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Kinetics, thermodynamics and equilibrium studies on the adsorption of Nickel (II), Copper (II) and Iron (III) by acid activated Nirgudi Leaf powder

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ABSTRACT

The study was performed to investigate the use of Acid Activated leaf powder of Nirgudi plant (L. Vitex negudo) as an adsorbent for the removal of transition metal ions like Ni (II), Cu (II) and Fe (III) from aqueous solution. FT-IR characterization of Acid Activated Nirgudi leaf powder (AANLP) was done by standard procedures. The adsorption process was carried by batch experiments by varying adsorbent dose, pH of the adsorbate (metal ion) solution, temperature and time. The percentage removal of Ni (II), Cu (II) and Fe (III) by AANLP under different condition during the findings was significant and is enlisted in the tabular form in TABLE 1. The order of adsorption during the findings on AANLP of metal ions were Ni > Cu >Fe. The equilibrium adsorption data were fitted with Freundlich, Langmuir Isotherms. A time variation study indicates that adsorption follows pseudo-first order kinetics.

KEYWORDS

Nirgudi plant powder;
Adsorption isotherm;
pH;
Freundlich;
Langmuir.

INTRODUCTION

Heavy metals such as Nickel (II), Copper, Cadmium, Lead and Zinc have harmful effects on human physiology and other biological systems when they exceed the tolerance level[1,2]. They pose serious healthy hazards through entry into the food chain; therefore, they must be removed from industrial waste effluents. 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[3-9]. Literature survey reveals that no work has been reported on thermodynamic and kinetic study by using Nirgudi Leaf powder (NLP) as an adsorbent for removal of Nickel, Copper and Iron from aqueous solution.

In the present investigation an attempt has been made to study the feasibility of Nirgudi Leaf powder as a cheap, locally and easily available medicinal plant for the adsorption of Nickel, Copper and Iron. The adsorption of heavy metal ions from aqueous solution was carried to study the effect of pH, adsorbent dose, temperature and variation in the initial concentration of adsorbate on the adsorption of Kinetics studies. The batch adsorptions Kinetics were carried for the first order reversible reaction.

EXPERIMENTAL

Adsorbent

The adsorbent used in the present investigation were leaves of Nirgudi Plants collected from Ahmednagar District of Maharashtra State (India). The leaves of Nirgudi 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°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 Nirgudi Leaf Powder (NLP)

The surface chemistry of NLP was determined by the type quantity and bonding of oxygen containing functional groups such as hydroxyl, carbonyl, carboxyl, nitro groups[10,11].

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

1. Medium based overlapping bands at 3399.89 cm^{-1} may be attributed to -OH group stretching present in tertiary alcohol of NLP.
2. The bands at 2913.31 cm^{-1} indicates C-H stretching assigned to secondary asymmetric carbon.
3. The bands at 2226.42 cm^{-1} ascribes to C-N stretching in the Cyanide group.
4. The bands at 1684.52 cm^{-1} indicates C=O stretching in α - β unsaturated Ketones.
5. The bands at 1518.67 cm^{-1} ascribes to NO_2 stretching in aromatic nitro compounds of NLP.
6. The bands at 1621.84 cm^{-1} attributes to NH_3- deformation.
7. The bands at 1132.97 cm^{-1} ascribes to C-O stretching in tertiary alcohol and also attributes to -OH deformation in tertiary alcohols of NLP.
8. The bands range of 600.70 cm^{-1} to 666.28 cm-1 ascribes to NH deformation in primary, secondary amines of NLP.

Preparation of adsorbate solution

Nickel, Copper and Iron were the metal ions selected for the present investigation. The chemicals used were of all of Analar 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[12]. All the metals were estimated following a suitable colorimetric method. Nickel was estimated by the dimethylglyoxime method[13], Copper and Iron by the thiocyanate methods[14,15].

