Development of modelling equations for the removal of Nickel (II) from aqueous solutions

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Abstract: This paper presents adsorption results concerning nickel (II) ions on the surface of 5Å molecular sieves. The parameters which tend to favour the adsorption of aqueous solution were optimized and the surface morphology of the molecular sieves was determined by means of Scanning Electron Microscopy (SEM) while the evidence of functional groups was highlighted by Fourier transform infrared spectroscopy (FTIR) measurements. These equilibrium & kinetic studies were compared by computer simulations to investigate the deviations. FTIR analysis revealed that –NH (bending), C-H (Stretching), C=O (Stretching) and –OH functional groups are responsible for Ni (II) adsorption. The experimental parameters investigated include initial solution pH, metal concentration, adsorbent dose and temperature.

Keywords: 5Å molecular sieves, Adsorption, Nickel (II), Isotherm, Kinetics, SEM, FTIR.

Introduction

The contamination of wastewater by toxic heavy metallic cations is a worldwide environmental problem. A number of techniques such as filtration, reverse osmosis; chemical precipitation, ion exchange, electro-deposition and adsorption have been used to remove the toxic metals from aquatic environment with varying degree of success. All these methods have inherent advantages and limitations[1]. Natural zeolites are hydrated aluminosilicate minerals of a porous structure with valuable physicochemical properties, such as cation exchange, molecular sieving, catalysis and sorption. The use of natural zeolites for environmental applications is gaining new research interests mainly due to their properties and significant worldwide occurrence. Application of natural zeolites for water and wastewater treatment has been realised and is still a promising technique in environmental cleaning processes. In the past decades, utilisation of natural zeolites has been focussed on ammonium and heavy metal removal due to the nature of ion exchange and some review papers have been appeared[2]. Molecular sieves are widely applied in catalysis, adsorption, and separation, as these processes benefit from their highly ordered channels and ion exchange abilities. Molecular sieves are usually prepared using hydrothermal or solvothermal synthesis methods. Moreover, the challenges associated with novel approaches for the synthesis of molecular sieves with exotic structures and properties continue to be of great importance in the field of molecular sieve materials[3].

2. Equilibrium Studies:

Materials

Molecular Sieves[4] or zeolites, Merck Ltd., Worli, and Mumbai are crystalline aluminum silicates of group IA and IIA elements used for the separation. Natural zeolites are good potential material for water and wastewater treatment. The potential advantages for application of natural zeolites in water and wastewater treatment are promising. Firstly, a benefit gained by using natural zeolites for water and wastewater treatment is their ability to undergo ion-exchange and adsorption. In addition, natural zeolites can be treated and modified in order to trap contaminants in water and wastewater. Also, natural zeolites exist abundantly low cost and only low technology systems are required. An additional benefit of using natural zeolites is their regenerative properties[5].

Preparation of stock solution

Nickel Sulphate solution was prepared by dissolving 9.567 g Nickel Sulphate salt in 1000 mL standard volumetric flask with de-mineralized water, which approximately gives 2000 ppm of Ni^{2+} in solution. From the stock solutions, experimental test solutions were prepared by diluting the primary stock solution with de-mineralized water. The pH range was adjusted by rational addition of specified mineral acid.

Methods:

Equilibrium studies

The experiments were carried out in 250 mL Erlenmeyer conical flasks, at a constant agitation speed (160 rpm) with 100 mL solution and required amount of adsorbent using orbital shaker (Kemi make). Initially the effect of contact time (0–360 min) on the sorption capacity of **5Å Molecular sieves** was evaluated. The equilibrium time was obtained and the experiments were conducted for the same time for all conditions. Batch experiments were carried out to investigate the adsorption behaviour of Ni^{2+} on **5Å Molecular sieve**.

Analysis of heavy metal ions

The concentrations of unadsorbed Ni^{2+}, in the sample solutions were determined using an Atomic Absorption Spectrophotometer (PerkinElmer model AA 400). The metal uptake (q_e) was calculated using the general definition:

$$q_e = \frac{V \times (C_T - C_e)}{M} \qquad (1)$$

where q_e is the metal uptake of mg $Ni^{2+}.g^{-1}$ adsorbent, V is the volume of metal containing solution in contact with the adsorbent in L, C_T and C_e are the total and equilibrium (residual) concentration of metal in the solution mg L^{-1}, respectively, and M is the amount of added adsorbent in g.

