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Research Article

Adsorption of Nickel (II), Copper (II) and Iron (III) On Raatrani Leaf Powder:Kinetics and Equilibrium Studies

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ABSTRACT

Removal of Nickel (II), Copper (II) and Iron (III) from aqueous solutions using the adsorption process on Raatrani plant material has investigated. Physical, Chemical and Liquid phase adsorption, FT-IR characterization of Raatrani Leaf Powder (RLP) done by standard procedures studies on the removal of Ni (II), Cu (II) and Fe (III) ions were attempted by varying adsorbate dose, pH of the metal ion solution and time in batch mode. The equilibrium adsorption data were fitted with Freundlich, Langmuir Isotherms and the Isotherms constant were evaluated. A time variation study indicates that adsorption follows pseudo-first order kinetics. pH was found to have significant role to play in the adsorption. The processes were exothermic and the thermodynamic parameters were evaluated.

Keywords: Raatrani, Adsorption isotherm, adsorbent dose, Freundlich

INTRODUCTION

Heavy metals such as Nickel, Copper, Cadmium, Lead and Zinc have harmful effects on human physiology and other biological systems when they exceed the tolerance level[1-2]. In recent past development of efficient and eco-friendly methods for removal of heavy metals are receiving attention by agro waste as adsorbent by various researchers[3-7]. Literature survey reveals that no work has been reported on thermodynamic and kinetic study by using Raatrani Leaf powder (RLP) as an adsorbent for removal of Nickel, Copper and Iron from aqueous solution. In the present work an attempt has been made to study the feasibility of RLP, a cheap, locally and easily available for the adsorption of Nickel, Copper and Iron. An additional goal was to establish the ability of Langmuir Freundlich isotherms to model the equilibrium adsorption data effect of pH, adsorbent dose, temperature and variation in the initial concentration of adsorbate on the adsorption of Kinetics studies. The batch adsorptions kinetics was carried for the first order reversible reaction.

MATERIALS AND METHODS

Adsorbent

The adsorbent used in the present investigation were leaves of Raatrani Plants collected from Ahmednagar District of Maharashtra State (India). The leaves of Raatrani were dried in shadow avoiding direct sunlight on them. The dried plant leaves were grinded into powder and were boiled in distilled water to remove the suspended and dust for one hour and filtered. The residue left was treated with formaldehyde and finally with very dilute solution of sulphuric acid, stirred for 30 minutes vigorously using mechanical stirrer at room temperature, it was filtered and washed with distilled water repeatedly to remove free acid. After chemical treatment residue was dried first in air and finally in oven at 90-100^{0}C for 8-10 hours and powdered using electric grinder. The homogeneous powder was then passing through mesh for desired particle size (9.8 - 41.8

micron). The adsorbent once prepared were used throughout the experimental work. The particle size selected for these experiments were on the basis of their settlement at the bottom of the system, so that the portion of the solution could be taken out conveniently from the supernatant liquid.

FT - IR Spectrum of Raatrani Leaf Powder (RLP)

The surface chemistry of RLP was determined by the type quantity and bonding of oxygen containing functional groups such as hydroxyl, carbonyl, carboxyl, nitro groups[8-9].

The FT - IR spectrum of RLP adsorbent can be summarized from the bands observed as:

(1) Medium based overlapping bands at 3398.92cm^{-1} may be attributed to -OH group stretching present in tertiary alcohol of RLP.

(2) The bands at 2903.31cm^{-1} indicates C-H stretching assigned to secondary asymmetric carbon.

(3) The bands at 1717cm^{-1} is ascribe to C=O stretching in Raatrani.

(4) The band at 1133.94 cm^{-1} is attributed to C-O stretching and also O-H deformation of tertiary alcohol of Raatrani.

(5) The bands range of 665.32cm^{-1} indicates N-H deformation (out of plane band) in primary, secondary amines of RLP.

Preparation of Adsorbate Solution

Nickel, Copper and Iron were the metal ions selected for the present investigation. The chemicals used were of all of A.R. grade and used without further purifications. The solutions were prepared in doubly distilled water. A distilled water prepared by using first metal distillation unit and then all quick fit glass assembly in permangantic condition, wherever necessary the prepared solutions were standardized as per literature[10]. All the metals were estimated following a suitable colorimetric method. Nickel was estimated by the dimethylglyoxime method[11], Copper and Iron by the thiocyanate methods[12-13].

