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ROLE OF *CALOTROPIS PROCERA* FOR REMOVAL OF Ni(II) ION FROM WASTE WATER

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ABSTRACT

The present work deals with the removal of Ni(II) ion using activated charcoal prepared from the stem of *Calotropis procera*. The Ni^{2+} adsorption was found to be dependent on adsorbent dose, initial concentration, pH and contact time. The removal of Ni ion is higher at lower conc. and gradually decreases as the concentration increases. The pH 6 was the most suitable for removal and removal of Ni(II) ion increases with the increase in the absorbent dose.

Keywords: Absorption, *Calotropis procera*, Activated carbon, Nickel ion, Isotherms.

INTRODUCTION

The problems of ecosystem are increasing with developing technology. Heavy metal pollution is one of the main problems[1]. Consequently removal of heavy metals from waste water and industrial waste has become a very important environment issue[2]. Heavy metals have been used extensively in electroplating and metal surface treatment processes generate significant quantities of waste water containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum and silver) from a variety of application. These heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organism, causing health problems in animals, plants and human being[3]. Various treatment method for the removal of heavy metal from industrial effluents like ion exchange, solvent extraction, reverse osmosis, precipitation and adsorption methods are in vogue[4]. The selection of removal method is ultimately dependent upon technology being validated in term as sustainability, efficiency, adaptation and cost effectiveness. But these technologies have limitation such as high operation and maintenance cost, when dealing with large volume of waste water with low metal concentration. Based on these criteria adsorption method is considered to be the most suitable for application in India[5].

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Activated charcoal is the main adsorbent used in industry. Different physical forms of activated charcoal are produced depending on their application. Granular (GAC) form to be used in adsorption column and powder (PAC) forms for use in batch adsorption followed by filtration[6]. Adsorption can produce high quality water while also being a process that is economically feasible. Low cost adsorbents like fly ash, coal, peat saw dust[7], sawdust lignite and wood have received considerable interest because of their local availability and their practically low cost[8]. The object of the work is to develop a better method for the removal of heavy metal using low cost adsorbent.

EXPERIMENTAL

Materials and methods

Preparation of activated carbon from *Calotropis procera*

The naturally dried stem of the plant *Calotropis procera* were obtained locally. It was cut into small pieces. The stem was treated with 2% v/v sulphuric acid in 1 : 1 ratio and was kept in an oven at 150°C for 24 hours. It was filtered and washed with distilled water repeatedly to remove sulphuric acid and finally dried. Chemical activation using sulphuric acid produces a high surface area and high degree of micro porosity. The adsorbent was sieved to 40-60-mesh size and dried at 110°C for 2 hrs[9].

Preparation of stock solution of Ni (II) ion

In order to have wastes of uniform characteristics and to avoid interferences of other metals the synthetic stock solution of waste water was prepared from AR grade chemical. A standard stock solution of Ni(II) ion (1000 mg/L) was prepared from $Ni(NO_3)_2.6H_2O$ in deionized water. A solution was diluted to 1 L with deionized water. Several concentrations (from 60 ppm to 150 ppm) were prepared from this standard stock. Absorbance value of these solutions was measured at a specified wavelength of 232 nm.

Experimental methods and measurement

The experiments were carried out in the batch mode for the measurement of the adsorption capacities. The bottles with 250 mL were filled with wastewater and adsorbent. The bottles were capped and shaken at room temperature on an electric shaker at 450 rpm for required time period. The separation of the adsorbent and solution was carried out by centrifugation. The concentration of the unabsorbed Ni ion in the solution was determined spectrophotometrically. Batch adsorption studies were carried out to study the effect of pH (3, 4, 5, 6, 7 and 8), contact time (15-135 min), adsorbent dose (2-6 g/L) and initial Ni ion concentration (60-150 ppm) at room temperature using stopper bottles. The initial pH of solution was adjusted by using 0.05 N HCl or 0.1 N NaOH without changing the volume of the sample. After agitating the sample for the required contact time, the contents were centrifuged and filtered through whatman No. 41 filter paper and unreacted Ni (II) ion in the filtrate was analyzed spectrophotometerically[10].

The removal efficiency (E) of adsorbent was defined as –

$$E (\%) = [(C_o - C_e) / C_o] \times 100$$

Where C_o and C_e is the initial and equilibrium concentration of metal ion solution (mg/L), respectively.

