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Potential of *Azadirachta indica* Leaves for Removal of Hexavalent Chromium from Aqueous Solution with Reference to Adsorption Isotherm

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Abstract:
Hexavalent chromium is considered as a serious environmental pollutant through industries. The main objective of present studies is to investigate the adsorption behaviour of Cr^{6+} ions on to Azadirachta indica leaves. Main parameters considered are pH, contact time, adsorbent dose and initial hexavalent chromium concentration during removal of Cr^{6+} using natural adsorbent by adsorption technique with Batch mode experiments. Present study shows that the Azadirachta indica leaves were found as an effective biosorbent for the removal of hexavalent chromium from aqueous solution. The optimum percentage removal of hexavalent chromium from aqueous solution obtained is 99.68 %, 99.63%, 98.79%, 98.99% for initial Cr (VI) concentration 50 mg/L ,75 mg/L, 100 mg/L, 125 mg/L at pH 6 , adsorbent dosage 5 g, contact time 4 hrs in jar test apparatus with 160 rpm. The results showed that the maximum adsorption capacity of hexavalent chromium on Azadiracta indica leaves observed is 6.202 (50mg/L), 8.307 (75mg/L), 9.546 (100mg/L) and 12.68 (125mg/L) at pH 6 after 4 hr. The values of coefficient of correlation (R^2) obtained was nearer to 1 for Azadirachta indica leaves are in good agreement with Langmuir, BET , Freundlich and Temkin adsorption isotherm models. For Langmuir and BET adsorption isotherm the adsorption capacity (Q_0) is observed highest 10.194 mg/g and (q_{max}) 5.8754 mg/g for 125 mg/L initial Cr(VI) concentration. Rate of adsorption (b) was also observed highest 7.0469 L/mg and 344.82 L/mg in case of Langmuir and BET adsoption isotherm for 125 mg/L initial Cr(VI) concentration, suggest better applicability of BET isotherm for Azadirachta indica leaves as adsorbent for Cr(VI) from aqueous solution. Azadirachta indica leaves data for all chromium concentration(50mg/L, 75mg/L, 100mg/L and 125mg/L) followed Freundlich model due to value of n obtained is 3.690, 4.115, 3.875 and 4.975 respectively . Freundlich adsorption isotherm is also better applicable for 125 mg/L initial Cr(VI) concentration as the highest value of adsorption capacity (K_f) is obtained 4.518 mg/g and intensity of adsorption (n) is 4.9751 L/mg. The Azadirachta indica leaves shows good agreement with Temkin isotherm for all initial concentration of Cr (VI) = 50 mg/L, 75 mg/L ,100 mg/L, 125 mg/L as the value of rate of adsorption (b) = 1.049 , 1.292, 1.646, 1.580 L/mg respectively. Here also, the value of adsorption capacity (a) was observed highest 3.939 mg/g for initial Cr(VI) concentration of 125 mg/L. The natural water/wastewater/effluent can be treated by adding suitable dose of low-cost, natural adsorbent Azadirachta indica leaf powder and by application of flocculator/other instrument with 160 rpm. The settled residue remained at the bottom can be taken out. The adsorbent and Cr^{6+} can be recovered by giving H_2SO_4 treatment to this sludge. The sludge of Azadirachta indica leaves is biodegradable. By using this cost effective, eco-friendly technique we can get rid of the hazardous sludge disposal problem-generated by chemical treatment of Chromium removal/recovery.

Keywords: *Hexavalent chromium, adsorption capacity, removal %, Azadirachta indica, Langmuir isotherm, BET isotherm, Freundlich isotherm, Temkin isotherm*

1. Introduction

The presence of heavy metals in the environment is of great concern because of their increased discharge, toxicity and threat to human life and environment. The majority of toxic metal pollutants are waste products of industrial and metallurgical processes. Their concentrations have to be reduced to meet over increasing legislative standards. Usually concentration of Cr^{6+} in industrial wastewaters range from 0.5 to 270 mg/L [1].

Major industries discharging Cr^{6+} in their effluents are chrome plating, textile, leather tanning, electro plating, pigment and dyes, metallurgical, metal finishing, photography, the production of dichromate, the production and use of alloys and wood preserving. Chromium exists in two oxidation states as Cr^{6+} and Cr^{3+}. The hexavalent form of chromium is 500 times more toxic than the trivalent [2].

Chromium exist in different oxidation states in nature , of which Cr^{6+} is the most water soluble and easily enter the living cells. As determined by the National Toxicity Program (NTP), the International agency for Research on Cancer (IARC), Cr^{6+} is a human carcinogen [3].