Batch Adsorption experiments

Each batch adsorption study was carried out by contacting the Raatrani leaf powder (RLP) with the metal ions Ni (II), Cu (II) and Fe (III) under different conditions for 60 minutes in a glass tube. Study was conducted in a thermostated water bath and the residual metal ions were analyzed. The amount of metal ions adsorbed from solution was determined by difference[14]. The effect of pH on the adsorption of Ni (II), Cu (II) and Fe (III) carried out within the range that would not influenced by the metal precipitation[15]. The pH range for adsorption study was kept in range of 3.5 to 7.2 and the temperature was maintained at 30^{0}C to examine the effect of initial solution pH on the adsorption of metals by contacting 0.9 g of the RLP with 100 ml. of Ni (II), Cu (II) and Fe (III) solutions in different glass tube. The pH of each solution was adjusted to the desired value with 0.1 M NaOH and / or 0.1 HCl (HNO_3).

RESULTS AND DISCUSSION

Effect of pH

The solution pH plays a vital role in the removal of heavy metals as the acidity of solution pH is one of the most important factors for controlling the uptake of heavy metals from wastewater and aqueous solution[16]. The maximum adsorption of Nickel, Copper and Iron on to the surface of RLP adsorbent was found to be at pH 3.5 which was rather acidic. Our findings have been supported by the earlier reported work[17]. The adsorption in acidic media may be attributed to link H^+ ion which are released from active sites and makes site available for the metal ions on to the surface of RLP, it is in good agreement with the findings of Devaprasath et al and others[18-19].

In the present investigation with increase in pH from 3.5 to 7.2 the degree of protonation of adsorbent functional group decreased gradually and hence the removal decreased as in Table 1**.** A close relationship between the surface basis of the adsorbents and the anions are evident where the interaction between oxygen free Lewis basic sites and the free electrons of anions as well as the electrostatic interaction between the anions and the protonated sites of the adsorbents are the main adsorption mechanism[20].The order of adsorption of metal ions on to the surface of RLP was Nickel > Copper > Iron.

Table 1. Removal of metal ions at different pH

	Nickel				Copper				Iron			
pH	3.5	4.4	5.8	7.2	3.5	4.4	5.8	7.2	3.5	4.4	5.8	7.2
% Removal	72.9	61.8	45.6	33.1	61.9	57.2	43.4	24.9	62	55.4	51	44.2

Effect of adsorbent dose

The present study reveals that as the adsorbent dose was increased from 0.5 gms to 0.8 gms there was increase in the adsorption of metal ions on to the surface of RLP, as in Table 2. This was in good agreement with the earlier reported work. The increase in adsorption with increase in RLP dose may be attributed to the increase in the availability of active sites, increase in the effective surface area[21].

Table 2. **Effect of adsorbent dose on removal of metal ions.**

	Nickel			Copper			Iron		
Adsorbent Dose (gm)	0.5	0.6	0.8	0.5	0.6	0.8	0.5	0.6	0.8
% Removal	44.4	47.8	56.6	40.5	49.0	52.5	45.2	42.5	52.0

Effect of Initial Concentration of metal ions

The feasibility and efficiency of a adsorption process not only depends on the properties of the adsorbents but also on the concentration of the metal ion solution the initial metal concentration provides an important driving force to overcome all the mass transfer resistances of the metal between aqueous and solid phase[22]. In the present investigation the removal of metal ions from the aqueous with variation in the initial concentration showed no regular trend and removals of metal ions found to be random as in figure 1. The decline in the adsorption capacity of RLP with increase in the concentration of metal ion (adsorbate) may be attributed to the availability of smaller number of surface sites on the adsorbents (RLP) for a relatively larger number of adsorbing species at higher concentration. The increase in metal concentration, also increases electrostatic interaction between the

metal ion and RLP adsorbent active sites and can be explained by the fact that more adsorption sites were covered as the metal ion increases[23].

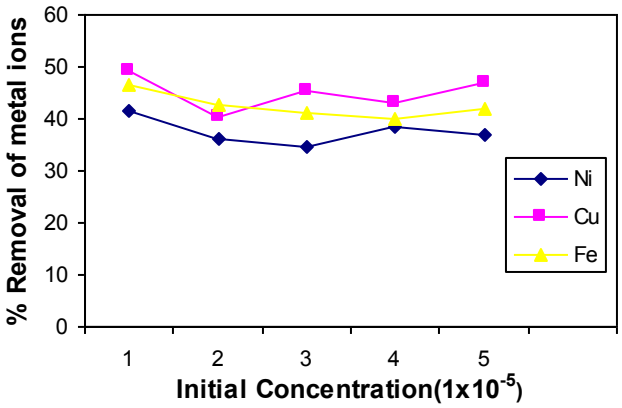

Figure 1. Effect of initial concentration on removal of metal ions.

