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Removal of Hexavalent Chromium from aqueous solution using an eco-friendly activated carbon adsorbent

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ABSTRACT

The present study is focused on removal of hexavalent chromium from aqueous solution using an eco-friendly adsorbent, activated carbon prepared from the pods of Delonix regia. The effect of optimum dosage, pH and initial concentration of adsorbate on the effective removal of hexavalent chromium has been studied. The results of the study show the adsorption of Cr(VI) to be concentration and pH dependent. The maximum removal of Cr(VI) was observed at pH 2. Removal of Cr(VI) increased from 70.58% to ~100% with increasing adsorbent dosage from 50 to 200 mg. The adsorption process was found to obey Langmuir adsorption isotherm and Freundlich adsorption isotherm. Hence the use of the low cost carbon prepared is of practical importance and is expected to be economical.

Keywords: Activated carbon, adsorption, hexavalent chromium, adsorbent, diphenyl carbazide method.

INTRODUCTION

The contamination of water by toxic heavy metals is a world wide problem. Heavy metal solutions are widely used in industrial activities such as metal finishing, electroplating, painting, dyeing, photography, surface treatment and printed circuit board manufacture[1]. One of the heavy metals that has been a major focus in water and waste water treatment is chromium and the hexavalent form of it has been considered to be more hazardous due to its carcinogenic properties [2]. Chromium has been considered as one of the toxic pollutants and because of its carcinogenic characteristics, it has become a serious health problem. Extensive use of chromium results in large quantities of chromium containing effluents which need sufficient treatments.

There are several methods of effluent treatment. Primary treatment involves sedimentation, equalization, neutralization etc.[3]. In secondary treatment, the dissolved and colloidal organic matter present in wastewater is removed by biological processes involving bacteria and microorganisms. The secondary treatment involves aerated lagoons, trickling filters, activated sludge process, oxidation ditch, oxidation pond, anaerobic digestion etc.[4]. Tertiary treatment aims at improving the waste water quality to the point at which it can be used. Other commonly employed treatment methods include: Ion Exchange[5,6], Electrodialysis [7], Evaporation [8], Chemical Precipitation[9], Reverse Osmosis , Electro deposition, Chemical Reduction, Adsorption etc.

Activated carbon has been found to be an effective adsorbent though it suffers from the disadvantage of possessing high cost. Several adsorbents like discarded automotive tyres, human hair, starch, xanthate and oxides of manganese etc.have been successfully tried. They are not easily and widely available, therefore agricultural products and byproducts like crushed coconut shell, saw dust, peat mass have been employed, as these adsorbents have a distinct advantage over activated carbon because of their low cost and easy availability [10]. The present study is focused on removal of hexavalent chromium form aqueous solution using an eco-friendly adsorbent- activated carbon prepared from the pods of *Delonix regia*. The effect of optimum dosage, pH and initial concentration of hexavalent chromium on the effective removal of hexavalent chromium has been studied.

MATERIALS AND METHODS

Plant profile

COMMON NAME	GULMOHUR
KINGDOM	PLANTAE
DIVISION	PHANEROGAMS
CLASS	DICOTYLEDONEAE
SUBCLASS	POLYPETALAE
SERIES	CALYCIFLORAE
ORDER	ROSALES
FAMILY	LEGUMINOSAE
SUB-FAMILY	CAESALPINEACEAE
GENUS	DELONIX
SPECIES	REGIA

Preparation of activated carbon

Pods of *Delonix regia* were collected from Avinashilingam Deemed University for Women campus, Coimbatore. The pods were cut into small pieces, dried in sunlight for 5 days and further dried in a hot air oven at 60°C for 24 hours. The completely dried material was powdered well and chemically activated by treating with concentrated sulphuric acid with constant stirring and kept for 24 hours. The carbonized material obtained was washed with water several times to remove excess acid and dried at 105-110°C for 24 hours. The adsorbent thus obtained was ground well and sieved through a 250 mesh and kept in an airtight container for further use.

Reagents

Preparation of Cr(VI) metal ion solution

All chemicals used were of analytical grade. In order to assess the performance of the low-cost adsorbent prepared and to avoid interference by other contaminants in waste water, the experiments were conducted with aqueous solution of Cr(VI) prepared by dissolving 283mg of potassium dichromate in one liter of double distilled water.