In general, Cr^{6+} is removed from wastewater by various methods such as chemical precipitation, electrochemical reduction, sulphide precipitation, ion-exchange, reverse osmosis, electro dialysis, solvent extraction, evaporation, etc. These methods are, however cost intensive and are unaffordable for large scale treatment of wastewater that is rich in Cr^{6+}[3].

Activated carbon in most cases has been used as an adsorbent for reclamation of municipal and industrial wastewater for almost last few decades [4]. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives instead of commercially activated carbon because it is costly.

Bio-sorption of heavy metals is one of the most promising technologies involved in removal of toxic metals from industrial waste streams and natural waters [5]. A biosorption technology uses biomass- based adsorbents called “biosorbents”. The biosorbent material is comprised of dead biological matter which has active group on its surface for the purpose of metal binding [6].

Chromium enters in body by breathing air, drinking water, or eating food containing chromium or through skin contact with chromium or chromium compounds. People who work in industries that process or use chromium or chromium compounds can be exposed to higher than normal levels of chromium. The maximum levels permitted in wastewater are 2mg/L for hexavalent chromium in wastewater and 0.005mg/L in drinking water[7].

Since most of the heavy metals are non-degradable into non-toxic end products, their concentrations must be reduced to acceptable levels before discharging them into environment. One of the heavy metals that have been a major focus in water and wastewater treatment is chromium and the hexavalent form of it has been considered to be more hazardous due to its carcinogenic properties [8].

Its removal from industrial effluent has been an intense challenge to the research chemist for the last two decades. Different adsorbents namely petiolar felt-sheath of palm, cotton boll , coconut copra meal, coir pith and *Moringa oleifera* (MO) seed powder, clay minerals , coal saw dust, rice husk, human hair, sun flower stalks ,tamarind seeds, coconut shell, waste tea, rice straw, tree leaves, peanut and walnut husks, Eucalyptus bark were used. These materials either used as such or modified by converting it into carbon and tried for the removal of heavy metals from wastewater.

Present study looks into a specific process, for the removal of toxic element (hexavalent chromium) with the help of low cost adsorbent developed from *Azadirachta indica* leaves. *Azadirachta indica* (neem) is most widely cultivated tree in India. The neem tree belongs to genus Azadirachta and meliaceae. Its seeds and leaves have been in use since ancient times to treat a number of human ailments and also as a household pesticide. The tree is also known as an air purifier [9]. Compounds like niacin, proline, salanin, azadirachtin, etc. are present in neem leaves which contain polar groups like $–NH_2$, -COOH, -OH etc. which contribute negative surface charge for the binding of hexavalent chromium. These ingredients contribute an electro negativity of 35.1% [10, 11].

2. Objective of the Study

The main objective of present studies is to investigate the adsorption behaviour of Cr^{6+} ions on to *Azadirachta indica* leaves. Main parameters considered are pH, contact time, adsorbent dose and initial hexavalent chromium concentration during removal of Cr^{6+} using natural adsorbent by adsorption technique with Batch mode experiments. (Table i)

3. Materials and Methods

Mature leaves of *Azadirachta indica* were collected from the available tree in my village, Taliyara, Amalsad, Gujarat, India.

3.1. Preparation of adsorbents

Azadirachta indica leaves were collected and wash with water to remove dust and water soluble impurities and were air dried in shadow until become crisp. After become crisp leaves were grinded in electrical grinder. After it was converted into powder form sieved to 0.250 mm size. The resulting neem leaf powder fractions were preserved in air tight glass bottles.

3.2. Reagents

Analytical reagent grade $K_2Cr_2O_7$, 1N NaOH, 1N H_2SO_4, Diphenyl-carbazide were used for experimental study.

3.3. Adsorbate solution

Hexavalent chromium ion solution is made by dissolving 5.462g of 99% $K_2Cr_2O_7$ in 1000 ml double distilled water to prepare 1000 mg/L of chromium stock solution. From this stock solution different standards of hexavalent chromium were prepared. (Table ii).

Sr. no.	**Parameter**	**Values investigated**
1.	Agitation time, t, h	1,2,3,4,5
2.	Adsorbent size, dp, 250µ	250
3.	Adsorbent dosage, w, g	1,2,3,4,5
4.	Initial concentration of Cr(VI) in Aqueous solution, Co, mg/L	50,75,100,125
5.	Volume of the aqueous solution, v, ml	200
6.	pH of the aqueous solution	2,4,6,8

Table 1: List of parameters during batch experiments

Concentration of chromium	**Volume of stock solution**	**Volume of distilled water**
50ppm	50ml	1000ml
75ppm	75ml	1000ml
100ppm	100ml	1000ml
125ppm	125ml	1000ml

Table 2: Preparation of adsorbate solution having different concentration

3.4. Experimental procedure

Adsorption studies at room temperature at 160 rpm using standard methods were carried out in batch experiments.

