptake of metal. It has been suggested that at highly acidic condition, adsorbent surface ligands would be closely associated with H_3O^+ that

restricts access to ligands by metal ions as a result of repulsive forces. It is to be expected that with increase in pH values, more and more ligands having negative charge would be exposed which result in increase in attraction of positively charged metal ions [17]. In addition at higher pH the lower binding is attributed to reduced solubility of the metal and its precipitation [18].

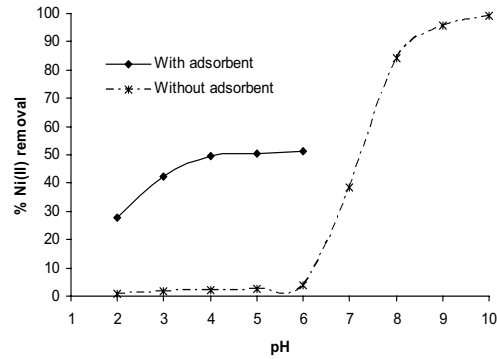


Fig. 4 Effect of pH on Ni(II) removal [Ni(II) conc = 100 mg L^{-1} ; adsorbent dose = 20.0 g L^{-1} ; contact time = 180 min; stirring speed = 180 rpm; temp = 25°C]

C. Effect of Adsorbents Dose

Effect of biosorbents dosage on percentage removal of Ni(II) was investigated by varying adsorbents dosage in the range of 4.0 g L^{-1} to 20.0 g L^{-1} . It was observed that the percentage removal of Ni(II) increases with the increase in the adsorbent dosage (Fig. 5). The maximum percentage removal of Ni(II) was 51.8% at 20.0 g L^{-1} of biosorbents dose and constant initial metal ion concentration of 100 mg L^{-1} . The phenomenon of increase in percentage removal of Ni(II) with increase in adsorbent dose may be explained as with increase in adsorbent dose, more and more surface becomes available for metal ion to adsorb and this increases the rate of adsorption [4]. Table II shows the uptake capacity at different adsorbent doses.

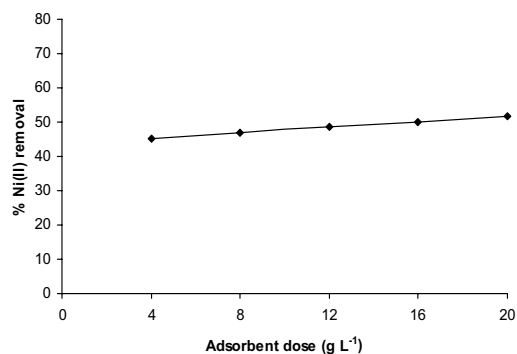


Fig. 5 Effect of adsorbent dose on Ni(II) removal [Ni(II) conc = 100 mg L^{-1} ; pH = 6.0; contact time = 180 min; stirring speed = 180 rpm; temp = 25°C]

D. Effect of Contact Time

Fig. 6 shows the effect of contact time on the extent of adsorption of Ni(II). It has been observed that adsorption rate

increased from 30.3% to 51.8% with increased in contact time from 10 to 180 min. Maximum Ni(II) removal was achieved within 120 min after which Ni(II) concentration in the test solution became constant. It may be explained by the fact that initially for adsorption large number of vacant sites was available, which slowed down later due to exhaustion of remaining surface sites and repulsive force between solute molecule and bulk phase [19].

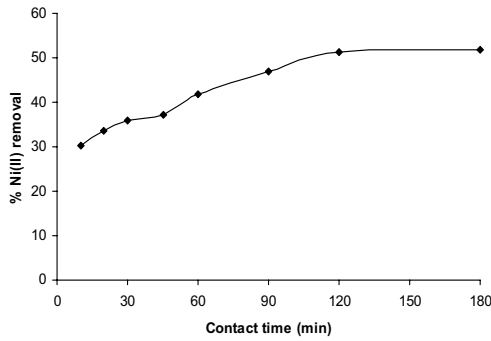


Fig. 6 Effect of contact time on Ni(II) removal [Ni(II) conc = 100 mg L⁻¹; pH = 6.0; adsorbent dose = 20.0 g L⁻¹; stirring speed = 180 rpm; temp = 25°C]

E. Effect of Initial Metal Ion Concentration

Fig. 7 shows the effect of initial metal concentration on the adsorption experiment. It was observed that adsorption of Ni(II) decreased from 82.5% to 30.5% with increased in metal concentration from 5 to 500 mg L⁻¹. At higher concentration, most of the Ni(II) are left unabsorbed due to saturation of adsorption sites. As the ratio of sorptive surface to ion concentration decreased with increasing metal ion concentration and so metal ion removal was reduced. At low initial concentration of metal ions, more binding sites are available. But as the concentration increases, the number of ions competing for available binding sites in the biomass increased [20]. Table II shows the uptake capacity of adsorbent at different initial concentration of nickel ions.