Metal % of removal by **5Å Molecular sieves** was determined by Eq. (2) as follows:

$$R\ (\%) = (C_T - C_e)/C_T *100 \qquad (2)$$

where R is the percentage of Ni(II) adsorbed by biomass, C_T is the total concentration of metal ions in mg L^{-1} and C_e is the concentration of metal ions at time t in mg L^{-1}.

Results and discussions

1. Effect of contact time:

Experiments were conducted to estimate the time required to reach the sorption equilibrium by taking an initial charge of 100 mL of aqueous solution containing Ni (II) ions and required quantities of biomass. The mixture was shaken in an orbital shaker; the samples were drawn at regular time intervals, and the metal concentration was estimated using AAS. The data of concentration of metal ion Ct in solution with time are shown for different quantities of biomass in fig1. Experimental results shows faster uptake at initial stages of

contact, and subsequent slowing down as the equilibrium is approached. In the initial stages of contact, large numbers of vacant sites are available, and hence the uptake is faster. The slowing down of metal uptake later is due to difficulty in occupying the remaining vacant sites. Repulsive forces between the adsorbed Pb (II) ions and aqueous Pb (II) may also most probably contribute to the slowing down of uptake of metal at equilibrium[6]. It can be observed from the graph the metal ion concentration decrease with time and reaches a plateau after 5 hours for Ni^{2+} using 5Å molecular sieves, indicating attainment of equilibrium for the present study. No significant change in the adsorption with further increase in contact time was noticed.
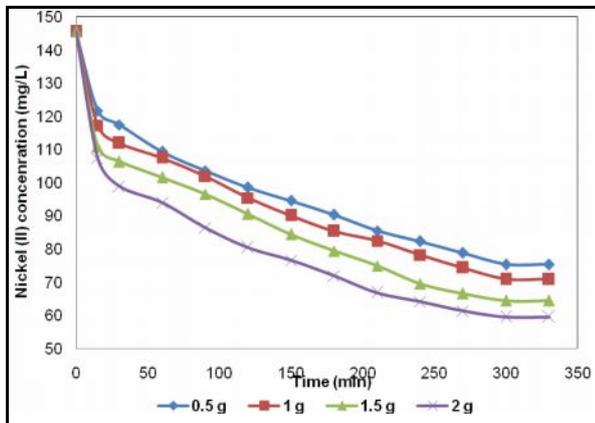
Fig.1. Variation of aqueous metal (Ni^{2+}) concentration with time using 5Å molecular sieves as an adsorbent at 25°C, 97.3 mg/L and pH 5.

Effect of pH

The pH of the solution after contact with synthetic zeolite MAP increased to 8.5–9.0 regardless of the initial pH (3.2 for the synthetic solution, 7.1 for the storm water). This is typical of synthetic zeolites and is due to hydronium ion exchange reducing the concentration of protons in solution[7]. The effect of pH on the adsorption of Ni^{2+} metal ion over 5Å molecular sieves were studied in the pH range 3–6.In case of 5Å molecular sieves the percent removal of adsorption was increased from 53.36% to 59.12% (Fig.2) at a total metal ion concentration of 95 mg/L as pH was increased from 3 to 5. The maximum adsorption was found to be 60.85% at pH 5 therefore all the subsequent experiment runs were conducted at pH 5 and pH beyond 5, the adsorption yield for Ni^{2+} ions showed a decline.
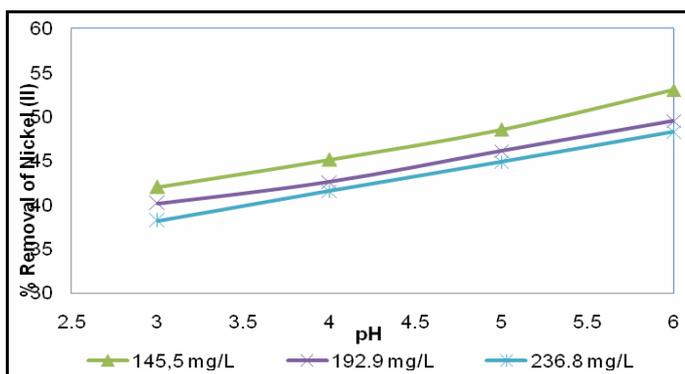
Fig2. Effect of pH on percent adsorption at various total metal ion (Ni^{2+}) concentration and at a temperature of 25°C and 20g/L, using   5Å molecular sieves.

