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Adsorption of Nickel (II), Copper (II) and Iron (III) on Jaswand Leaf Powder: A Case Study

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Abstract

The study was performed to investigate the use of Jaswand plant material (Hibiscus rosa-Sinensis) as an adsorbent for the removal of Ni (II), Cu (II) and Fe (III) from aqueous solution. FT-IR characterization of Jaswand Leaf Powder (JLP) 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 JLP under different condition during the findings was significant and is enlisted in the tabular form as:

Condition	Percentage removal of metal ions	
	Minimum	Maximum
p^H	23.80	74.50
Adsorbent dose	37.00	63.70
Initial Conc. of Adsorbate	43.00	53.08
Temperature	55.60	70.50

The order of adsorption during the findings on JLP 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: Jaswand Leaf Powder, Adsorption isotherm, pH, Freundlich, Langmuir

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INTRODUCTION

Industrial and mining waste water is the major source of pollution of heavy metals. Furthermore in the developing countries like India, many industries are operated at small or medium scale or even a family business within the residential premises of owner. These smaller units can generate a considerable pollution load which in many cases is discharge directly into the environment

without any waste water treatment. This is because capital investment, turnover and profit for these industries are also small. In India, such a situation exists and the discharge of waste water containing chemicals and metallic ions into nearby water sources.

In recent years increasing awareness of the environmental impact of heavy metals has prompted a demand for the purification of industrial waste water prior to discharge into natural water [1]. Conventional methods like Ion-exchange, chemical precipitation, ultra-filtration of electro-chemical deposition do not seem to be economically feasible for such industries because of their relatively high cost. Therefore, there is a need to look into alternatives to investigate a low cost method which is effective, economic and can be used by such industries.

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 [2-7]. Literature survey reveals that no work has been reported on thermodynamic and kinetic study by using Jaswand Leaf powder (JLP) 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 JLP, a cheap, locally and easily available for the adsorption of metal ions. The optimum temperature (range 30 to 45^0C), p^H (range 3 to 7), contact time (60 minutes) for the present study were selected by carrying trial experiments and was found to be maximum removal of metal ions by JLP in this range. The batch adsorptions kinetics was carried for the first order reversible reaction.

MATERIALS AND METHODS

Experimental

Adsorbent

The adsorbent used in the present investigation were leaves of Jaswand Plants collected from Ahmednagar District of Maharashtra State (India). The leaves of Jaswand 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 90-100^0C for 8-10 hours and powdered using electric grinder. The homogeneous powder was then passed 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 Jaswand Leaf Powder (JLP)

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

(1) Medium based overlapping bands at 3310.21cm^{-1} may be attributed to -OH group stretching present in secondary alcohol of JLP.

(2) The bands at 2917.77cm^{-1} indicates C-H stretching assigned to secondary asymmetric carbon.

(3) The bands at 1730.8 cm^{-1} indicates C=O stretching in α - β unsaturated Ketones.

(4) The bands range of 668.21cm^{-1} ascribed to N-H deformation (out of plane band) in primary, secondary amines of JLP.

Preparation of Adsorbate Solution

Nickel, Copper and Iron were the metal ions selected for the present investigation. The chemicals used were 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 Jaswand leaf powder (JLP) 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 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 JLP 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 enhances the adsorption capacities as the surface oxide functions as ligands for the metal ions on to the surface of JLP, 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 shown in figure 1 and The order of adsorption of metal ions on to the surface of JLP was found to be Ni > Cu > Fe

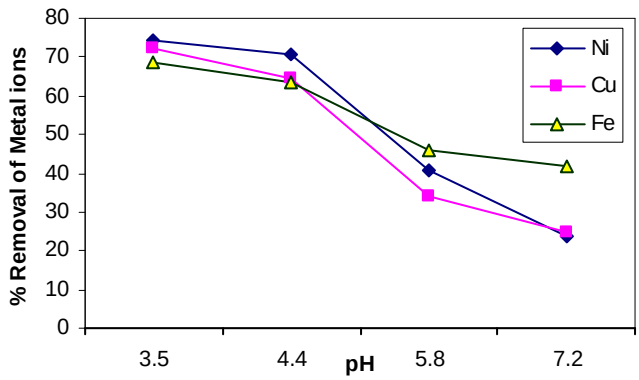

Figure 1- Effect of pH on removal of metal ions

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 JLP, as in figure 2. This is in good agreement with the earlier reported work [20]. The increase in adsorption with increase in JLP dose may be attributed to the increase in the availability of active sites, increase in the effective surface area [21].