3.5. Experimental set up to study effects of pH

Take 200 ml of the hexavalent chromium solution of 75 mg/L concentration in 500 ml beakers. Prepare such 5 sets. The pH of each chromium solution in each beakers were varied as 2, 4, 6, 8 by adding the required volume of 1N H_2SO_4 and 1N NaOH. Now add 1 g of the leaves adsorbent in all beakers and keep the system run for 60 minutes in jar test apparatus at 160 rpm. Take about 20 ml of solution from beaker and these metal bearing suspensions were allowed to settle. Then suspension was filtered using what man 42 filter paper. Then filtrate was collected to determine the amount of hexavalent chromium by Systronic make, model no. 104 spectrophotometer. Same experiments were performed for various dosage of adsorbent.

3.6. Experimental set up for the effect of agitation time, initial concentration of Cr^{6+} and adsorbent dosage.

Take 200 ml of the hexavalent chromium solution of different initial concentration (50mg/L, 75mg/L, 100mg/L, 125mg/L) in 500ml of beakers. Prepare different sets for different initial concentration. The pH of solution in each beaker were kept 6 by adding 1N H_2SO_4 and 1N NaOH. Now add 1,2,3,4 and 5 g of the adsorbent respectively in each beaker and keep the system run for different agitation time i.e. 1,2,3,4,5 hours respectively at 160 rpm. Take 20 ml suspension from beaker after completion of agitation time and allowed to settle. The suspension is filtered through what man 42 filter paper.

3.7. Experimental set up to determine the hexavalent chromium by using spectrophotometer

The amount of hexavalent chromium was determined in collected filtrate by using Systronic make, model no. 104 spectrophotometer. This method is known as Diphenyl carbohydrazide method and its range is 0.01mg/L to 0.07 mg/L Cr^{6+}.

Accuracy was checked by standard addition method. Hexavalent chromium is determined by 1, 5 Diphenylcarbohydrazide method using diphenylcarbazide solution. This reagent reacts to give a purple colour when hexavalent chromium is present. Test results are measured at 540 nm.

Prepare a series of standards ranging from 0.01 to 0.1 mg of chromium by taking the 2,4,6,8,10 ml of standard chromium working solution in 100 ml S.M.F. Add 2.5 ml of dilute H_2SO_4 and make it up to 100 ml. Add 2 ml of diphenylcarbazide solution, mix and allow to stand for 10 minutes for full colour development. Read the absorbance at 540 nm and draw a calibration curve.
After that take 7 ml of sample and do same as above for measuring unknown amount of Cr (VI).

3.8. Batch isotherm studies

Isotherm experiments were conducted to investigate the relationship between the solid phase concentration of an adsorbate and the solution phase concentration of adsorbent at an equilibrium condition.
The removal percentage (R %) of chromium was calculated for each run by following equation:

$R (\%) = [(C_i - C_e)/C_i] \times 100$ (1)

Where, C_i and C_e are the initial and final concentration of hexavalent chromium in the solution.
The adsorption capacity of the adsorbent for each concentration of hexavalent chromium ions at equilibrium were calculated using following equation.

$q_e\ (mg/g) = [(C_i - C_e)/M] \times V$ (2)

Where, C_i and C_e were the initial and final concentration of hexavalent chromium (mg/L) in the test solution respectively. V is the volume of solution (L) and M is the mass of adsorbent (g) used [12].

3.9. Adsorption isotherms

In the present study various adsorption isotherm models have been used to study the adsorption capacity and equilibrium coefficients for adsorption. Four commonly used isotherms (Langmuir, BET, Freundlich and Temkin isotherm) were studied to observe the adsorption pattern.

- **The Langmuir adsorption isotherm** has the simplest form and shows reasonable agreements with a large number of experimental isotherms. Therefore, the Langmuir adsorption model is probably the most useful one among all isotherms describing adsorption, and often serves as a basis for more detailed developments [13].

Langmuir's equation is a commonly used for isotherm modelling, which involves two parameter, expressed as follows. Langmuir isotherm equation is derived from simple mass kinetics, assuming chemisorptions. This model is based on two assumptions that the forces of interaction between sorbed molecules are negligible and once a molecule occupies a site no further sorption will take place. Also these equations can reduce to Henry's law at lower initial concentrations. Alternatively at higher concentrations, it predicts a monolayer sorption capacity [14]. It assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The linear form of Langmuir adsorption isotherm is represented as:

$C_e/q_e = [1/Q_0 b + 1/Q_0 \times C_e]$ (3)

Where, C_e is the equilibrium concentration of adsorbate (mg/L) and qe is the amount of Cr^{6+} adsorbed per gram at equilibrium (mg/g), Q_0 (mg/g) and b (L/mg) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The values of Q_0 and b were calculated from the slop and intercept of the Langmuir plot of C_e versus C_e/q_e [12].