Adsorption Kinetics

Kinetics of adsorption describing solute uptake rate, which is turn governs the contact time of adsorption process, is one of the important characteristics defining the efficiency of adsorption. The pseudo first order equation of Lagergren as cited by Ho.et.al[24] and was employed for studying the adsorption kinetics. The pseudo - first order equation of Lagergren is expressed as follows:

$$\text{Log } (q_e - q_t) = \log q_e - K_1 t / 2.303 \quad \ldots\ldots\ldots\ldots\ldots \quad 1$$

In the present study a plot of log $(q_e - q_t)$ versus't' gives a straight line confirming the applicability of first order rate expression of Lagergren[25]. The summarized rate constant (Kr) value range after applying different conditions is given in tabular form (Table-3).

Table 3- Rate constant values for different condition of adsorption process.

Adsorbate	pH	Adsorbent Dose	Initial Concentration	Temperature
Nickel	2.675×10^{-2} to 3.511×10^{-2} m^{-1}	2.224×10^{-2} to 3.866×10^{-2} m^{-1}	2.779×10^{-2} to 2.997×10^{-2} m^{-1}	3.442×10^{-2} to 4.463×10^{-2} m^{-1}
Copper	2.301×10^{-2} to 3.092×10^{-2} m^{-1}	2.866×10^{-2} to 3.838×10^{-2} m^{-1}	3.191×10^{-2} to 3.204×10^{-2} m^{-1}	3.893×10^{-2} to 4.427×10^{-2} m^{-1}
Iron	2.029×10^{-2} to 2.947×10^{-2} m^{-1}	2.879×10^{-2} to 3.947×10^{-2} m^{-1}	1.685×10^{-2} to 1.729×10^{-2} m^{-1}	3.747×10^{-2} to 4.080×10^{-2} m^{-1}

The present study reveals that with increase in pH during adsorption process, there was increase in the rate constant. In order to know the effect of adsorbent dose viz varying the amount of RLP adsorbent (0.5 gms, 0.6 gms and 0.8 gms respectively) The kinetics carried by keeping other parameters constant, showed that the rate constant increases with increase in the quantity of adsorbent, which indicates that adsorption depends on surface area of adsorbents. The effect of temperature on adsorption was used to calculate energy of activation and the data was fitted to Arrhenius equation.

$$K = Ae^{-Ea/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2$$

Where Ea is energy of activation, R is gas constant and T is the temperature.
The equation was modified as logK = logA - Ea / 2.303 RT 3

The plot of logK Vs 1/T gave a straight line with negative slope and was used to calculate energy of activation. Energy of activation (Ea) for Nickel (8361.21J), Copper (8577.92J) and Iron (8983.46J). Thus Ea for the metal ions was found to be in the order of Iron > Nickel > Copper

The Ea value for Nickel found to be minimum which may be attributed to higher binding of Nickel on to the surface of RLP. The energy barrier was less and therefore, its rate of adsorption was maximum. The dispersion force between the metal ions and RLP during adsorption at equilibrium increases with increase in initial concentration which may be attributed to the positively charged ions approaching the RLP surface inducing negative charge on it and hence attraction between the two dipoles lowers potential energy between them and brings adsorption.

Effect of Temperature

Temperature has two major effects on the adsorption process one is that increasing the temperature will increase the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbate particles because liquid viscosity decreases as temperature increases and the other one is that it effects the equilibrium capacity of the adsorbate depending on whether the process is exothermic or endothermic[26]. The effect of temperature on adsorption of metal ion on RLP is given in figure 2. The increased adsorption at higher temperature with some exception during the present investigation may be attributed to acceleration of some originally slow step, creation of new activation sites on adsorbent surface decrease in the size of adsorbing species, this could well occur due to progressive dissolution of the metal ion as the solution temperature increases. Our findings are in good agreement with the findings of different researchers[27].

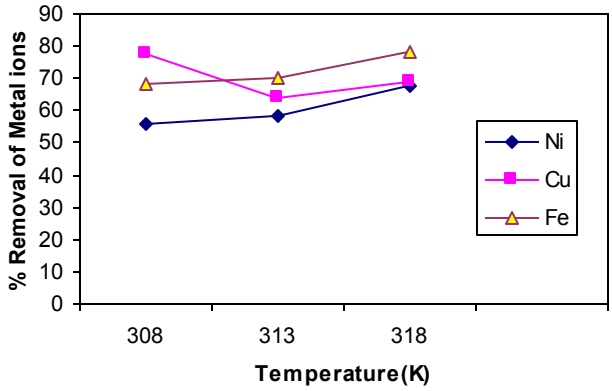

Figure 2- Effect of temperature on removal of metal ions.