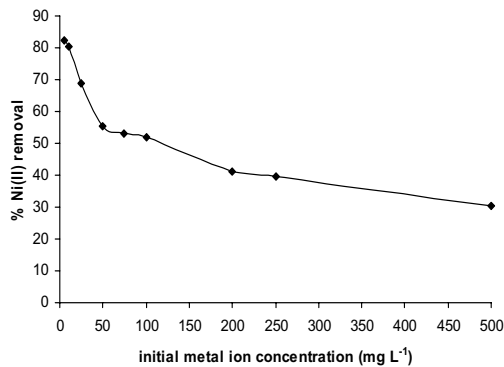


Fig. 7 Effect of initial metal ion concentration on Ni(II) removal [adsorbent dose = 20.0 g L⁻¹; pH = 6.0; contact time = 180 min; stirring speed = 180 rpm; temp = 25°C]

F. Effect of Temperature

Fig. 8 shows the effect of temperature on the adsorption of Ni(II). From the results it is evident that there is gradual

increase in the removal percentage from 46.9% to 65.4%. The above results also showed that the adsorption was endothermic in nature. Since adsorbent is porous in nature and possibilities of diffusion of adsorbate cannot be ruled out therefore, increase in the sorption with the rise of temperature may be diffusion controlled which is endothermic process, i.e. the rise of temperatures favors the adsorbate transport with in the pores of adsorbent [21].

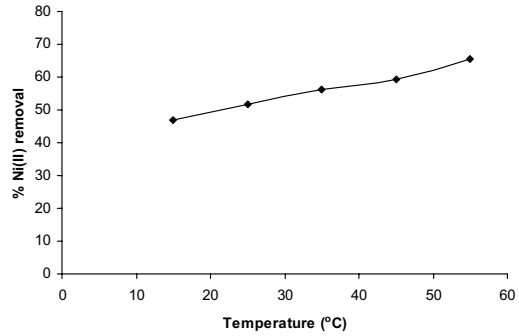


Fig. 8 Effect of temperature on Ni(II) removal [Ni(II) conc = 100 mg L⁻¹; adsorbent dose = 20.0 g L⁻¹; pH = 6.0; contact time = 180 min, stirring speed = 180 rpm]

TABLE II
ADSORPTION CAPACITY OF ADSORBENT AT DIFFERENT INITIAL NICKEL CONCENTRATIONS AND DIFFERENT ADSORBENT DOSES

Parameter	Adsorption Capacity (q _e , mg g ⁻¹)
<i>Initial nickel conc (mg L⁻¹)</i>	
5	0.21
10	0.40
25	0.86
50	1.39
75	1.98
100	2.59
200	4.11
250	4.94
500	7.63
<i>Adsorbent dose (g L⁻¹)</i>	
4	11.3
8	5.86
12	4.06
16	3.13
20	2.59

G. Adsorption Isotherms

The Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models have been tested in this study. These isotherms relate the amount of solute adsorbed at equilibrium per unit weight of adsorbent, x/m (mg g⁻¹), to the adsorbate concentration at equilibrium, C_e (mg L⁻¹). The Langmuir model represents one of the first theoretical treatments of non-linear sorption and suggests that the uptake occurs on a homogenous surface by monolayer sorption without interaction between the adsorbed molecules. The linear form of the Langmuir adsorption isotherm is represented as:

$$C_e / q_e = [1 / Q_o b + 1 / Q_o \times C_e] \quad (1)$$

where, C_e is the equilibrium concentration of adsorbate (mg L⁻¹), and q_e is the amount of nickel adsorbed per gram of the

