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Biosorption of Chromium (VI) from Industrial Effluent using Neem Leaf Adsorbent

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Abstract

Industrial water pollution is a potential threat to human health mainly because of the non-biodegradable, hazardous heavy metals. Among these heavy metals chromium is of considerable concern. Various methods adopted for removal of heavy metals include chemical precipitation, membrane separation, ion exchange and adsorption. In case of adsorption, the generally used adsorbents like activated carbon, silica, alumina, etc. are expensive. This has prompted the use of natural materials as adsorbents in order to develop cheaper alternatives, which can be disposed off without regeneration due to their lower cost. Azadirachta indica leaf powder is tried for the removal of chromium. The newly developed adsorbents should be as effective as the conventional ones. Hence in the present work, Azadirachta indica (Neem) leaf powder is studied for their adsorptive capacity to remove chromium (VI) from aqueous solution. The equilibrium studies are systematically carried out in a batch process covering various process parameters that include agitation time, adsorbent dosage, temperature and initial concentration of chromium. The adsorption behavior is finding to follow the Freundlich Adsorption Isotherm.

Keywords: Adsorption, Neem leaf, chromium solution, isotherm.

Introduction

Advances in science and technology have brought tremendous progress in many spheres of development, but in the process, also contributed to degradation of environment all over the globe due to very little attention paid to the treatment of industrial effluents. Industrial pollution continues to be a potential threat affecting the water. Heavy metals like Cu, Zn, Ni, Pb, Cd, and Cr into water stream is hazardous because the consumption of polluted water causes various health problems. Among these heavy metals, pollution by chromium is of major concern as the metal is used in electroplating, leather tanning, metal finishing, and chromate preparation. Chromium occurs in aqueous systems in trivalent and hexavalent forms. But the latter form is of particular concern due to its greater toxicity. When chromium enters the gastric system, epigastric pain, nausea, vomiting, severe diarrhea, corrosion of skin, respiratory tract and lungs carcinoma are noticed. The discharge limit of chromium from industries is less than 1 mg/l. Chromium is hazardous to health when its limit in potable water exceeds 0.5 mg/L.

Conventional methods for removing Cr (VI) ions from industrial wastewater include reduction[1], reduction followed by chemical precipitation, adsorption on activated carbon[2-4], low cost adsorbent[5], adsorption on the steel wool[6], solvent extraction[7], freeze separation, reverse osmosis[8], and electrolytic methods. This has prompted the use of natural materials as adsorbents in order to develop cheaper alternatives.

Bio-sorption refers to passive metal uptake by different forms of biomass, which may be dead or alive. It is a promising alternative method to treat industrial effluents, mainly because of its low cost[9] and high metal binding capacity. Fly ash from thermal power plant[10], waste slurry from a fertilizer plant[11], and Fe (III)/Cr (III) hydroxide obtained from the petrochemical industry[12], blast furnace flue dust[13], and photo film waste sludge[14], has been examined for the removal of hexavalent chromium.

The adsorption of Cr (VI) on bituminous coal[15], sphagnum peat moss[16], coconut husks and palm pressed fibers[17], sawdust[18], sugarcane bagasse, sugarbeetpulp and maize cob, distillery sludge[19], has been reported.

Azadirachta indica A. Juss *(*Neem*)* leaf powder is tried for the removal of chromium. The presence of niacin, praline, glutamic acid, aspartic acid, glutamine, tyrosine and alanine which contain polar groups like $–NH_2$, –COOH, –OH etc. in neem powder contribute to the negative surface charge. The ingredients contribute an electro negativity of 35.1%. This study aims at evaluation of neem leaf powder for removal of Cr (VI) from aqueous solution.

Material and Methods

Preparation of Adsorbent: The Neem leaves were collected from our college campus. The collected Neem leaves were washed thrice to remove soluble impurities. After the removal of impurities the leaves were dried in an oven until the leaves become crisp. Then it was crushed by using domestic mixture. It was screen analyzed by using a set of sieves in a sieve shaker. Powders of size 0.4 to 0.5 mm were chosen for adsorption studies.