Effect of metal ion concentration

An increase in total Ni^{2+} concentration of 48.59 mg/L to 236.81 mg/L decreased the percent of removal 56.61 to 49.09% (Fig. 5.3.3.2.C) at Sorbent dose of 20g/L, temperature 25^0C and pH 5 using 5Å molecular sieves shown in fig3.
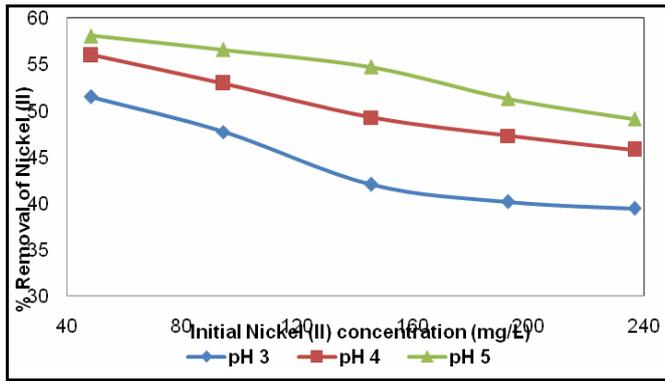
Fig.3.Variation of % removal of Ni^{2+} with various total concentration of Ni^{2+} at temperature of 25°C, 20 g/L of 5Å molecular sieves.

Effect Of Adsorbent Dosage

In case of 5Å molecular sieves, the % obtained increased from 48.82 to 59.63% (Fig.4) at total Ni^{2+} Concentration of 145mg/L and the uptake capacity showed a decrease from 13.30 to 4.37 mg/g.
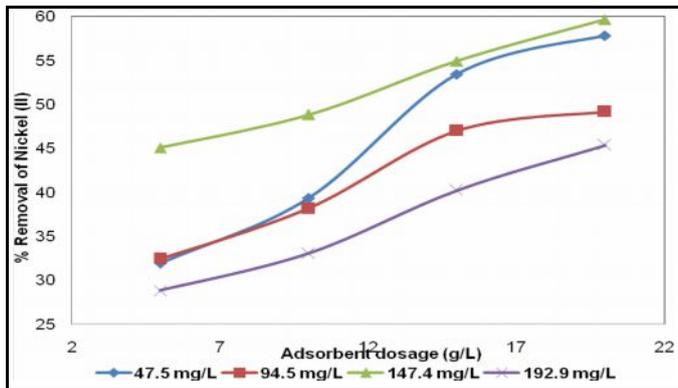

Fig.4.Variation of % Ni^{2+} adsorption with various adsorbent weights at various total metal ion concentration, at temp of 25°C and pH 5 using 5Å molecular sieves.

Effect of Temperature

The experiments with Ni^{2+} were conducted in the temperature range of 15-40°C. The adsorption capacity of Ni^{2+} increased from 50.82 to 57.83 % with an increase in temperature in the range 15-40°C (see at a total concentration of 24 mg/L in Fig.5 using 5Å molecular sieves.
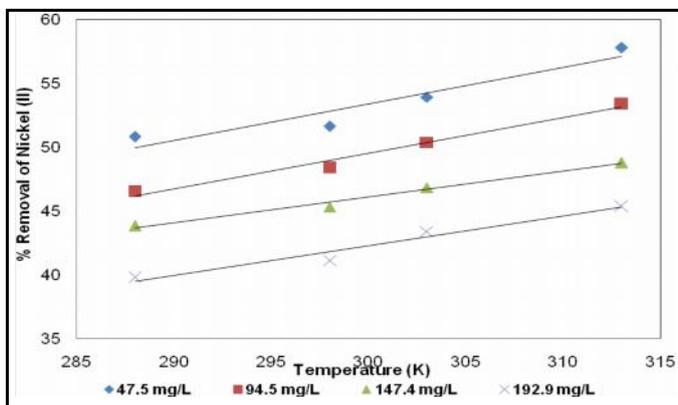

Fig.5.Variation of percent adsorption of Ni^{2+} metal ion with temperature using 5Å molecular sieves as adsorbent at different total metal ion concentrations and at pH of 5.