adsorbent at equilibrium (mg g^{-1}). Q_0 (mg g^{-1}) and b (L mg^{-1}) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The values of Q_0 and b were calculated from the slope and intercept of the Langmuir plot of C_e versus C_e/q_e (Fig. 9, Table III). The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter, R_L [22] which is defined as given below:

$$R_L = 1/(1 + bC_0) \quad (2)$$

where b is the Langmuir constant (L mg^{-1}) and C_0 (mg L^{-1}) is the initial concentration of nickel. The R_L parameter is considered as a reliable indicator of the adsorption. There are four probabilities for the value of R_L : (i) for favourable adsorption, $0 < R_L < 1$, (ii) for unfavourable adsorption, $R_L > 1$, (iii) for linear adsorption, $R_L = 1$, (iv) for irreversible adsorption, $R_L = 0$. The values of R_L for the studied system at different initial concentrations were found to be in between 0 and 1 which indicate favourable adsorption of nickel onto the adsorbent (Table IV).

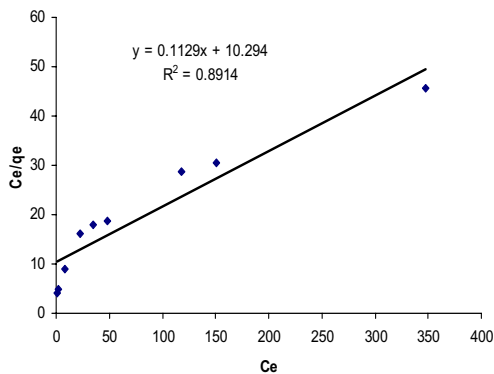


Fig. 9 Langmuir isotherm for the adsorption of Ni(II) [initial Ni(II) conc = 5-500 mg L^{-1} ; pH = 6.0; adsorbents dose = 20.0 g L^{-1} ; temperature = 25°C]

The Freundlich model can be applied for non-ideal sorption onto heterogeneous surfaces involving multilayer sorption. The linearized Freundlich model isotherm was applied for the adsorption of nickel and is expressed as:

$$\log_{10} q_e = \log_{10} (K_f) + (1/n) \log_{10} (C_e) \quad (3)$$

where, q_e is the amount of nickel adsorbed at equilibrium (mg g^{-1}), and C_e is the equilibrium concentration of nickel in solution (mg L^{-1}). K_f and n are the constants incorporating all factors affecting the adsorption process (adsorption capacity and intensity). Values of K_f and n were calculated from the intercept and slope of the plot (Fig. 10) and are given in Table III. Both the parameters, K_f and 'n' affect the adsorption isotherm. The larger the K_f and 'n' values, the higher the adsorption capacity.

The magnitude of the exponent n gives an indication of the favourability of the adsorption. It is generally stated that values of n in the range 2-10 represent good, 1-2 moderately difficult and less than 1 poor adsorption characteristics [23] Based on the correlation coefficient values, it has been deduced that Freundlich model better fitted to the

experimental data (Table III).

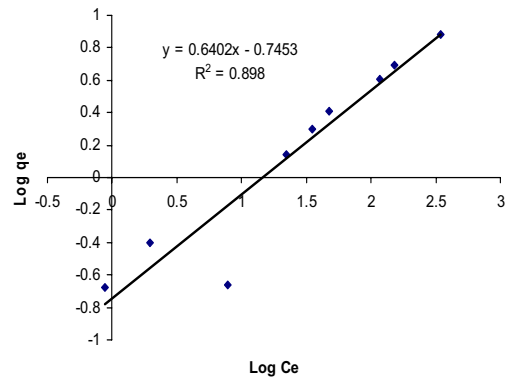


Fig. 10 Freundlich isotherm for the adsorption of Ni(II) [initial Ni(II) conc = 5-500 mg L^{-1} ; pH = 6.0; adsorbents dose = 20.0 g L^{-1} ; temperature = 25°C]

The Dubinin-Radushkevich (D-R) model was applied to the equilibrium data to determine if sorption had occurred by physical or chemical processes. The D-R adsorption isotherm is represented as:

$$\text{Log}_{10} q_e = \text{Log}_{10} q_D - 2B_D R^2 T^2 \text{Log}_{10} \left(1 + \frac{1}{C_e}\right) \quad (4)$$