Preparation of complexing reagent

The complexing reagent was prepared by dissolving 250mg of diphenyl carbazide in 50ml of acetone. The reagent (0.5% in acetone) was kept in an amber bottle and used for the study.

Equipments

- ◆ Elico pH meter was used to measure pH.
- ◆ Elico CL157 colorimeter was used for spectrophotometric work.
- ◆ Genuine Equipment Manufacturers mechanical shaker was used for the shaking of solution containing adsorbent and adsorbate.

Effect of variation of initial concentration of Cr(VI) solution on the adsorption of Cr(VI)

100ml of Cr(VI) standard solutions containing 0.06, 0.08, 0.1 and 0.12 $\mu\text{g}/100\text{ml}$ of Cr(VI) was added with 100mg of the adsorbent taken in Pyrex bottles and shaken in an electrical horizontal bench shaker for various time intervals (10 to 180 minutes) at room temperature and at constant $\text{pH}4\pm0.02$. The solutions were filtered and Cr(VI) concentrations in the filtrate were estimated colorimetrically by diphenyl carbazide method [11].

Effect of variation of pH on the adsorption of Cr(VI)

The optimum pH for the maximum Cr(VI) adsorption was found by varying the pH from 2.0 to 4.0. The pH of the solution was adjusted using dilute sulphuric acid and it was measured using Elico pH meter. 100ml samples containing 0.12mg of Cr(VI) were contacted with 100mg of adsorbent by altering the pH of the solution. These solutions were shaken for various time intervals (10 to 180 minutes) in an electrical horizontal bench shaker. The solutions were filtered and analyzed colorimetrically to find the adsorption potential of Cr(VI) from aqueous solution for the variation of pH from 2 to 4.

Effect of variation of adsorbent dosage on the adsorption of Cr(VI)

100ml of the Cr(VI) standard solutions containing 0.12mg/l of Cr(VI) was taken in Pyrex bottles containing 50, 100, 150 and 200mg of the adsorbent at $\text{pH}2\pm0.02$. The system was equilibrated thoroughly on a horizontal bench shaker at room temperature for 180 minutes. Then the solutions were filtered and analyzed colorimetrically, to find the amount of Cr(VI) adsorbed.

RESULTS AND DISCUSSION

Effect of variation of initial concentration of Cr(VI) solution on adsorption of Cr(VI) from aqueous solution

The adsorbate concentrations were varied from 0.06 to 0.12 mg/l and batch studies were performed to optimize the initial concentration of the adsorbate. The percentage removal of Cr(VI) with variation in initial concentration of Cr(VI) solution is given in table - 1. The increase

in percentage removal Cr(VI) when the adsorbate concentration was varied from 0.12 to 0.06 mg/l may be probably due to the fact that for a fixed adsorbent dose, the total available adsorption sites are limited thereby adsorbing almost the same amount of Cr(VI) causing a decrease in percentage removal of Cr(VI) corresponding to an increased initial adsorbate concentration.

Table – 1: Adsorption potential of Cr(VI) with variation of initial concentration of Cr(Vi) solution
Conditions

Adsorbent dosage :100mg ; pH :~ 4.00; Temperature: 32°C; Contact time: 10-180 minutes

Time in minutes	Removal of Cr(VI) in percentage			
	0.06 mg/l	0.08mg/l	0.1mg/l	0.12mg/l
10	25.72	15.25	15	11.75
20	28.5	21.75	17.5	13.25
30	31.43	28.25	22.81	14.67
40	34.33	30.38	24.6	16.17
50	37.17	32.35	26.3	22.08
60	42.83	34.75	28.1	23.5
90	51.5	39.13	31.6	26.5
120	57.17	43.5	35.1	30.92
150	60	45.6	38.6	32.33
180	65.67	52.13	43.9	36.75

Effects of pH variation on Cr(VI) removal from aqueous solution

In order to optimize the pH for maximum Cr(VI) removal, experiments were conducted with 100 ml of 0.12 mg/l of Cr(VI) solution with 100 mg adsorbent by varying the pH, pH - 2 to 4 at various contact time and the results are depicted in table - 2 .The results indicated a maximum adsorption of (90.12%) at pH 2 in 180 minutes of contact time. The decrease in adsorption at higher pH may be due to the negative charges on the surface of the adsorbent repelling the negatively charged chromate ions

Table – 2: Adsorption potential of Cr(VI) with pH variation
Conditions

Adsorbent dosage: 100mg; Temperature:32°C; Concentration of Cr(VI) solution: 0.12mg/l; Contact time :10-180 minutes