Adsorption isotherm models

The Langmuir and Freundlich equations are commonly used for describing adsorption equilibrium of adsorbate onto the adsorbent. The Langmuir isotherm is applicable to monolayer chemisorptions while Freundlich isotherm is used to describe adsorption on surface having heterogenous energy distribution:

Langmuir isotherm

A basic assumption of the Langmuir theory[8] is that sorption takes place at specific homogeneous sites within the sorbent. This model can be written in non-linear form and is represented by the equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (3)$$

where q_m is the maximum amount of the metal ion per unit weight of adsorbent to form a complete monolayer on the surface bound at high C_e (mg.g^{-1}), and b is a constant which accounts for the affinity of the binding sites (L mg^{-1}). From the plots between (C_e/q_e) and Ce the slope ($1/q_m$) and the intercept ($1/b\ q_m$) can be calculated. The linear Langmuir adsorption isotherms of Ni^{2+} for the adsorbent obtained at different temperatures are given in **Fig.6**.constant values at different metal ion concentrations was calculated and the values were shown in Table 1.
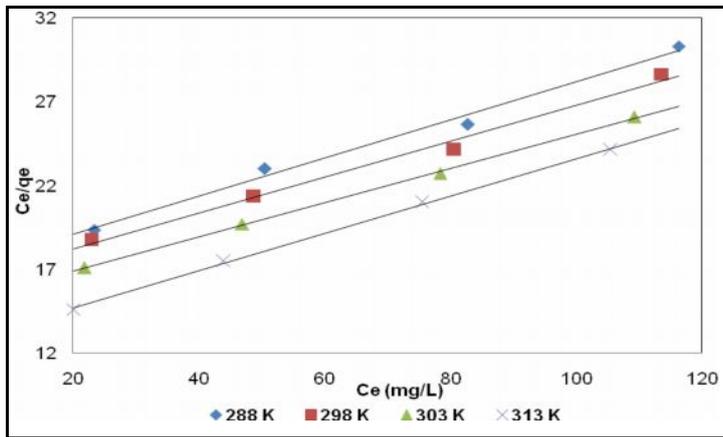
Fig.6. Langmuir plot for adsorption of Ni^{2+} over 5Å molecular sieves as adsorbent at various temperatures for adsorbent weight 20g/L and at pH 5.

Freundlich isotherm

Freundlich isotherm[9] is the earliest known relationship describing the adsorption equation and is often expressed as: $q_e = K_f C_e^{\frac{1}{n_f}}$ (4)

Taking logarithm on both sides:

$$\log q_e = \log K_f + \frac{1}{n_f} \log C_e \qquad (5)$$

Where 'qe' is equilibrium adsorption capacity (mg/g), 'Ce' is the equilibrium concentration of the adsorbate in solution, 'K$_f$' and nf are constants related to the adsorption process such as adsorption capacity and intensity respectively. The plots in Fig.8 shows linear that the isotherm drawn for adsorption of Ni^{2+} onto **5Å** Molecular sieves and fitted well at various temperatures shown in fig7.
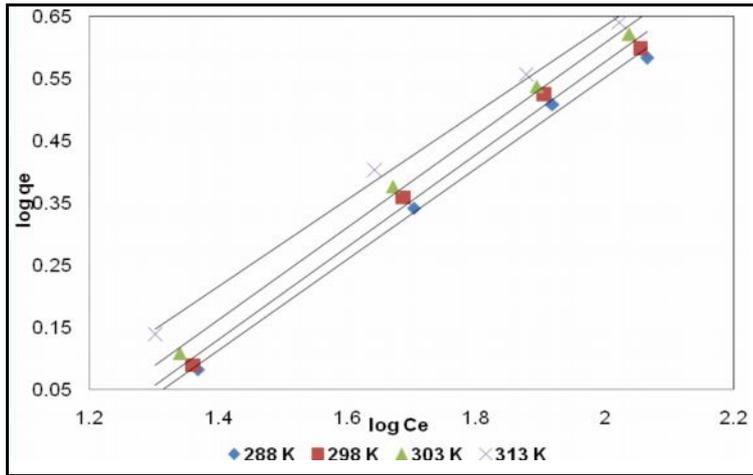
Fig.7.Freundlich plot for adsorption of Ni^{2+} over 5Å molecular sieves at different temperatures for adsorbent weight 20g/L and at pH 5.