Experimental Procedure: 200 mg/l of chromium solution was prepared. From that solution 100 ml of chromium was treated with 1g of adsorbent in 250 ml beaker for 3 hours by agitating with magnetic stirrer at room temperature. The sample was allowed to settle and then filtered through an ordinary filter paper. The filtrate of the sample was analyzed using Standard titration method of analyses[20] of chromium solution for the final concentration of chromium in aqueous solution. The percentage removal of chromium (VI) was calculated as
% Removal = $((C_o-C_t)/C_o)$ x 100

where, C_o: Initial concentration of chromium, C_t: Chromium concentration at equilibrium after treatment with adsorbent.

The same experimental procedure was repeated for different agitation times. The effect of other parameters such as initial concentration, adsorbent dosage and temperature of chromium in aqueous solution, on percentage removal of chromium (VI) was obtained at the equilibrium agitation time by following the procedure described above. The values of variables studied in this investigation are given in table 1.

Table-1
Experimental conditions investigated

Parameter	Values investigated for neem leaf
Agitation time (min)	30 – 180
Adsorbent dosage (gm)	0.25 – 3
Initial Concentration of Chromium (mg/L)	100 – 350
Temperature, (°C)	29- 50

Results and Discussion

Effect of agitation time: In order to estimate the adsorption capacity of the adsorbent accurately, it was very much important to allow significant time for the experimental solution to attain equilibrium.

As the time increases, chromium getting adsorbed by the adsorbent increases, but at a particular point of time, the solution attains equilibrium. Equilibrium agitation time is defined as the time required for the heavy metal concentration to reach a constant value.

The equilibrium agitation time is determined by plotting the % removal of chromium against agitation time. Results obtained for effect of agitation time are shown in table 2.

Table-2
Effect of agitation time on the removal of chromium

Agitation time (min)	Percentage Removal (%)
30	22.00
60	56.66
90	65.33
120	82.66
150	92.50
180	100.00

As the agitation time is increased the % removal increased and at 180 min of agitation time 100% removal of chromium is observed as shown in figure-1.

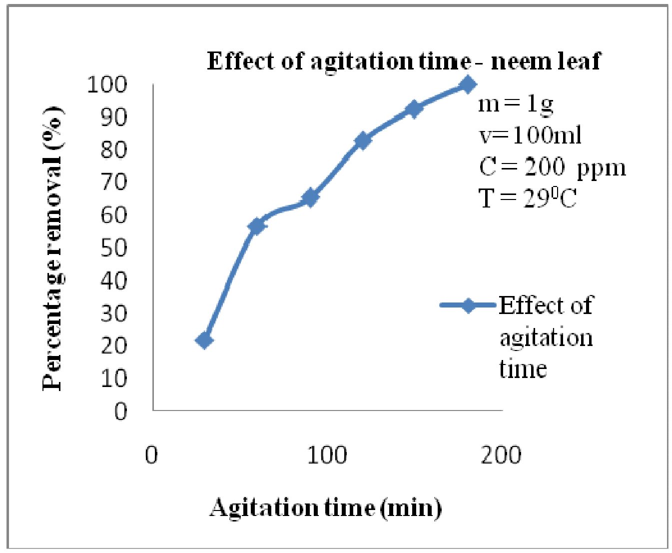

Figure-1
Effect of Agitation Time on the Removal of Chromium using Neem

Effect of Initial Concentration of Chromium: As the initial concentration of chromium increased, the % removal of chromium was decreased for the same agitation time of 180 min.

The % removal decreased from 100% to 75.26 % with the increase in initial chromium concentration from 100 mg/l to 350 mg/l as shown in figure 2.