- **Freundlich isotherm** assumes that the uptake of metal ions occurs on a heterogeneous surface by multilayer adsorption. The linearized Freundlich model isotherm was applied for adsorption of Cr^{6+} and is expressed as:

$\text{Log}_{10}\ q_e = \log_{10}(K_f) + (1/n) \log_{10}(C_e)$ (4)

Where, q_e is the amount of Cr^{6+} adsorbed at equilibrium (mg/g), and C_e is the equilibrium concentration of chromium in solution (mg/L). K_f and n are the constants incorporating all factors affecting the adsorption process [12]. The values of K_f and n were calculated from the intercept and slope of the Freundlich plot of log C_e versus log q_e.
Temkin isotherm model is given by the following equation:

$X = a + b \ln C$ (5)

Where, C is the equilibrium concentration of solution (mg/L), X is the amount of metal adsorbed per gram weight of adsorbent (mg/g), a and b are constants related to adsorption capacity and intensity of adsorption and related to the intercept and slope of the plots of ln C versus X. [15].

- **BET isotherm** was developed by Brunauer, Emmett and Teller as an extension of Langmuir isotherm, which assumes that first layer of molecules adhere to the surface with energy comparable to heat of adsorption for monolayer sorption and subsequent layers have equal energies. Equation in its linearized form is expressed as:

$C_f/(C_f - C_s)\, q = 1/Bq_{max} + (B-1/Bq_{max})(C_f/C_s)$ (6)

Where, C_s is the saturation concentration (mg/L) of the solute, C_f is solute equilibrium concentration. B and q_{max} are two constants and can be evaluated from the intercept and slope [16].

4. Results

4.1. Effect of pH

pH is an important factor controlling the process of adsorption as it affects the surface charge of the adsorbents, the degree of ionization and the species of adsorbate. Here in (Fig.1) it shows that, % removal of Cr^{6+} increases from 29.15 to 37.13%, 55.32 to 67.27%, 70.35 to 83.94%, 83.29% to 93.2% and 88.67 % to 98.6% for 1 g,2 g, 3 g, 4 g and 5 g of adsorbate respectively in solution containing 75 mg/L chromium concentration up to pH 6. After pH 6, % removal is decreased with increasing pH. Maximum percentage removal of hexavalent chromium is obtained at pH 6. At low pH, hydrogen ions compete with chromium ions for appropriate sites on the adsorbent. As pH approaches to 7, the competition of hydrogen ions becomes negligible and more chromium ions are bound to the adsorbent [9].

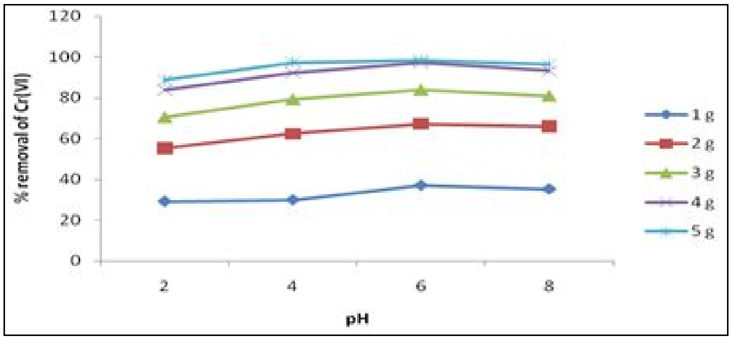


Figure 1: Effect of pH on % removal of Cr (VI) from 75 mg/L solution By A. indica leaves at 1 hour agitation time

4.2. Effect of adsorbent dosage

The effect of adsorbent dose on the adsorption of hexavalent chromium by *Azadirachta indica* leaves are presented in(Fig.2). It is evident from experimental data that the rate of adsorbent increases from 50.35 to 98.59% (1hr), 58.36 to 99.57%(2 hr), 60.01 to 99.57%(3hr), 62.01 to 99.67%(4 hr) and 61.89 to 99.68%(5 hr) for 50mg/L initial Cr(VI) concentration,37.13 to 98.29%(1 hr), 45.52 to 98.98%(2 hr), 50.78 to 99.02%(3 hr), 55.38 to 99.23%(4 hr) and 55.89 to 99.63%(5 hr) for 75 mg/L initial Cr(VI) concentration, 32.89 to 97.42%(1 hr), 45.09 to 98.85(2 hr), 49.73 to 98.93%(3 hr), 52.27 to 99.13%(4 hr) and 55.43 to 99.23%(5 hr) for 100mg/L initial Cr(VI) concentration and 25.00 to 95.77%(1 hr), 42.03 to 98.66%(2 hr), 49.12 to 98.82%(3 hr), 51.53 to 98.93%(4 hr) and 58.23 to 98.99%(5 hr) for 125mg/L initial Cr(VI) concentration with increase in adsorbent dosage from 1 to 5 gm. Cr(VI) removal efficiency was increased with increase in adsorbent dose, since contact surface of adsorbent particles increased and it would be more probable for $HCrO_4^-$ and $Cr_2O_7^{-2}$ ions to be adsorbed on adsorption sites and thus adsorption efficiency was increased. Higher is the dose of adsorbent in the solution, greater is the availability of exchangeble sites for metal ions and greater is the surface area [17].