Table 1. Langmuir & Freundlich isotherm model parameters and R$_L$ values at different initial metal ion concentrations for Ni^{2+} adsorption by 5Å Molecular sieves

Temp. (K)	Langmuir constants			Freundlich constants			Separation factor	
	q$_m$(mg/g)	b(L/mg)	R^2	k$_f$	n$_f$	R^2	C$_T$(mg/L)	R$_L$
288	8.7489	0.0068	0.9901	0.1215	1.3629	0.9956	47.521	0.755
298	9.3023	0.0066	0.9903	0.1213	1.3397	0.9933	94.51	0.612
303	9.7656	0.0069	0.9993	0.1321	1.3457	0.9963	147.415	0.495
313	8.9766	0.0089	0.9992	0.1715	1.4267	0.9967	192.97	0.367

Adsorption kinetic models:

Pseudo-first-order/Lagergren kinetic model

The pseudo-first-order or Lagergren kinetic rate equation for the adsorption of liquid–solid system was derived based on solid adsorption capacity. It is one of the most widely used adsorption rate equations for adsorption of a solute from a liquid solution. The pseudo first order kinetic equation can be expressed as:

$$\frac{dq}{dt} = k_1(qe - qt) \qquad ----- (6)$$

After integration and applying the boundary conditions, for q$_t$= 0 at t= 0 and q$_t$= q$_t$ at t= t, the integrated form of Eq. (6) becomes:

$$\log(q_e - q_t) = \log q_e - k_1 t \qquad -------- (7)$$

In the present study Pseudo first order and Pseudo second order kinetic models have been attempted. The plots between *log(q$_e$ –q$_t$)* and time, t of Eq.7 show that the Lagergren pseudo-first order kinetic model does not fit well for the adsorption of metal ions in the present study, as they do not follow a straight line shown in Fig.8.

Pseudo-second-order kinetic model

In view of the above the fitness of the sorption data was tested using pseudo-second-order reaction model. The pseudo-second-order reaction model could be expressed by the rate expression as :

$$\frac{dq}{dt} = k_2(q_e - q_t)^2$$

(8)

On integration for boundary conditions when t = 0 to t > 0 and qt = 0 to qt > 0 and further simplifications, Eq. (8) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

(9)

The plot (Fig.10) of t/q_t vs. t of Eq. (9) gave a linear relationship from which the q_e and k_2 values were determined. The rate constants and the correlation coefficients for pseudo-second-order kinetic model were calculated and summarized in Table 2. These values showed that the pseudo-second order kinetic plots fit well the adsorption data of cadmium metal for the adsorbent.
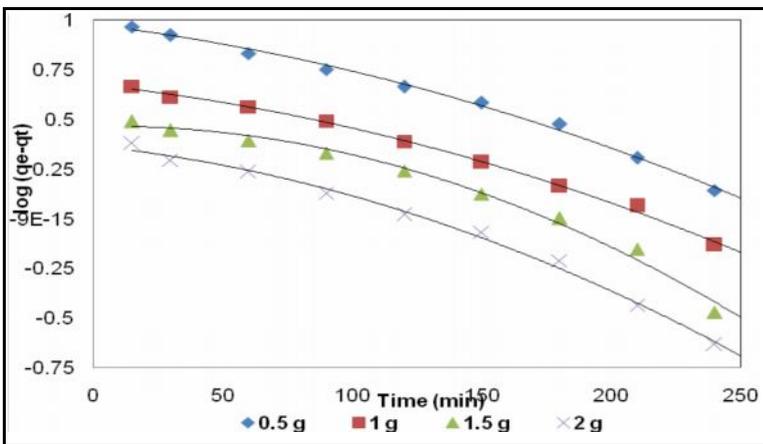