Influence of each parameter (pH, initial metal ion concentration, and adsorbent particle size and carbon concentration) was evaluated in an experiment by varying parameter under evaluation while all the parameters in the experiments were maintained as constant[11].

Table 1: The parameters for Ni treatment from waste water

S. No.	Particular	Optimum data
1.	Time (min.)	105
2.	pH	6
3.	Dose (g/L)	5
4.	Max. % removal of dye	85.6

Isothermal study: Known isotherm models like Freundlich and Langmuir isotherm fit the adsorption equilibrium data of metal.

Langmuir adsorption isotherm

The Langmuir equation is derived from simple mass-action kinetic, assuming chemisorption. This model is based on two assumptions that the forces of interaction between adsorbed molecules are negligible and once a molecule occupies a site and no further sorption takes place. The saturation value is reached beyond which no further sorption takes place. The saturation monolayer can then be represented by the expression:

$$C_e/q_e = 1/Q_o b + C_e/Q_o \quad ...(1)$$

Where, C_e is equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium time per unit adsorbent (mg/g) and Q_o and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

The essential characteristic of a Langmuir isotherm can be express in term of a dimensionless constant separation factor or equilibrium parameter RL. It is defined by −

$$RL = 1/(1+bC_O) \quad \text{…(2)}$$

Where C_O is initial adsorbate concentration (mg/L) and b is the Langmuir constant (mg/L). Values of dimensionless equilibrium parameter RL show the adsorption to be favorable (0 < RL < 1).

Freundlich adsorption isotherm

The relation between the metal adsorbed by the adsorbent and metal equilibrium concentration in solution is given by Freundlich adsorption isotherm. The Freundlich equation is used for heterogeneous surface energies in which the energy term, Qo in the Langmuir equation varies as a function of the surface coverage, q_e strictly due to variations in the heat of adsorption:

$$q_e = k_f\, C_e 1/n \quad \text{…(3)}$$

The linear form of the equation (3) or the log form is –

$$\log q_e = \log k_f + 1/n \log C_e \quad \text{...(4)}$$

k_f and n are Freundlich constants; n gives an indication of the favorability and k_f the capacity of the adsorbent. Value of n between 1 and 10 indicates good adsorption.

The equilibrium concentration was calculated using following formula:

$$C_e = C_o - (\%\ \text{adsorption x } C_o/100) \quad \text{…(5)}$$

The amount of dye adsorbed per unit weight of an adsorbent q, was calculated using following formula:

$$q = (C_o - C_e) \text{ x } V/m \quad \text{…(6)}$$

Where C_e is the equilibrium concentration (mg/L), C_o is the initial concentration (mg/L), m is the mass of the adsorbent (gm) and V is the volume of the solution (L).

The Langmuir and Freundlich constants increase with the rise in temperature. The values of the n lie between 1 to 10 indicating good sorption potential of the sorbent. The co-relation coefficients (r) for Freundlich and Langmuir isotherms are merely equal. Therefore from the present adsorption study, it can be stated that Freundlich and Langmuir adsorption equations are found to be better fitted. (r ~ 0.996 as shown in Table 3).

Table 2: Parameters of Langmiur and Freundlich adsorption isotherm for adsorption of Ni(II) ion

Adsorbent dose (g/L)	Langmuir isotherm (Linear equation)	Freundlich isotherm (Linear equation)
2 g/L	y = 0.012 x + 0.465	y = 0.580 x + 0.692
3 g/L	y = 0.018 x + 0.577	y = 0.560 x + 0.591
4 g/L	y = 0.024 x + 0.620	y = 0.531 x + 0.583
5 g/L	y = 0.031 x + 0.607	y = 0.499 x + 0.547
6 g/L	y = 0.038 x + 0.673	y = 0.485 x + 0.497

Table 3: Langmiur and Freundlich constant for adsorption of Ni(II) ion at 105 minute and optimum dose of 5 g/L

Dose	Freundlich isotherm					Langmuir isotherm				
	K_f	n	c	r	r^2	Q_o	b	RL	r	r^2
5 mg/L	3.523 709	2.004 008	0.547	0.995	0.992	32.25 806	0.051 071	0.246 08	0.998	0.997

RESULTS AND DISCUSSION

Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process. It affects both the surface charge of adsorbent and the degree of ionization of the metal salt in solution. Fig. 1 demonstrates the influence of pH on the adsorption of Ni (II) ion by activated charcoal surface at equilibrium time. It was found that 85.6% removal of Ni(II) ion achieved at pH 6 and thereafter the percent removal decreases with increases in pH at 7 and 8. Thus the optimum adsorption pH for removal of dye was found to be 6.