Where q_D is theoretical saturation capacity (mg g^{-1}) and B_D is a constant related to adsorption energy ($\text{mol}^2 \text{K J}^{-2}$), R is the gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$) and T is the temperature (K). The slope of the plot $\log_{10} q_e$ versus $\log_{10} (1+1/C_e)$ gives the q_D and B_D values (Fig. 11). The constant B_D gives an idea about the mean free energy E_D (kJ mol^{-1}) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the D-R isotherm constant B_D using following equation [22]:

$$E_D = 1/\sqrt{2B_D} \quad (5)$$

This sorption energy is independent of the temperature but varies depending on the nature of the adsorbent and adsorbate. The magnitude of E_D provides information on the nature of the sorption process, i.e. whether it is chemical or physical, with values in the range $E_D = 1-8 \text{ kJ mol}^{-1}$ corresponding to physical sorption and in the range $9-16 \text{ kJ mol}^{-1}$ to chemisorption. The calculated E_D value was found to be 1.25 kJ mol^{-1} (Table III). E_D value less than 8 kJ mol^{-1} as indicated by our results shows that the adsorption process of nickel on rice husk follows physical adsorption.

H. Adsorption Kinetic Study

In the present study, pseudo-first-order and pseudo-second-order kinetic models have been tested at different concentrations. The first-order-model can be expressed as follows:

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

where q_e (mg g^{-1}) is the mass of nickel adsorbed at equilibrium, q_t (mg g^{-1}) is the mass of nickel at any time 't' and k_1 (min^{-1}) is the equilibrium rate constant of pseudo-first-order adsorption. The values of k_1 and q_e are determined from the slope and intercept of the plot of $\log (q_e - q_t)$ versus t ,

respectively (Fig. 12) and are given in Table V.

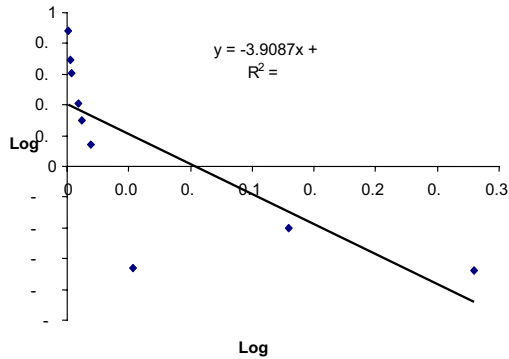


Fig. 11 Dubinin-Radushkevich isotherm for the adsorption of Ni(II) [initial Ni(II) conc = 5-500 mg L⁻¹; pH = 6.0; adsorbents dose = 20.0 g L⁻¹; temperature = 25°C]

TABLE III
LANGMUIR, FREUNDLICH AND DUBININ-RADUSHKEVICH MODEL'S REGRESSION CONSTANTS FOR ADSORBENT

Parameters	Value
Langmuir Isotherm	
Q ₀ (mg g ⁻¹)	: 8.86
b (L mg ⁻¹)	: 0.011
R ²	: 0.8914
Freundlich Isotherm	
K _f (mg g ⁻¹)	: 0.18
n (L mg ⁻¹)	: 1.56
R ²	: 0.898
D-R isotherm	
q _D (mg g ⁻¹)	: 2.56
B _D (mol ² kJ ⁻²)	: 0.32
E _D (kJmol ⁻¹)	: 1.25
R ²	: 0.5689

TABLE IV
SEPARATION FACTOR (R_L) OF ADSORBENT AT DIFFERENT INITIAL CONCENTRATIONS OF NICKEL

Initial nickel conc. (mg L ⁻¹)	R _L
5	0.95
10	0.90
25	0.78
50	0.64
75	0.55
100	0.48
200	0.31
250	0.27
500	0.15

The pseudo-second-order model, which leads to the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where k₂ is the pseudo- second-order rate constant (g mg⁻¹ min⁻¹) The value of q_e is determined from the slope of the plot of t/q_t versus t (Fig. 13). The calculated q_e value from the

pseudo-second-order model is in good agreement with experimental q_e value. This suggests that the sorption system followed the pseudo second-order model. The values of kinetic constants and q_e values of nickel sorption onto adsorbent are given in Table V.