Fig.8.First order kinetic plot for adsorption of metal ion (Ni^{2+}) at 25°C, C$_0$ 50 mg/L and pH 5, using 5Å molecular sieves.
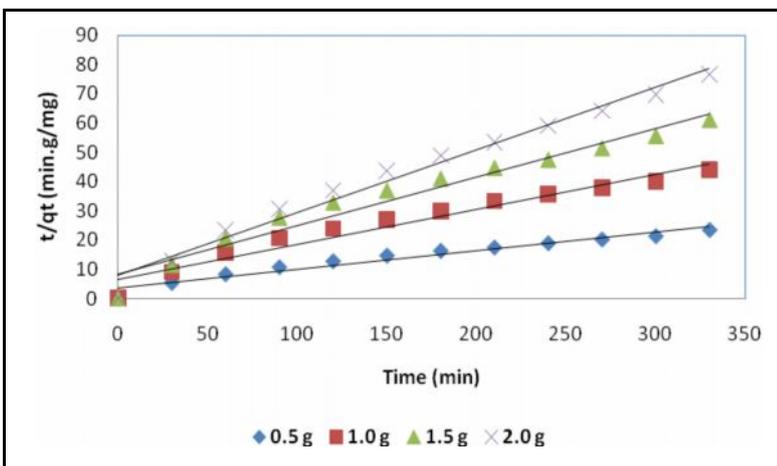
Fig.9.Second order kinetic plot for adsorption of metal ion (Ni^{2+}) at 25°C, C$_0$ 50 mg/L and pH 5, using 5Å molecular sieves.

Thermodynamic parameters and their determination

Thermodynamic parameters Gibbs free energy $\Delta G^°$ is the basic criterion for deciding whether the chemical process does occur/proceed or not. The spontaneity of the reaction can also be judged by the sign and magnitude of $\Delta G°$. A negative sign for $\Delta G°$ is an indicative of the spontaneity of any chemical process.

The thermodynamic parameters such as changes in standard free energy change $\Delta G°$, enthalpy $\Delta H^{'}$, entropy $\Delta S^{'}$ for any given adsorption process could be determined from the Equation:

$$\Delta G° = -RT \ln K_C \qquad \textbf{(10)}$$

where $\Delta G^{'}$,is the free energy change, expressed as J mol^{-1}. b is the Langmuir equilibrium constant for the process. The values of b (Table 1) at different temperatures were processed according to the following Van't Hoff equation.

$$\log \frac{Cad}{C_e} = -\frac{\Delta H°}{2.303RT} + \frac{\Delta S°}{2.303R} \qquad \textbf{(11)}$$

where b is in L mg^{-1}, R is universal gas constant (8.314 J/mol.K) The enthalpy changes ($\Delta H^{°}$) and entropy changes ($\Delta S^{'}$) for the adsorption process of Ni^{2+} using 5Å Molecular sieves were obtained from the plot of $\log \frac{Cad}{C_e}$ drawn against 1/T (Fig.11)and were compiled in Table 3.

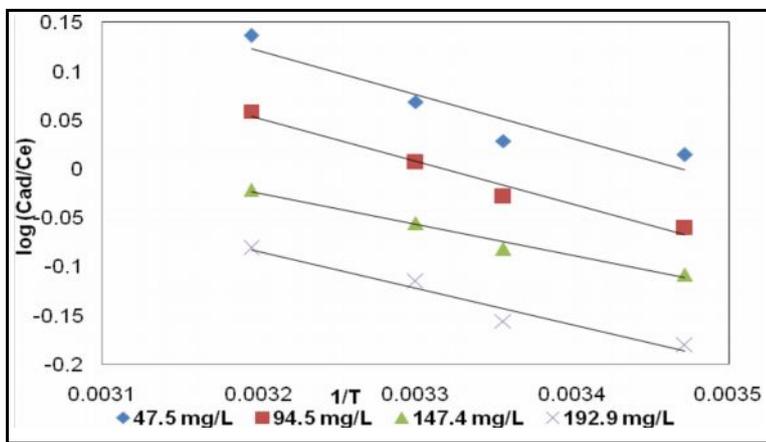**Fig.10.Vant Hoff plot for adsorption of Ni^{2+}over 5Å molecular sieves as adsorbent Plotted log Cad/Ce vs 1/T at different total metal ion concentration using 20g/L adsorbent at pH 5.**

Table 2. Kinetic parameters for Ni^{2+} adsorption on 5Å Molecular sieves   .