The principle force for metal ion adsorption is the electrostatic interaction that is, attraction between adsorbent and adsorbate. The greater the interaction higher is the adsorption of heavy metal. Neem leaf powder contains 35.1 % electronegative components [10,11]. As the concentration of Cr(VI) ion was constant , the dose of adsorbent increases the surface area for adsorption. Since the adsorbent particle size is almost constant, the surface area was directly proportional to the dose of the adsorbent in the system [18].

The results shows that maximum adsorption capacity of Hexavalent chromium on *Azadirachta indica* leaves were obtained 6.202 mg/g for 50mg/L, 8.307mg/g for 75mg/L, 9.547mg/g for 100mg/L and 12.68mg/g for 125mg/L initial chromium concentration at pH 6 and contact time 4 hour. As adsorbent dosage increases adsorbent capacity (mg/g) is decreased, because more surface area are provided for attachments of ions.

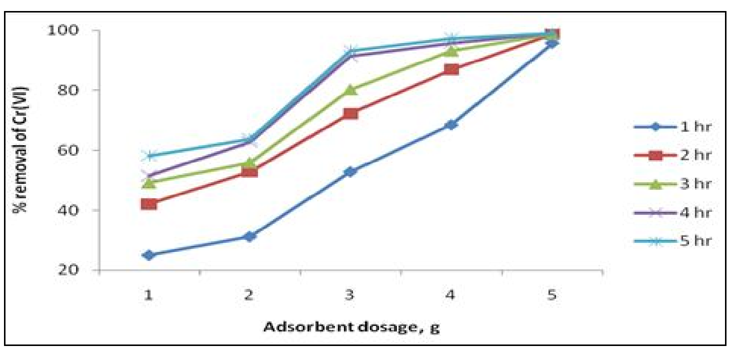


Figure 2: Effect of adsorbent dosage of A.indica leaves on % removal of Cr(VI) from 125mg/L solution at pH 6

4.3. Effect of Agitation time

Agitation time or contact time is one of the effective factors in batch adsorption process. It is evident that time has significant influence on the adsorption of Cr (VI) in this stage. As shown in (Fig.3) for all experimental condition the amount of adsorption of Cr(VI) was increased with increase in all NLP(neem leaf powder) dosages and all conentration. It has been observed that adsorption rate increased from 98.59% to 99.68%(50mg/L), 98.29% to 99.63%(75mg/L), 97.42% to 98.79%(100mg/L) and 95.77% to 98.99%(125mg/L) respectively for initial Cr(VI) concentration with increase in agitation time from 1-5 hrs, at 5 g dosage and pH 6. But there is no much difference in % removal and adsorption capacity between 4-5 hr and all isotherms best fit for 4 hour so 4 hour contact time is considered as optimum agitation time for hexavalent chromium removal from aqueous solution.

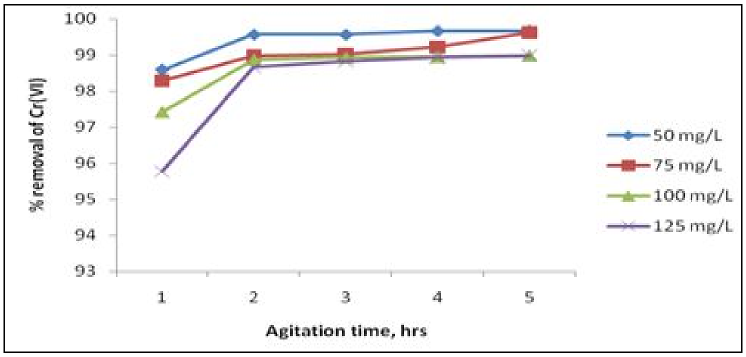


Figure 3: Effect of agitation time on % removal of Cr(VI) from different initial Cr(VI) in aqueous solution at 5 g dosage, pH 6.

