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Adsorption of Nickel (II), Copper (II) and Iron (III) from aqueous solution using Ashoka Leaf Powder

R. S. Shelke[1], B. R. Madje[2], J. V. Bharad[2] and M. B. Ubale[2]*

[1]Pemraj Sarda College, Ahmednagar (M. S.) India.

**[2]Post Graduate Department of Chemistry, Vasantrao Naik Mahavidyalaya,
Aurangabad. 431 003 (M. S.) India.**

***Corres.author: mbubale@yahoo.com
*Mobile: +919422201217**

Abstract: Removal of Nickel (II), Copper (II) and Iron (III) from aqueous solutions using the adsorption process on Ashoka plant material [Polyathia lonifolia (sonn)] has investigated. A treated plant leaf powder of Ashoka (ALP) utilized as an adsorbent tested for their ability to remove transition metal ions from aqueous solution. Physical, Chemical and Liquid phase adsorption, FT-IR characterization of ALP done by following 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: Ashoka, Adsorption isotherm, pH, adsorbent dose, Freundlich.

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 Ashoka Leaf powder (ALP) 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 ALP, 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 were carried for the first order reversible reaction.

Experimental

Adsorbent

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

The surface chemistry of ALP 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 ALP adsorbent can be summarized from the bands observed as:

1) Medium based overlapping bands at 3313.11cm^{-1} may be attributed to -OH group stretching present in tertiary alcohol of ALP.
2) The bands at 1730.8 cm^{-1} indicates C =O stretching in saturated ketones.
3) The bands at 1515.78 cm^{-1} ascribes to C-H deformation in methyl / methylene group of ALP.
4) The bands at 1057.76 cm^{-1} indicates C-O stretching in acyclic anhydride of ALP.
5) The bands at 587.218 cm^{-1} ascribes to N-H stretching in primary, secondary amines.

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 Ashoka leaf powder (ALP) 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 ALP was carried systematically and at temperature 30^{0}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 thermostated 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^{0}C to examine the effect of initial solution pH on the adsorption of metals by contacting 0.9 g of the ALP 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).

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

$$\text{Freundlich} \quad q_e = K_F\, C_e^{\,(1/n)}$$
$$\text{Langmuir} \quad q_e = K_L\, C_e / (1 + b\, C_e) = q_m\, bce / (1 + b\, C_e)$$

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.

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[18]. The maximum adsorption of Nickel, Copper and Iron on to the surface of ALP 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 link H^+ ion which are released from active sites and makes site available for the metal ions on to the surface of ALP, it is in good agreement with the findings of Devaprasath et al and others[20-22].

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 shown in figure 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[23-26]. The order of adsorption of metal ions on to the surface of ALP was Nickel > Copper > Iron.

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 ALP, as shown in figure 2. This was in good agreement with the earlier reported work. The increase in adsorption with increase in ALP dose may be attributed to the increase in the availability of active sites, increase in the effective surface area[27-29]. ALP showed sharp increase in adsorption of Copper on to the surface of ALP than Nickel and Iron but, however the order of adsorption of metal ion was found to be random on to the surface of ALP.

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 as shown in figure 3.

The decline in the adsorption capacity of ALP with increase in the concentration of metal ion (adsorbate) may be attributed to the availability of smaller number of surface sites on the adsorbents (ALP) 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 ALP adsorbent active sites and can be explained by the fact that more adsorption sites were covered as the metal ion increases[34].

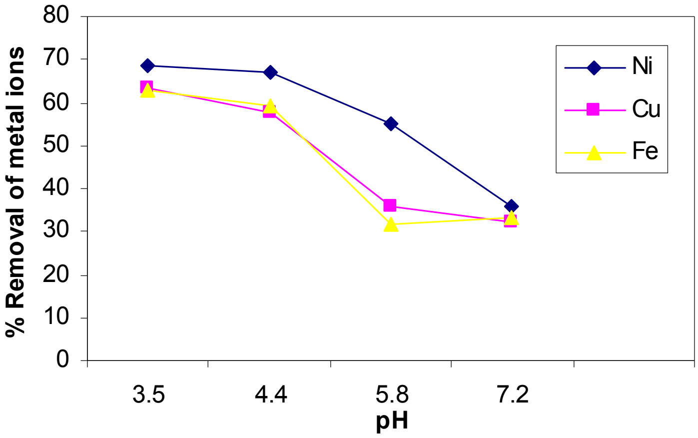

Fig.1. Effect of pH on removal of metal ions.

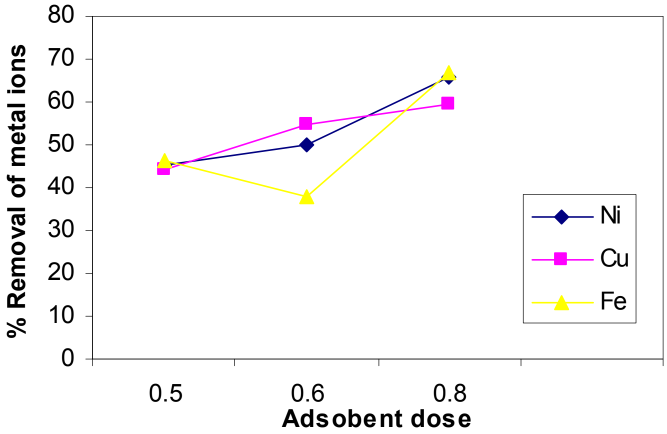

Fig. 2. Effect of adsorbent dose on removal of metal ions.