W(g L^{-1})	K$_2$(gmg^{-1} min^{-1})	q$_e$ (the) mg.g^{-1}	q$_e$ (exp) mg.g^{-1}	R^2
5	0.0006	17.6678	3.0094	0.9807
10	0.0012	9.2936	1.7315	0.9767
15	0.0018	6.6622	1.3098	0.9775
20	0.0035	5.0025	1.161	0.9913

Table3. Thermodynamic parameters for Ni^{2+} adsorption 5Å Molecular sieves

C$_0$ (mg L^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1}K)	ΔG^0 (kJ mol^{-1})	Temp. (K)
47.521	8.5930	29.8082	-8.57619	288
94.51	8.3958	27.8533	-8.2919	298
147.415	6.11483	19.0935	-5.77922	303
192.97	7.1372	21.2169	-6.63377	313

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Biomass characterization

Fourier transform infra red spectroscopy analysis.

The FTIR spectrum of 5Å molecular sieves before and after adsorption was shown in Fig.11&12. The broad band at 3397.55 cm^{-1} is due to corresponding to the OH-stretching vibration[10].The band at 2115.38 cm^{-1} indicated –C≡C– stretch, alkynes. The band at 1975.86 cm^{-1} indicated that the presence of combinational functional groups of aromatic aryl rings.
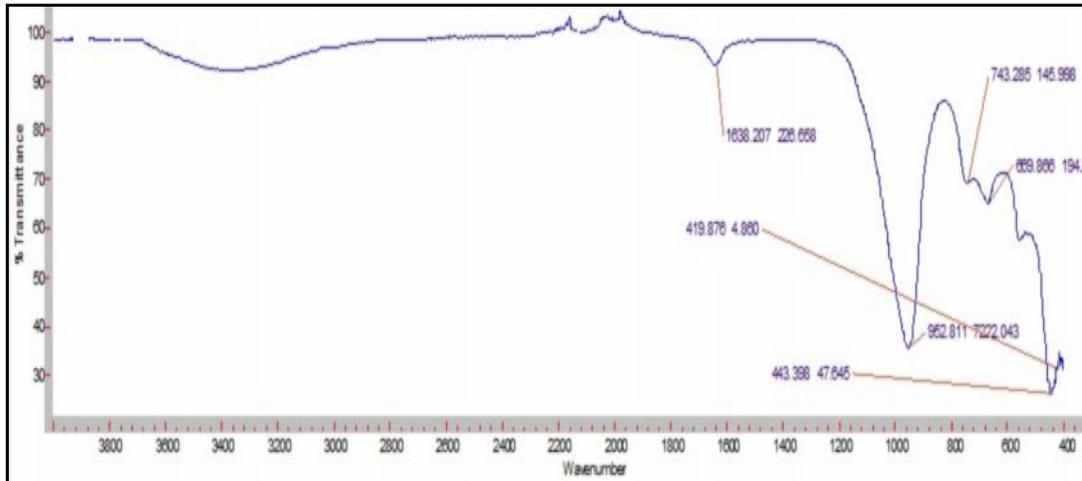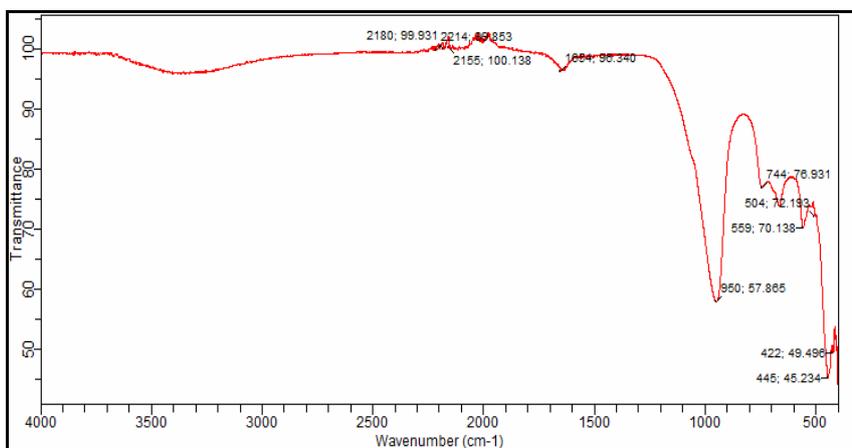