4.4. Effect of initial Cr(VI) concentration

The effect of initial concentration of chromium is shown in (Fig.4). Results shows that % removal of chromium was decreased from 62.01 to 51.53%(1 g), 94.89 to 62.79%(2 g), 98.78 to 91.39%(3 g), 98.88 to 95.82%(4 g) and 99.03 to 98.01%(5 g) with adsorbent dosage respectively as initial concentration increase from 50 mg/L to 125 mg/L for 4 hr time period. The trend is same for all experimented agitation time.

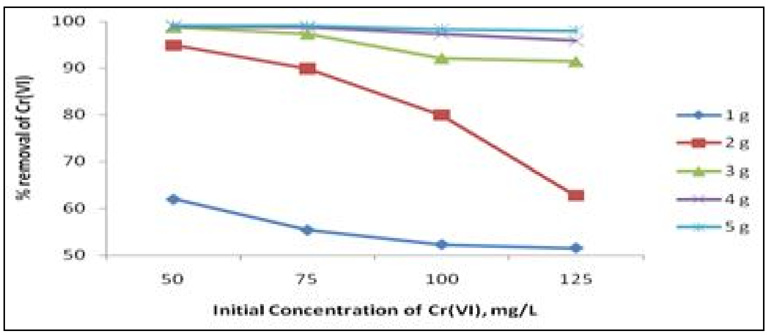


Figure 4: Effect of initial Cr(VI) concentration of aqueous solution on % removal of Cr(VI) at 4 hour time, pH 6 and different dosage

4.5. Comparison of adsorption capacity of Azadirachta indica with other adsorbent

In the present study, *Azadirachta indica* has been compared with other adsorbents based on their maximum adsorption capacity for hexavalent chromium removal from aqueous solution (Table iii).

Adsorbents	**Adsorp-tion capacity (mg/g)**	**pH**	**Co (mg/L)**	**Reference no.**
Raw rice bran	0.07	2	5	[19]
EHDDMA-zeolite	0.42	-	-	[20]
CETYL-amended zeolite	0.65	-	-	[20]
Activated rice husk carbon	0.8	2	10	[21]
Wheat bran	0.942	3	5	[22]
Walnut shell	1.33	-	-	[23]
Exhausted coffee	1.42	-	-	[23]
Nut shell	1.47	-	-	[23]
Waste tea	1.55	-	-	[23]
Activated alumina	1.6	4	10	[21]
Modified oak saw dust	1.7	3	-	[24]
Saw dust	4.44	-	-	[25]
Copper coated moss	7.1	-	-	[26]
Saw dust	10.1	-	-	[27]
Modified wool	17	-	-	[28]
Irish sphagnum moss peat	43.9	-	-	[16]

Orange peel(white inner)	125	-	-	[16]
Senna leaves	250	-	-	[16]
Orange peel(outer skin)	275	-	-	[16]
Moringa oliefera leaves	2.375	2	25	[29]
Moringa oliefere seeds	2.489	2	25	[29]
Moringa oliefera bark	2.483	2	25	[29]
Neem leaves	6.202	6	50	Present study
Neem leaves	8.307	6	75	Present study
Neem leaves	9.546	6	100	Present study
Neem leaves	12.68	6	125	Present study

Table 3: Comparison of adsorption capacities of Cr^{6+} with other adsorbents

4.6. Adsorption isotherm

The best fit of Langmuir, Freundlich, Temkin and BET isotherms for studied adsorbent for various concentrations are shown in (Fig.5-9). Results of modelling of the isotherm of Cr^{6+} adsorption from aqueous solution by *Azadirachta indica* leaves according to Langmuir, Frueundlich, Temkin and BET models are summarized in (Tables iv and v). The values of coefficient of correlation (R^2) for *Azadirachta indica* leaves are in good agreement with Langmuir, Freundlich, Temkin and BET isotherms. The value of R^2 found were nearly equal to 1 indicates favourable adsorption. Compounds like niacin, proline, salanin, azadirachtin, etc. are present in neem leaves which contain polar groups like $-NH_2$, -COOH, -OH etc. which contribute negative surface charge for the binding of hexavalent chromium. These ingredients contribute an electro negativity of 35.1% [10, 11].

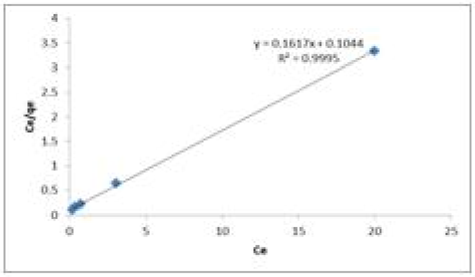
For Langmuir and BET adsorption isotherm the adsorption capacity (Q_0) is observed highest 10.194 mg/g and (q_{max}) 5.8754 mg/g for 125 mg/L initial Cr(VI) concentration. Rate of adsorption (b) was also observed highest 7.0469 L/mg and 344.82 L/mg in case of Langmuir and BET adsoption isotherm for 125 mg/L initial Cr(VI) concentration, suggest better applicability of BET isotherm. It indicates first layer of molecules adhere to the surface with energy comparable to heat of adsorption for monolayer sorption and subsequent layers have equal energies. Here we can say that BET isotherm as an extension of the Langmuir isotherm to account for multilayer adsorption and Langmuir isotherm applies to each layer [30].