Adsorption Isotherms

The capacity of adsorption isotherm provides a panorama of the course taken by the system under study in a concise form, indicating how efficiently an adsorbent will adsorb and allows an estimate of the economic viability of the adsorbents commercial applications for the specified solute. The Langmuir and Freundlich models are the most widely used models, in case of adsorption of metal ions by adsorbents even though the metal uptake may not exactly follows the monolayer adsorption mechanism. The Freundlich model[28] is perhaps the most popular adsorption model for a single solute system and is an empirical relation equation based on the distribution of solute between the solid phase and the aqueous phase at equilibrium.

In the present study the Freundlich model is found to be linear the coefficient of correlation value (r^2) was maximum. It was in good agreement with the findings of Shilpi et. al[29]. A smaller value of 1/n indicates better adsorption mechanism and formation of relating strong bond between adsorbate and adsorbent. The rate of attachment to the surface should be proportional to a driving force times on area. The affinity between the adsorbent and the different metals can be quantified by fitting the obtained adsorption values to the Langmuir Isotherm[30]. The Langmuir equation and Freundlich model describes the isotherm of Ni (II), Cu (II) and Fe (III) adsorption with high correlation coefficient (r^2 = 0.99). In our present findings isotherm data reveals that the adsorption process follows both Freundlich and Langmuir isotherm and suggest favorable adsorption. The dimensionless equilibrium parameter R_L also known as separation factor was defined by Hall et.al.[31] and given by the equation,

$$R_L = \frac{1}{1 \text{ x } b \text{ } C_0}$$

Where 'b' is Langmuir constant (1/mg) and C_0 is the initial concentration (mg/L). In the present investigation the values of R_L for Nickel (0.011), Copper (0.0108) and Iron (0.010) which lies in the range between 0 to 1 and shows favorable adsorption. Our findings are good agreement with the findings reported by Patil et al and others[32].

Thermodynamic Parameters

Thermodynamic Parameters evaluates the nature of adsorption of adsorbate and its magnitude during adsorption process. The change in Gibbs free energy (ΔG), enthalpy changes (ΔH) and entropy change (ΔS) were calculated and are summarized in the tabular form in Table 4. According to Laura[33] (i) ΔG upto -15KJ/mole are connected with the physical interaction between adsorption site and metal ions (physical adsorption), (ii) ΔG when more than -30KJ/mole involves charge transfer from adsorbent surface to the metal ion to form a co-ordination bond. In the present investigation ΔG values for nickel (II), copper (II) and iron (III) are below -15KJ/mole indicates adsorption mechanism as the physical interaction between adsorption sites and metal ion (physical adsorption). The negative value of ΔH shows the exothermic nature of adsorption of metal ions on to the surface of RLP. Our observations are supported by the work carried by Soon-Yong et.al[34]. The positive value of ΔS suggest increased randomness at the solid - liquid interface solvent (water) molecules which are displaced by the adsorbed species, gain more translational entropy than was lost by the adsorbate ions. Furthermore before adsorption process takes place the adsorbate ions are heavily solvated (the system is more ordered) and this order may be lost when the ions are adsorbed on the surface, due to the release of solvated water molecules.

Table 4: Thermodynamic Parameters at different temperature.

Adsorbate	Temperature /K	-ΔG /KJ	-ΔH /KJ	ΔS / J
Nickel	308	3.229	14.146	32.803
	313	2.947		
	318	3.029		
Copper	308	3.761	19.316	50.287
	313	3.275		
	318	3.710		
Iron	308	3.825	7.045	10.510
	313	3.720		
	318	3.480		

CONCLUSION

The experimental data generated by the present investigation shows that acid treated RLP is an efficient adsorbent for the removal of Ni (II), Cu (II) and Fe (III) from solution. The important advantage of using RLP as an adsorbent creates no effluent problem and easily biodegradable. Metal ion adsorption is a reasonably fast process on the surface of RLP as more than 50% of metal ion is adsorbed within 20-30 minutes. The Langmuir and Freundlich isotherms are found to be applicable in the present metal ion adsorption, which may be attributed to the formation of monolayer on the surface of the adsorbent. The values of thermodynamic parameters ΔG, ΔH, ΔS are indicative of spontaneous process. The plant material such as RLP will open new area of using various abundantly available plant materials as adsorbent in the removal of toxic effluents.

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