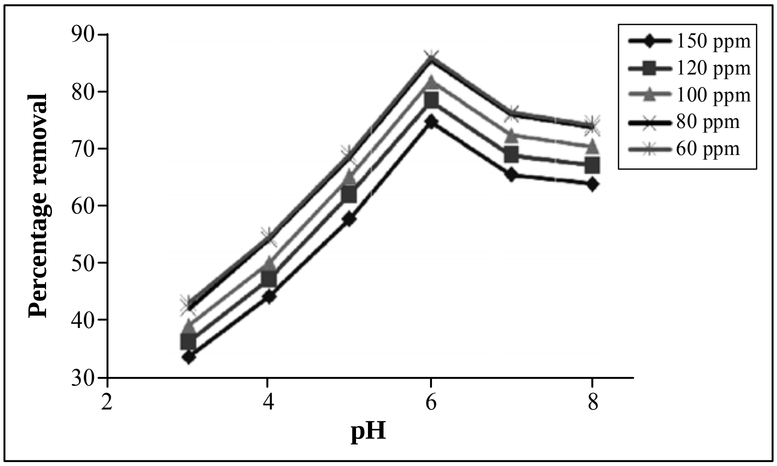

Fig. 1: Effect of pH on removal of Ni (II) ion at different concentrations by 0.5 g/L of activate carbon at constant contact time 105 min.

Effect of contact time

In adsorption system, the contact time play a vital role irrespective of the other experimental parameters, affecting the adsorption kinetics. Fig. 2 depicts that there was an appreciable increase in percent removal of Ni(II) ion upto 105 min. thereafter further increase in contact time the increase in removal was very small (at 120 min, 135 min). Thus the effective contact time (equilibrium time) is taken as 105 min. and it is independent of initial concentration 60 ppm.

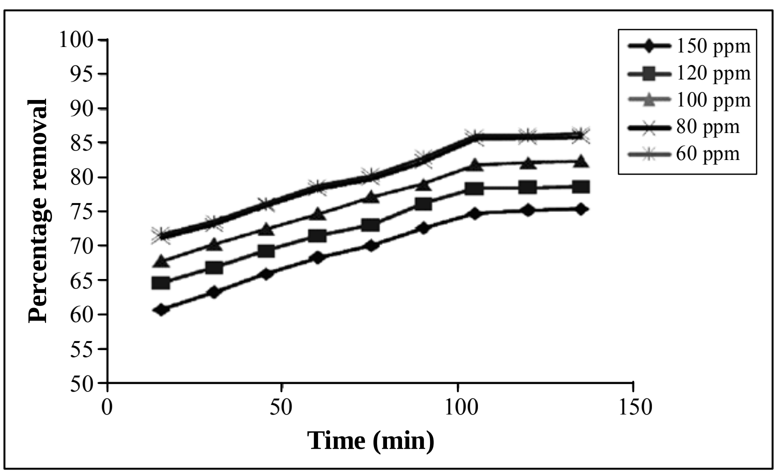

Fig. 2: Effect of contact time on removal of Ni(II) ion at different concentration by activated carbon at pH 6

Effect of adsorbent dose

The effect of adsorbent dose on percent removal of Ni(II) ion is shown in Fig. 3. Adsorbent dose was varied (2, 3, 4, 5, 6 g/L) and performing the adsorption studies at pH 6. The present study indicated that the amount of metal ion adsorbed on activated charcoal increase with increase in the charcoal dose up to 5 g/L and thereafter further increase in dose the increase in removal was very small. Thus the effective dose is taken as 5 g/L.