**Fig.11.FT-IR Spectrum of unloaded 5Å molecular sieves**

Fig.12.FTIR Spectrum of Ni^{2+} loaded 5Å molecular sieves

Characterization of 5Å Molecular sieves using SEM Studies

The SEM images were taken by applying 10 kV voltage with different magnification times for the clarification of surface. The SEM micrographs of 5Å molecular sieves powder before and after adsorption were studied and are depicted in Fig.13&14. SEM images of pure 5Å molecular sieves (Fig.13) show that number of pores with different diameters and different pore areas. Further, pores facilitate the good possibility for metal ions to be adsorbed[11]. The SEM observation revealed its complex and porous surface texture. Pores and internal surface are requisite for efficient adsorption.
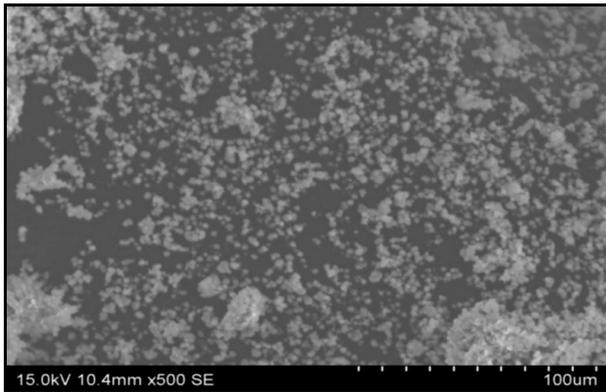
Fig.13.SEM of powder 5Å molecular sieves without metal ions
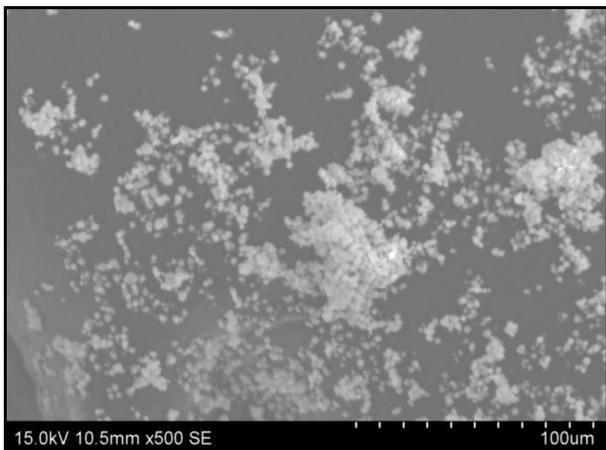
Fig.14. SEM of powder 5Å molecular sieves loaded with Ni^{2+} ions.

Regression analysis

Regression analysis also carried out to calculate the standard deviation and average deviation of the equilibrium data by Force 2.0 software. The standard and average deviations have represented in the below developed equation. The values of different constants obtained by both graphical analysis and regression analysis are in good agreement.The below equation predicts the metal uptake very well with an average deviation of 15-20%. The FORTRAN program used for regression analysis. The equilibrium metal uptake capacity (q_e) is given by

$$q_e = f (C_e, C_H, L/S, T) \quad \text{----------------------- (12)}$$

$$qe= 0.374*10^{-4} (C_e)^{0.8432} (C_H)^{-0.0813} (L/S)^{0.5308} (T)^{0.8219} \text{-------------------(13)}$$

Average Deviation=10%,Standard Deviation=13%.

Conclusions

The time required to reach equilibrium for 5Å molecular sieves was found to be 5 hours for Ni^{2+}.An increase in aqueous metal concentration increased metal adsorption for all conditions of the study.Decreases in pH of aqueous phase decreased metal adsorption due to the preferential adsorption of H^{+} ion compared to metal ions. pH 5 was to be found to favor metal adsorption of all metal ions. Increase in weight of molecular sieves leads to slightly increases percent adsorption and the equilibrium metal uptake decreases in all the conditions of present study. Increasing temperature increases metal adsorption from 288K to 313K in the removal of metal ions in the present study, indicating that endothermic in nature.

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