Batch adsorption experiments

Each batch adsorption study was carried out by contacting the Nirgudi leaf powder (NLP) with the metal ions [Nickel (II), Copper (II) and Iron (III)] under different conditions for 60 minutes in a glass tube. The uptake of metal ions study on NLP was carried systematically and at temperature 30°C to evaluate effect of initial solution pH, adsorbent dose initial metal ion concentration on adsorption of metal ions. The effect of temperature on the adsorption was carried out in order to study the thermodynamics of the process. Each study was conducted in a thermo stated water bath and the residual metal ions were analyzed. The amount of metal ions adsorbed from solution was determined by difference[16]. The effect of pH on the adsorption of Nickel (II), Copper (II) and Iron (III) carried out within the range that would not influenced by the metal precipitation[17]. The pH range for adsorption study was kept in range of 3.5 to 7.2 and the temperature was maintained at 30°C to examine the effect of initial solution pH on the adsorption of metals by contacting 0.9 g of the NLP 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).

Batch Kinetics experiments were first conducted using freshly prepared NLP to determine the time needed by Ni (II), Cu (II) and Fe (III) binding process to reach the equilibrium state. Based on Kinetic experimental results, all experiments were conducted for a period of 60 minutes. For equilibrium study the glass tubes containing the mixture were kept in thermostated water bath for 24 hours. The adsorbent (NLP) were removed from solution by decantation 10ml discarded by using Whatmann Filter paper no.41. The residual Nickel (II), Copper (II) and Iron (III) concentration in the solution were determined. All the studies were conducted in triplicates and the mean value were determined for each. Subsequent adsorptions studies were carried at pH 3.5 to 7.2, variation in adsorbent dose, temperature and Initial concentration variation of adsorbate (metal ion).

The equilibrium adsorption data were then fitted to Freundlich, Langmuir adsorption isotherms equations.

Freundlich,

$$q_e = K_F C_e^{(1/n)}$$

Langmuir,

$$q_e = K_L C_e / (1 + b C_e) = q_m bce / (1 + b C_e)$$

Where q_e is the adsorption capacity in mg/g, C_e is the equilibrium concentration of adsorbate (mg/L); K_F and n are Freundlich Constant K_L and b are Langmuir constants, q_m is the Langmuir monolayer adsorption capacity.

RESULT 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[18]. The maximum adsorption of Nickel, Copper and Iron on to the surface of NLP adsorbent was found to be at pH 3.5 which was rather acidic. Our findings have been supported by the earlier reported work[19]. The adsorption in acidic media may be attributed to the exposure of negative sites of the adsorbents through dissolution of more protons and thus enhances the adsorption capacities as the surface oxide functions as ligands for metal ions. Hence the adsorption phenomenon is attributed solely to the chemical interaction namely inner-sphere complexation between the metal ions on to the surface of NLP, it is in good agreement with the findings of Devaprasath et al and others[20-22].

In our finding the adsorption of metal ions onto the surface of NLP adsorbent decreases by the drift in solution pH from acidic to alkaline medium i. e. increase in pH from 3.5 to 7.2 as shown in figure 1. Similar findings were reported by Oboh and others[23-26]. The order of adsorption of metal ions on to the surface of NLP was Nickel > Copper > Iron.

Effect of adsorbent dose

The present study reveals that as the adsorbent dose increased from 0.5 gms to 0.8 gms there was increase in the adsorption of metal ions on to the surface of NLP, as shown in figure 2. The increase in adsorption with increase in NLP dose may be attributed to the increase in the availability of active sites, increase in the effective surface area[27-29]. The adsorption of metal ion onto the surface of NLP was at random order.

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[30,31]. There are many factors which contribute to the adsorbate concentration effect. The first and important one is that adsorption sites remain unsaturated during the adsorption reaction; the second cause is aggregation / agglomeration of adsorbent particles at higher concentration. Such aggregation leads to a decrease in the total surface area of the adsorbent particles available for adsorption and an increase in the diffusional path for adsorption and an increase in the diffusional path length[32]. 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