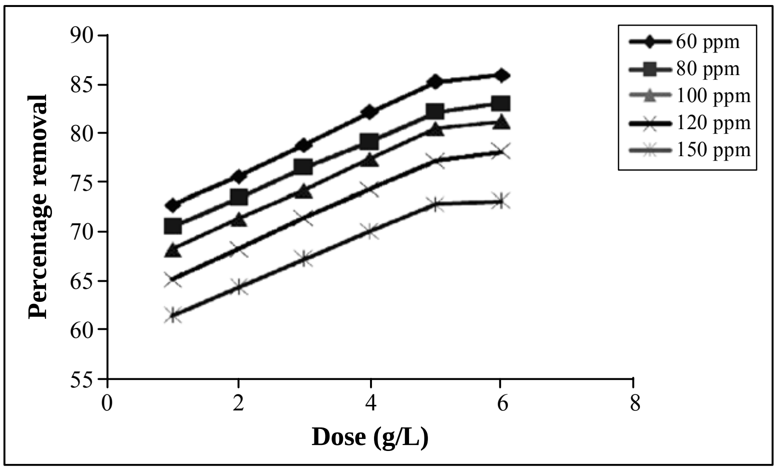

Fig. 3: Effect of activated carbon dose on percent removal of Ni(II) ion at equilibrium contact time 105 min. and pH 6

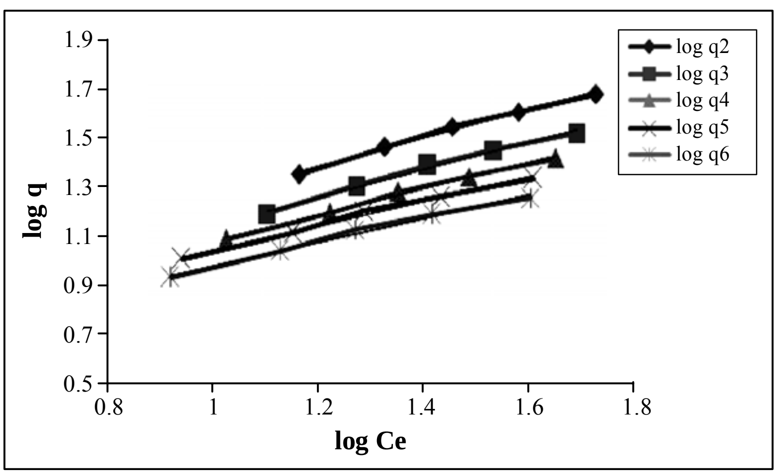

Fig. 4: Freundlich isotherm plot for Ni(II) ion adsorption by activated carbon at optimum conditions

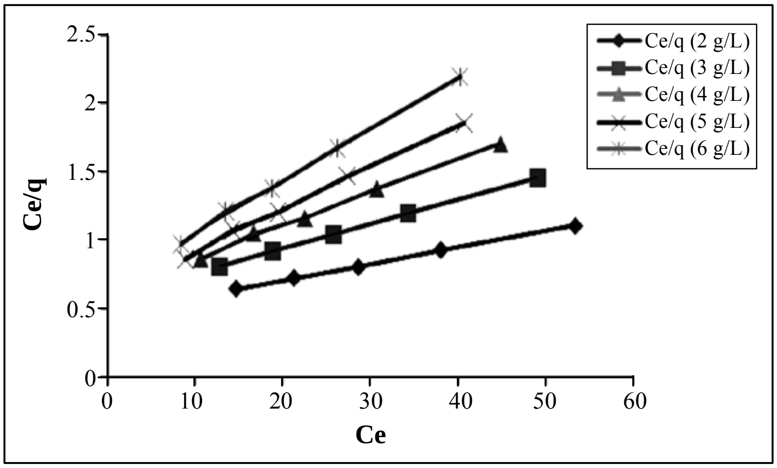

Fig. 5: Langmuir isotherm plot for Ni(II) ion adsorption by activated carbon at optimum conditions

Effect of nickel ion concentration

It was observed that the % removal of Ni(II) ion decreases with an increase in the concentration of Ni ion from 60 to 150 ppm.

CONCLUSION

The prepared activated carbon from the dry stem of *Calotropis procera* has a high ability for removing the Ni(II) ion from aqueous solutions. The percentage removal of the Ni(II) ion by the activated charcoal increases with the increase in adsorbent dose and decrease with increase in initial Ni^{2+} concentration. The uptake of Ni(II) ion on charcoal surface increased when the pH increased from 3 to 5.

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