For Freundlich isotherm the larger the K_f and n values, the higer is the adsorption capacity. The magnitude of the exponent n gives an indication of favourability of the adsorption. [29] *Azadirachta indica* leaves data for all chromium concentration(50mg/L, 75mg/L, 100mg/L and 125mg/L) followed Freundlich model due to value of n obtained 3.690, 4.115, 3.875 and 4.975 respectively . The value of n in the range of 2-10 represent good, 1-2 moderately difficult and less than 1 poor adsorption characteristics [31]. Freundlich adsorption isotherm is also better applicable for 125 mg/L initial Cr(VI) concentration as the highest value obtained of adsorption capacity (K_f) 4.518 mg/g and intensity of adsorption (n) 4.9751 L/mg.

The *Azadirachta indica* leaves shows good agreement with Temkin isotherm for all initial concentration of Cr (VI) = 50 mg/L, 75 mg/L ,100 mg/L, 125 mg/L as the value of rate of adsorption (b) = 1.049 , 1.292, 1.646, 1.580 L/mg respectively. Here also, the value of adsorption capacity (a) was observed highest 3.939 mg/g for initial Cr(VI) concentration of 125 mg/L.The *Moringa oleifera* leaves also followed Temkin isotherm for chromium removal from aqueous solution as the value of b is 1.868 [15] and value of b is 3.153[29]. The Temkin isotherms fit the present data because it takes into account for the occupation of the more energetic adsorption sites at first. For natural unmodified materials such as the studied one it is highly probable that their adsorption sites are energetically nonequivalent [32].

Initial concentration of Cr(VI)	Langmuir isotherm			BET isotherm		
	Q_0 (mg/g)	b (L/mg)	R^2	q_{max}	B	R^2
50 mg/L	6.211	0.648	0.9995	3.8789	322.26	0.998
75 mg/L	7.880	1.849	0.9959	4.6253	-270.27	0.996
100 mg/L	10.627	6.939	0.8934	5.0968	-131.57	0.989
125 mg/L	10.194	7.0469	0.8107	5.8754	344.82	0.956

Table 4: Langmuir and BET model constants for Azadirachta indica leaves for different concentration



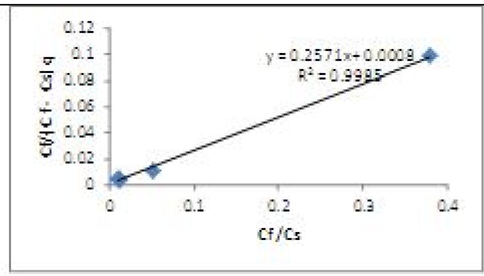
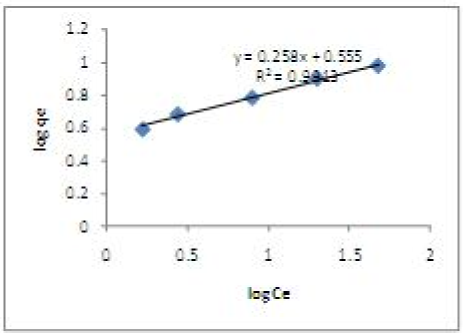


Figure 5: Langmuir plot for Cr (VI) adsorption isotherm for 50 mg/L
Figure 6: BET plot for Cr(VI) adsorption isotherm for 50 mg/L

Initial concentration of Cr(VI)	Freundlich isotherm			Temkin isotherm		
	K_f (mg/g)	n (L/mg)	R^2	a(mg/g)	b (L/mg)	R^2
50 mg/L	3.062	3.690	0.8328	3.248	1.049	0.9415
75 mg/L	3.801	4.115	0.9566	3.912	1.292	0.9931
100 mg/L	3.589	3.875	0.9913	3.053	1.646	0.9931
125 mg/L	4.518	4.975	0.8073	3.939	1.580	0.7059

Table 5: Freundlich and Temkin model constants for Azadirachta indica leaves for different concentration