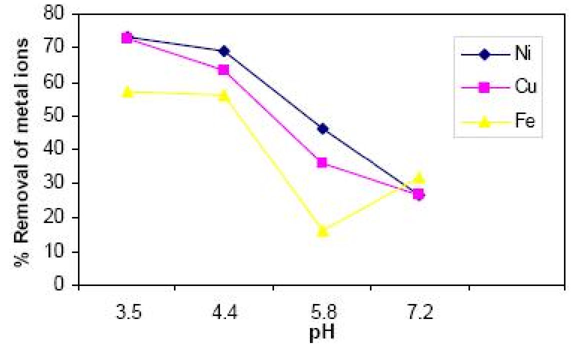

Figure 1 : Effect of pH on removal of metal ions

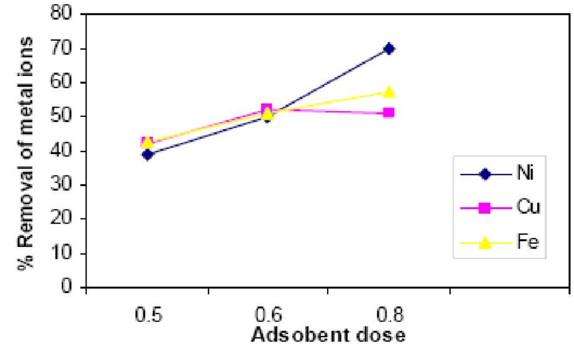

Figure 2 : Effect of adsorbent dose on removal of metal ions

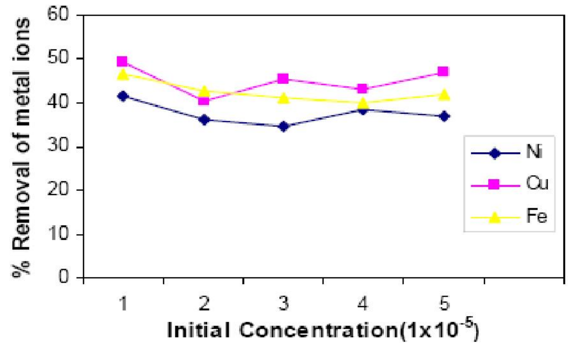

Figure 3 : Effect of initial concentration on removal of metal ions

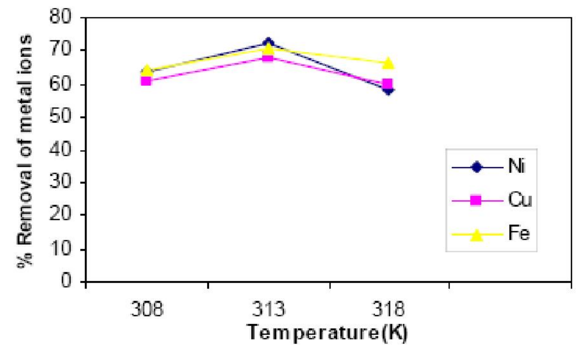

Figure 4 : Effect of temperature on removal of metal ions

as shown in figure 3.

The decline in the adsorption capacity of NLP with increase in the concentration of metal ion (adsorbate) may be attributed to the availability of smaller number of surface sites on the adsorbents (NLP) for a relatively larger number of adsorbing species at higher concentration[33]. The increase in metal concentration, also increases electrostatic interaction between the metal ion and NLP adsorbent active sites and can be explained by the fact that more adsorption sites were covered as the metal ion increases[34]. In the present investigation the copper has more affinity to the surface of NLP than Nickel and Iron.

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 important physicochemical study which helps in the evaluation of the basic qualities of a good adsorbent is adsorption kinetics and equilibrium[35]. In order to estimate the adsorption capacity of the adsorbent accurately, it is important to allow sufficient time for the experiment system to reach equilibrium. The pseudo first order equation of Lagergren as cited by Ho.et.al.[36] and was employed for studying the adsorption kinetics. The pseudo - first order equation of Lagergren is generally expressed as follows:

$$\mathrm{Log}\,(q_e - q_t) = \log q_e - K_1\, t / 2\text{-}303 \quad (1)$$

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[35,37,38].

The present study reveals that after carrying adsorption in different conditions, from the observations made, it can be concluded that rate constant is independent of initial concentration of metal ions with some exception.