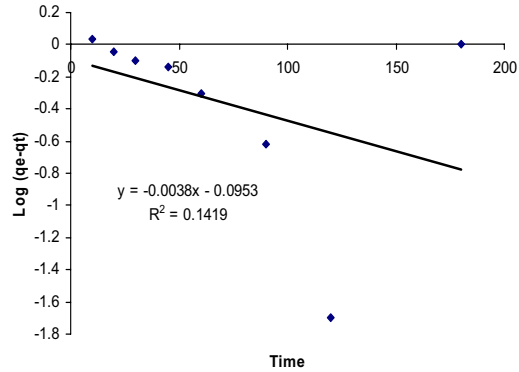


Fig. 12 Pseudo-first order model for Ni(II) adsorption [initial Ni(II) conc = 100 mg L⁻¹; contact time = 10-180 min]

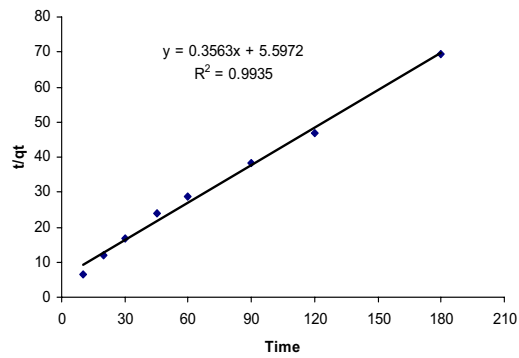


Fig. 13 Pseudo-second order model for Ni(II) adsorption [initial Ni(II) conc = 100 mg L⁻¹; contact time = 10-180 min]

TABLE V
KINETIC PARAMETERS FOR THE REMOVAL OF NICKEL

Reaction order	Kinetic parameters
Pseudo first order	
q _{e, exp} (mg g ⁻¹)	2.59
k ₁ (min ⁻¹)	0.0088
q _{e, cal} (mg g ⁻¹)	0.8
R ²	0.1419
Pseudo second order	
q _{e, exp} (mg g ⁻¹)	2.59
k ₂ (g mg ⁻¹ min ⁻¹)	0.023
q _{e, cal} (mg g ⁻¹)	2.81
R ²	0.9935

I. Desorption

Desorption studies are helpful to explore the possibility of recycling the adsorbent. Fig. shows the desorption of Ni(II) by KI and HCl respectively. A range from 0.0125 to 0.150 M

concentrations of KI and HCl solutions were tested to remove metal from the adsorbent. The results showed that the maximum desorption of Ni(II) was 60.19% and 78.93% from BRH, by KI and HCl (0.15 M) respectively. When KI and HCl were used as a desorption agent, the biosorbents surface were covered with K^+ and H^+ ions while the coordination spheres of chelated Ni(II) ions was disrupted. Thereafter the Ni(II) ions could not compete with K^+ and H^+ ions for exchange sites and subsequently heavy metal ions were released from the solid surface into the solution.

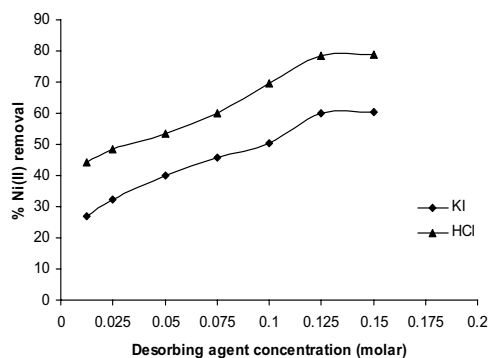


Fig. 14 Desorption plot of the Ni(II) by KI and HCl [desorbing agent volume = 50 ml; Ni(II) conc = 100 mg L⁻¹; adsorbent dose = 20.0 g L⁻¹; contact time = 60 min; temperature = 25°C; stirring speed = 180 rpm]

IV. CONCLUSION

The effect of various process parameters showed that percent adsorption decreased with increase in initial metal ion concentration while it increased with increase in adsorbent dose. Maximum nickel removal by adsorbent was at pH 6.0. Equilibrium adsorption showed that system followed both Langmuir and Freundlich model. According to Dubinin-Raduskevich model, the adsorption of nickel was physical in nature. The kinetics studies concluded that nickel removal followed pseudo second-order rate equation. Desorption studies indicated the good possibility of reusing the adsorbent. Results in the present study showed that rice husk can be used for the removal of nickel from dilute wastewater.

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