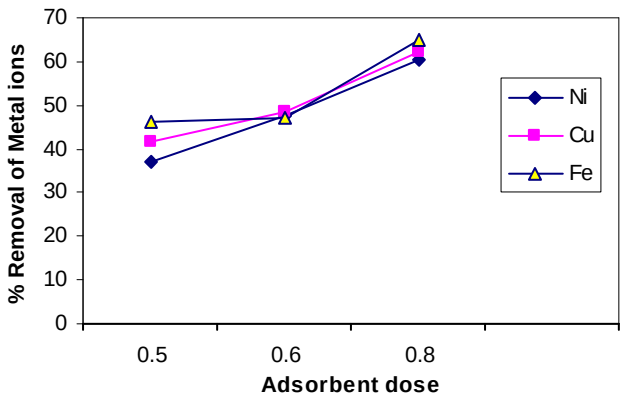

Figure 2- Effect of adsorbent dose on removal of metal ions

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 3. The decline in the adsorption capacity of JLP with increase in the concentration of metal ion (adsorbate) may be attributed to the availability of smaller number of surface sites on the adsorbents (JLP) 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 JLP adsorbent active sites and can be explained by the fact that more adsorption sites were covered as the metal ion increases [23].

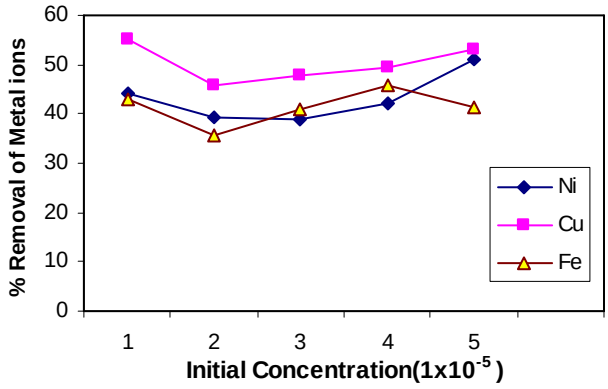

Figure 3- Effect of initial concentration on removal of metal ions

Effect of Temperature

Temperature has two major effects on the adsorption process increases the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbate particles due to decrease in liquid viscosity at higher temperature and the other effects is the equilibrium capacity of the adsorbate depending on nature of the process i.e. exothermic or endothermic [24]. The effect of temperature on adsorption of metal ion on JLP 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 [25].

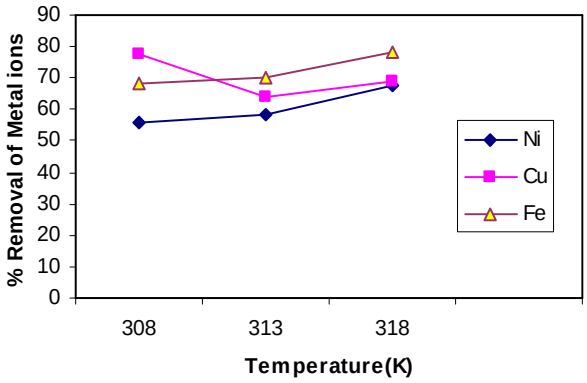

Figure 4- Effect of temperature on removal of metal ions

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 [26] 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 is in good agreement with the findings of Shilpi et. al [27]. 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 [28]. 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. [29] and given by the equation,

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

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 (0.0102), Copper (0.0102) and Iron (0.0101) 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 [30].

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 no. 1. According to Laura [31] (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 JLP. Our observations are supported by the work carried by Soon-Yong et.al [32].

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 which 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 1- Thermodynamic Parameters at different temperature

Adsorbate	Temperature (K)	-ΔG (KJ)	-ΔH (KJ)	ΔS (J)
Nickel	308	3.571	12.797	29.978
	313	3.400		
	318	3.271		
Copper	308	3.744	13.429	31.568
	313	3.472		
	318	3.428		
Iron	308	3.663	16.62	11.891
	313	3.221		
	318	3.782		

CONCLUSIONS

The experimental data generated by the present investigation shows that acid treated JLP is an efficient adsorbent for the removal of Ni (II), Cu (II) and Fe (III) from solution. The important advantage of using JLP as an adsorbent creates no effluent problem and easily biodegradable. Metal ion adsorption is a reasonably fast process on to the surface of JLP 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 JLP will open new area of using various abundantly available plant materials as adsorbent in the removal of toxic effluents.

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