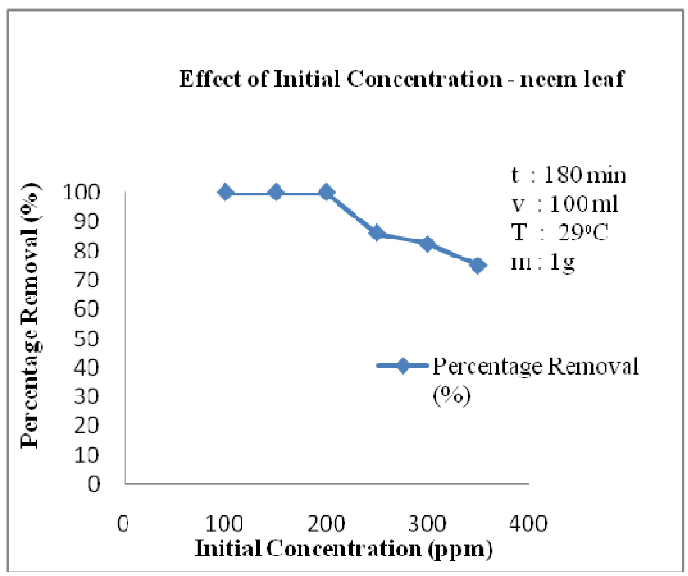

Figure-2
Effect of Initial Concentration on the Removal of Chromium using Neem

The results obtained for the effect of initial concentration of chromium are shown in table 3.

Table-3
Effect of Initial concentration on the removal of chromium

Initial Concentration of Chromium (mg/L)	Percentage Removal (%)
100	100.00
150	100.00
200	100.00
250	86.13
300	82.60
350	75.26

Effect of Adsorbent Dosage: The percentage removal of chromium for the same agitation time of 180 minutes increased with the increase in adsorbent dosage.

The results obtained for the effect of adsorbent dosage are shown in table 4.

Table-4
Effect of Adsorbent dosage on the removal of chromium

Adsorbent Dosage (gm)	Percentage Removal of Chromium (%)
0.25	13.73
0.50	39.33
0.75	65.43
1.00	100.00
1.25	100.00
1.50	100.00
1.75	100.00
2.00	100.00
2.25	100.00
2.50	100.00
2.75	100.00
3.00	100.00

The percentage removal increased from 13.7% to 100% as the amount of neem powder was increased from 0.25gm to 3gm as shown in figure 3.

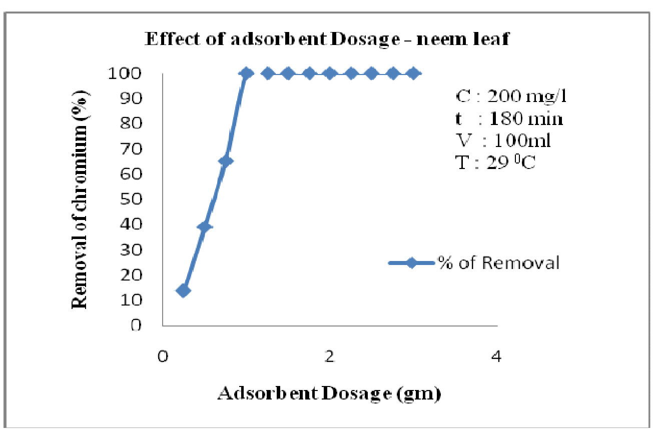

Figure-3
Effect of Adsorbent Dosage on the Removal of Chromium using Neem

Effect of Temperature: The percentage removal of chromium decreased with increase in temperature, substantiating the fact that the adsorption of chromium on neem leaf was physical adsorption.

The results obtained for the effect of temperature are shown in table 5.

Table-5
Effect of Temperature on the Removal of Chromium

Temperature (^{0}C)	Percentage Removal (%)
29	100.0
35	73.9
40	47.9
45	30.6
50	21.9

The percentage removal decreased from 100% to 21.9% as the temperature was increased from 29^{0}C to 50^{0}C as shown in figure 4.

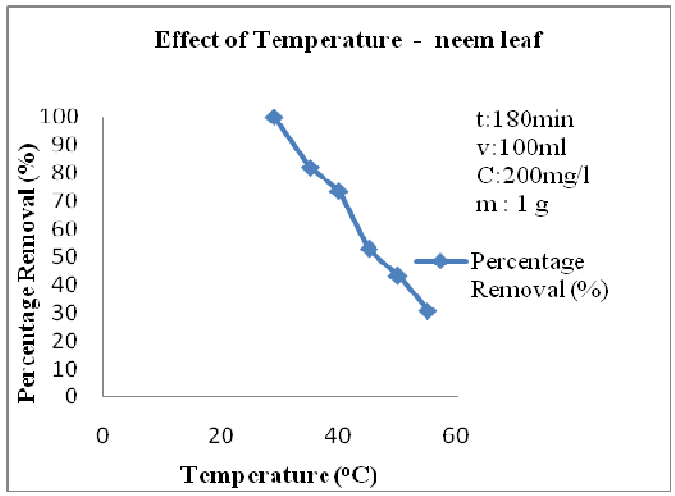

Figure-4
Effect of Temperature on the Removal of Chromium using Neem

Adsorption Isotherm: Freundlich Adsorption Isotherm: The Freundlich adsorption isotherm is tried for the adsorption of Cr (VI) on neem leaf.