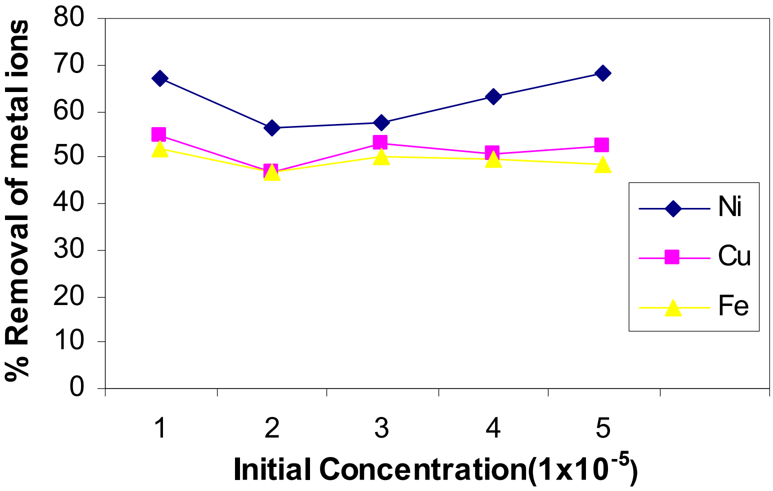

Fig. 3. Effect of initial concentration on removal of metal ions.

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 important physico-chemical 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:

$\text{Log}\,(q_e - q_t) = \log q_e - K_1\, t / 2\text{-}303$ ….. (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 summarized rate constant (Kr) value range after applying different conditions is given in tabular form as:

Table 1. Rate constant values for different condition of adsorption process.

Adsorbate	Rate constant values for different condition of adsorption process			
	pH	Adsorbent Dose	Initial Conc.	Temp.
Nickel	2.036×10^{-2} to 2.777×10^{-2} m^{-1}	2.853×10^{-2} to 3.610×10^{-2} m^{-1}	2.920×10^{-2} to 3.311×10^{-2} m^{-1}	4.924×10^{-2} to 5.995×10^{-2} m^{-1}
Copper	2.945×10^{-2} to 3.672×10^{-2} m^{-1}	2.710×10^{-2} to 3.177×10^{-2} m^{-1}	2.688×10^{-2} to 2.708×10^{-2} m^{-1}	4.424×10^{-2} to 5.187×10^{-2} m^{-1}
Iron	2.256×10^{-2} to 3.089×10^{-2} m^{-1}	2.921×10^{-2} to 3.675×10^{-2} m^{-1}	2.781×10^{-2} to 2.807×10^{-2} m^{-1}	4.443×10^{-2} to 5.035×10^{-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 ALP 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 log K Vs 1/T gave a straight line with negative slope and was used to calculate energy of activation. Energy of activation (Ea) for Nickel (3637.48 J), Copper (8544.80 J) and Iron (8617.71 J). Thus Ea for the metal ions was found to be in the order of

Iron > Copper > Nickel.

The Ea value for Nickel found to be minimum which may be attributed to higher binding of Nickel on to the surface of ALP. The energy barrier was less and therefore, its rate of adsorption was maximum. The dispersion force between the metal ions and ALP during adsorption at equilibrium increases with increase in initial concentration which may be attributed to the positively charged ions approaching the ALP 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

Temperature plays a major role in the adsorption of heavy metals on adsorbent surface. Although, the magnitude of the heat effects for the adsorption process is one of the most important criteria for the efficient removal of heavy metals from the waste-water[40]. 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[41-42]. The effect of temperature on adsorption of metal ion on ALP 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].

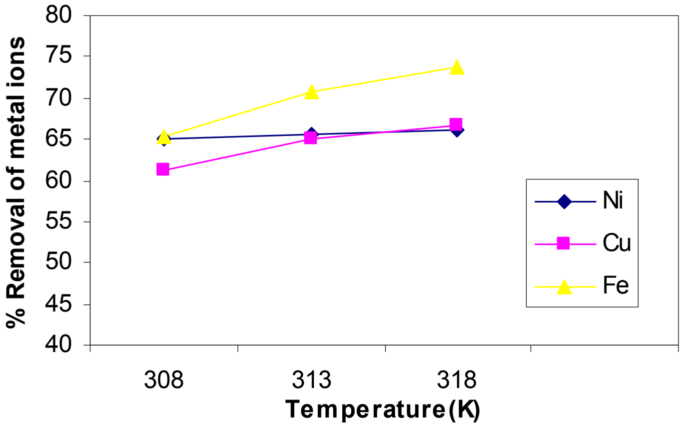

Fig. 4. Effect of temperature on removal of metal ions.

Adsorption Isotherms

The capacity of adsorption isotherm is fundamental and plays an important role in determination of the maximum capacity of adsorption. 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 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 (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,

$$R_L = \frac{1}{1 \times b\, C_0}$$

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 (0.0103), Copper (0.0103) and Iron (0.0105) 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 such as change in Gibbs free energy (ΔG), enthalpy changes (ΔH) and entropy change (ΔS) were calculated and are summarized in table no. 2

According to Laura[55] (i) ΔG upto -15Kg/mole are connected with the physical interaction between adsorption site and metal ions (physical adsorption), (ii) ΔG when more than -30Kg/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 ALP. 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 and this order may be lost when the ions are adsorbed on the surface, due to the release of solvated water molecules.

Table 2. Thermodynamic Parameters at different temperature.

Adsorbate	Temperature (K)	-ΔG (KJ)	-ΔH (KJ)	ΔS (J)
Nickel	308	3.229	9.298	19.905
	313	2.947		
	318	3.029		
Copper	308	3.270	1.206	14.493
	313	3.302		
	318	3.415		
Iron	308	3.080	7.608	36.618
	313	3.148		
	318	3.480		

Conclusions

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

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