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 NLP 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 and therefore, increase in quantity furnishes more surface area and hence adsorption increases at the same time rate of adsorption also increases. The effect of temperature on adsorption was used to calculate energy of activation and the data was fitted to Arrhenius equation.

$$K = Ae^{-Ea/RT}$$

where Ea is energy of activation, R is gas constant and T is the temperature.

The equation was modified as,

$$\log^{K} = \log^{A} - Ea / 2.303\, RT$$

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 (732.9085), Copper (2354.935) and Iron (2650.54). Thus Ea for the metal ions was found to be in the order of Copper > Iron > Nickel.

The Ea value for Nickel found to be minimum which may be attributed to higher binding of Nickel on to the surface of NLP. The energy barrier was less and therefore, its rate of adsorption was maximum. The dispersion force between the metal ions and NLP during adsorption at equilibrium increases with increase in initial concentration which may be attributed to the positively charged ions approaching the NLP surface inducing negative charge on it and hence attraction between the two dipoles lowers potential energy between them and brings adsorption[39].

Effect of temperature

The magnitude of the temperature effects for the adsorption process is one of the most important criteria for the efficient removal of heavy metals from the wastewater[40]. Temperature has two major effects on the adsorption process one is that increasing the temperature increases 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[41,42]. The effect of temperature on adsorption of metal ion on NLP is given in figure 4.

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[43,44].

Adsorption isotherms

The capacity of adsorption 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[18]. It is a graphical representation showing the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium[43]. 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[45]. The Freundlich model[46] 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.[47,48]. A smaller value of 1/n indicates better adsorption mechanism and formation of relating strong bond between adsorbate and adsorbent[49-52]. The Langmuir adsorption isotherm has been used traditionally to quantify and contrast the performance of different adsorbents. The Langmuir adsorption isotherm is based on the assumptions. (I) All sites are equivalent. (II) A molecule is adsorbed on a site independent of the neighboring adsorbed molecules. (IV) Coverage is independent of binding energy[45] and (V) constant temperature.

The rate of attachment to the surface should be proportional to a driving force times on area. The driving force is the concentration is fluid and the area is the amount of bare surface. The affinity between the adsorbent and the different metals quantified by fitting the obtained adsorption values to the Langmuir Isotherm.

The Langmuir equation and Freundlich model describes the isotherm of Nickel (II), Copper (II) and Iron (III) adsorption with high correlation coefficient

TABLE 1 : The percentage removal of Ni (II), Cu (II) and Fe (III) by AANLP under different condition during the findings

Condition	Percentage removal of metal ions	
	Minimum	Maximum
p^H	26.30	73.00
Adsorbent dose	39.00	70.00
Initial conc. of adsorbate	34.66	49.10
Temperature	58.20	72.30

TABLE 2 : Thermodynamic parameters at different temperature

Adsorbate	Temperature /K	-ΔG /KJ	-ΔH /KJ	ΔS / J
Nickel	308	3.206	3.849	23.019
	313	3.423		
	318	3.436		
Copper	308	2.954	15.144	58.722
	313	3.209		
	318	3.542		
Iron	308	3.080	9.289	40.021
	313	3.148		
	318	3.480		

(r^2 = 0.99)[36,47]. 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.[47] and given by the equation,

$$R_L = \frac{1}{1 \times b\,C_o}$$

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 (0.0067), Copper (0.0105) and Iron (0.0106) 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[49,53-55].

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 2

According to Laura[55] (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 NLP. Our observations are supported by the work carried by Soon-Yong et.al.[56]. 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.

CONCLUSIONS

The experimental data generated by the present investigation shows that acid treated NLP is an efficient adsorbent for the removal of Nickel (II), Copper (II) and Iron (III) from solution. The important advantage of using NLP as an adsorbent creates no effluent problem and easily biodegradable. Metal ion adsorption is a reasonably fast process on the surface of NLP as more than 50% of metal ion is adsorbed within 20-30 minutes. The adsorption of metal ions onto the surface of NLP adsorbent is first order process with low activation energy which is indicative of rapid adsorption process. 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 NLP will open new area of using various abundantly available plant materials as adsorbent in the removal of toxic effluents. Thus NLP is suitable adsorbent for adsorption of metal ions from aqueous solution.

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