The function of Freundlich:
$x/m = k_f Ce^n$

x/m = adsorbed substance per gram neem powder, Ce = equilibrium adsorbate concentration, K_f, n = specific constants.

The above equation can be written as,
$q_e = k_f Ce^n$

The empirical Freundlich relationship does not indicate a finite uptake capacity. This relationship can be reasonably applied to the low or intermediate concentration ranges.

The above equation is linearised as,
$\log q_e = \log k_f + n \log Ce$

The present data, when plotted shows good linearity for Freundlich relationship (correlation coefficient, R^2=0.973) in case of neem. The slope of isotherm (n) also satisfies the condition of 0<n<1 for favorable adsorption**.** The following equation is obtained for neem as shown in figure 5.

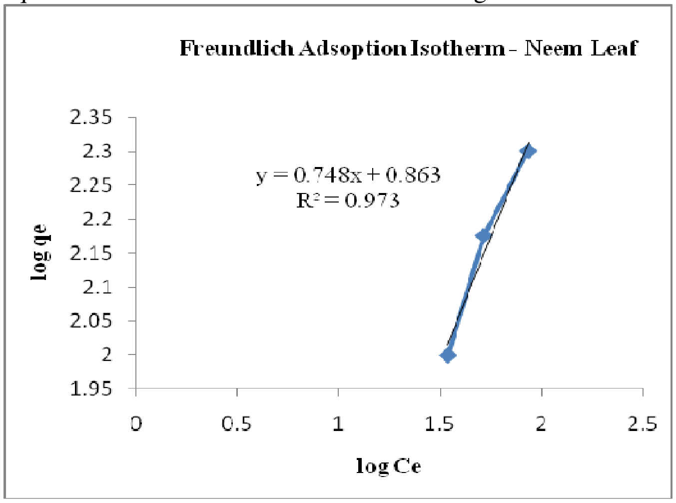

Figure-5
Freundlich Adsorption Isotherm on the Removal of Chromium using Neem

logqe = 0.003 + 0.049 log Ce

Langmuir adsorption isotherm: The Langmuir adsorption isotherm is given by,
$q_e = q_m K_L C_e / 1 + K_L C_e$

which is linearized to,
$C_e / q_e = 1/q_m K_L + C_e / q_m$

where, C_e – The equilibrium liquid phase concentration (mg/l), q_e – The equilibrium solid phase concentration (mg/l), q_m – The maximum adsorption capacity (mg/g), K_L – The Langmuir constant.

This model assumes that monolayer adsorption take place and that all the available adsorption sites are homogeneous. Furthermore, the model does not consider any interactions among the metal ions that are adsorbed with their neighboring sites [21]. All adsorption energy is constant and does not depend on the level of occupation of the adsorbent active sites. The dimensionless co-efficient (R_L) of the model is given by,

$R_L = 1 / (1 + K_L C_o)$

Depending on the values of R_L of isotherm can be linear (R_L=1), un favorable (R_L>1), favorable (0<R_L<1) and irreversible (R_L=0).

The Langmuir adsorption isotherm is given in figure 6.

Temkin Adsorption Isotherm: This model is given by,
$q_e = (RT / b) \ln A C_e$

It's linear expression, $q_e = (RT / b) \ln A + (RT / b) \ln C_e$

Where A is the equilibrium binding constant related to the heat of adsorption. The plot of q_e Vs ln C_e is used to determine the isotherm constant A and b. The basic assumptions of this model are that the heat of adsorption of the metal ions in a layer decreases linearly due to the adsorbent – adsorbate interaction and that the binding energies are uniformly distributed [22].

The Temkin Adsorption Isotherm is given in figure 7.