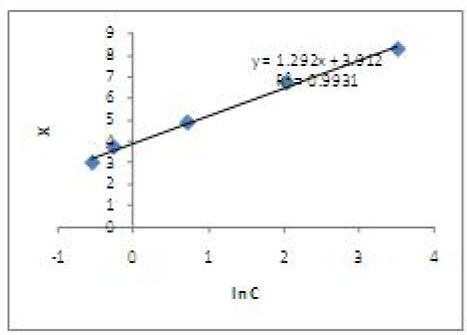


Figure 7: Freundlich plot for Cr(VI) adsorption isotherm for 100 mg/L
Figure 8: Temkin plot for Cr(VI) adsorption isotherm for 75 mg/L

5. Conclusion

Present study shows that the *Azadirachta indica* leaves were found as an effective biosorbent for the removal of hexavalent chromium from aqueous solution. The optimum percentage removal of hexavalent chromium from aqueous solution is 99.68 %, 99.63%, 98.79%, 98.99% for initial Cr (VI) concentration 50 mg/L ,75 mg/L, 100 mg/L, 125 mg/L at pH 6 , adsorbent dosage 5 g, contact time 4 hrs,.

The results showed that the maximum adsorbent capacity of hexavalent chromium on *Azadiracta indica* leaves were observed 6.202 (50mg/L), 8.307 (75mg/L), 9.546 (100mg/L) and 12.68 (125mg/L) at pH 6 after 4 hr. The values of coefficient of correlation (R^2) obtained was nearer to 1 for *Azadirachta indica* leaves obtained are good in agreement with Langmuir, BET , Freundlich and Temkin isotherms.

For Langmuir and BET adsorption isotherm the adsorption capacity (Q_0) is observed highest 10.194 mg/g and (Q_{max}) 5.8754 mg/g for 125 mg/L initial Cr(VI) concentration. Rate of adsorption (b) was also observed highest 7.0469 L/mg and 344.82 L/mg in case of Langmuir and BET adsoption isotherm for 125 mg/L initial Cr(VI) concentration, suggest better applicability of BET isotherm.

Azadirachta indica leaves data for all chromium concentration(50mg/L, 75mg/L, 100mg/L and 125mg/L) followed Freundlich model due to value of n obtained 3.690, 4.115, 3.875 and 4.975 respectively . Freundlich adsorption isotherm is also better applicable for 125 mg/L initial Cr(VI) concentration as the highest value obtained of adsorption capacity (K_f) 4.518 mg/g and intensity of adsorption (n) 4.9751 L/mg.

The *Azadirachta indica* leaves shows good agreement with Temkin isotherm for all initial concentration of Cr (VI) = 50 mg/L, 75 mg/L ,100 mg/L, 125 mg/L as the value of rate of adsorption (b) = 1.049 , 1.292, 1.646, 1.580 L/mg respectively. Here also, the value of adsorption capacity (a) was observed highest 3.939 mg/g for initial Cr(VI) concentration of 125 mg/L.

6. Recommendation

The data may be useful in designing and fabrication of an economic treatment plant for the removal od Cr^{6+} ions from wastewaters as shown in (Fig.9). This technology is suitable for chrome recovery section and composite wastewater of tannery industries [23]. Petrolium refinery – mining mud water effluent [24] .

The effluent of any ETP/CETP in which concentration of hexavalent chromium is up to 125mg/L can be treated by this technology. The effluent can be treated by adding suitable dose of adsorbent of *Azadirachta indica* leaves and by application of flocculator/ or in CSTR(contineous stirred tank reactor) with 160 rpm. Maintaine pH 6 for 4 hour contact time for maximum removal up to 99% . The settled residue/ sludge remained at the bottom of clarifier can be taken out by rotatinng scraper with pump. The adsorbent and Cr(VI) can be recovered by giving H_2SO_4 treatment to the sludge. This adsorbent can recycled or sent for biodegradation. The sludge of *Azadirachta indica* leaves is biodegradable. By using this eco-friendly technique we can get rid of the hazardous sludge disposal problem- generated by chemical treatment for chromium removal/ recovery.

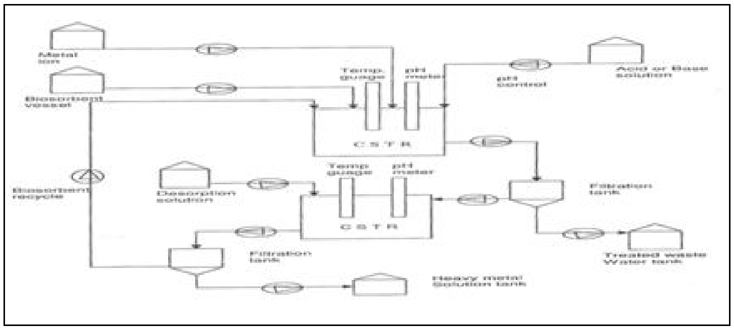


Figure 9: Recommended flow diagram of treatment plant for removal of Hexavalent chromium(heavy metal) from wastewater

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