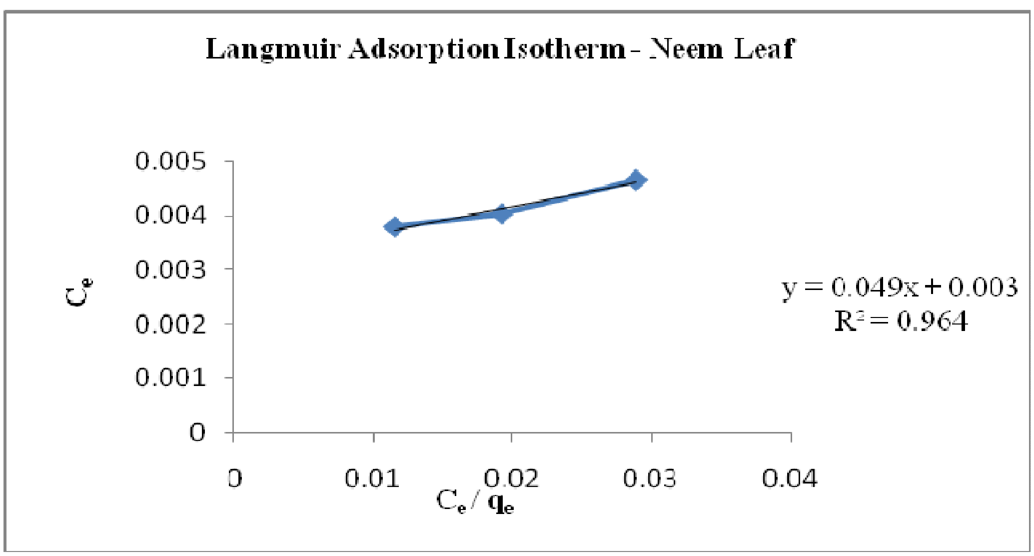

Figure-6
Langmuir Adsorption Isotherm on the Removal of Chromium using Neem

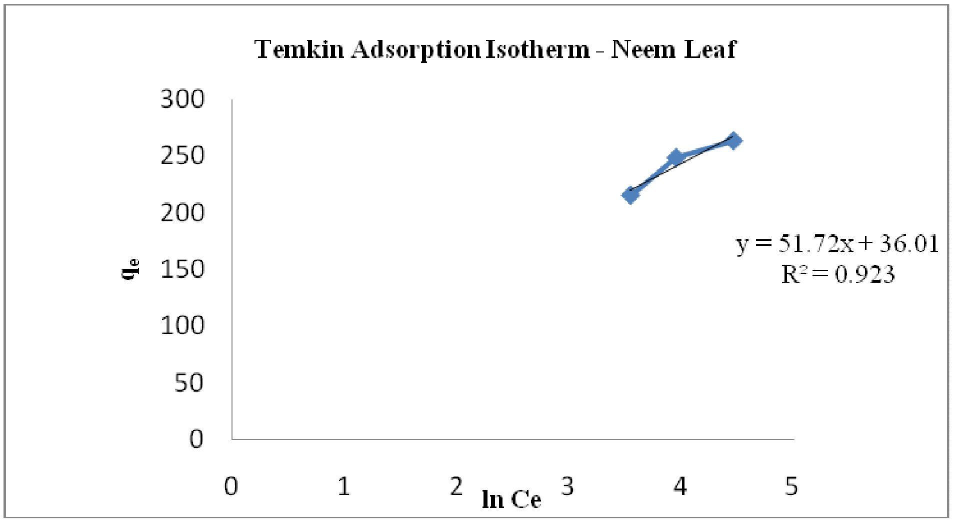

Figure-7
Temkin Adsorption Isotherm on the Removal of Chromium using Neem

Conclusion

The equilibrium agitation time for the adsorption of chromium was determined to be 3 hr. The percentage removal of chromium in aqueous solution increased with increase in the adsorbent dosage and time. The percentage removal of chromium in aqueous solution decreased with increasing initial concentration and temperature. The adsorption isotherm data can be satisfactorily explained by Freundlich Adsorption Isotherm. Higher sorption capacity of this sorbent indicates that neem leaf can be used for the treatment of chromium effluent.

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