Time in minutes	Removal of Cr(VI) in percentage				
	pH 2	pH 2.5	pH 3	pH 3.5	pH 4
10	42.58	22.9	22.42	20.58	11.75
20	49.25	26.25	28.33	23.5	13.25
30	59	29.5	32.83	25	14.67
40	65.58	36.08	34.25	26.5	16.17
50	68.83	39.33	35.83	27.92	22.08
60	72.13	42.58	37.33	29.42	23.5
90	80.33	49.25	38.83	30.92	26.5
120	85.17	56.58	40.3	33.83	30.92
150	88.5	60.67	43.25	39.67	32.33
180	90.12	65.58	44.75	41.17	36.75

Effect of adsorbent dosage on Cr(VI) removal from aqueous solution

The effect of variation of adsorbent dosage was determined by varying the adsorbent dosage from 50 to 200 mg with 100ml of 0.12mg/l of Cr(VI) solution. The results have been tabulated in Table-3 . It is evident from the table that adsorption potential of the adsorbent increases with increasing the dosage. The maximum adsorption of Cr(VI) was noted with 200 mg of adsorbent dosage. The increase in percentage adsorption of Cr(VI) with increase in the adsorbent dosage may be due to the availability of more surface area of the adsorbent for adsorption of Cr(VI) species.

Table – 3: Adsorption potential of Cr(VI) with dosage variation
Conditions

pH: ~2.00 ; Temperature: 32°C, Concentration of Cr(VI) solution:0.12mg/l; Contact time: 10-180 minutes

Time in minutes	Removal of Cr(VI) in percentage			
	50mg	100mg	150mg	200mg
10	39.67	42.58	45.42	61.75
20	42.67	49.25	53	75
30	45.58	59	65.17	80.91
40	50	65.58	71.25	86.75
50	51.5	68.83	78.75	91.12
60	52.92	72.13	86.33	95.59
90	55.92	80.33	95.5	100
120	60.33	85.17	98.5	100
150	64.67	88.5	100	100
180	70.58	90.12	100	100

Adsorption Isotherms

The data obtained in this study by varying the initial concentration of Cr(VI) solution was fitted with Langmuir and Freundlich adsorption isotherms.

Langmuir adsorption isotherm

Langmuir adsorption isotherm is based on the assumption that points of valency exists on the surface of the adsorbent and that each of these site is capable of adsorbing only one molecule. Thus the adsorbed layer will be one molecule thick. Further it is assumed that all the adsorption sites have equal affinities for the adsorbate and that the presence of adsorbed species at one site will not affect the adsorbed species at an adjacent site.

The Langmuir adsorption isotherm is commonly given by ,

$$X/m = (k_1^1 C_e / 1 + k_1 C_e)$$

x - Amount of Cr(VI) adsorbed (mg/l)

m - Weight of adsorbent (mg)

C_e - Concentration of Cr(VI) at equilibrium

k₁ and k¹ – are the Langmuir constants which are the measures of maximum energy of adsorption and adsorption capacity respectively.

On rearranging

$$1/x/m = 1/k_1^1 /k_1 + 1 / k^1 C_e$$

The plots of (1/x/m) versus 1/C_e were linear with slope equal to 1/k₁ and intercept (1/k¹/k₁). The slope, intercept and separation factor are calculated and given in the table 4. The linear plots of

$1/C_e$ Vs m/x shows the applicability of Langmuir model for the present system indicating the formation of monolayer coverage of adsorbate on the surface of the adsorbent.

Separation factor - R_L

The essential characteristics of Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter ' R_L ' which is defined by $R_L = 1 / (1 + bC_i)$

Where, C_i = initial concentration of Cr(VI) in mg/l ; b = Langmuir constant (k_1^{-1})

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$R_L < 1$	Favorable

The R_L values obtained (in the table V)are less than unity for Cr(VI) adsorption onto a low - cost adsorbent used in this study. This showed the feasibility of the Cr(VI) adsorption process at all initial concentration of aqueous solution of Cr(VI) used in this study.

Table 4: Interpretation of results of adsorption of Cr(VI) in terms of Langumir adsorption isotherm for variation of concentration of Cr(VI) solution

Time in minutes : 1 hour

Time in minutes	Initial concentration in mg/l	$1/C_e$	m/x	Separation factor R_L	Intercept k_1 / k_1^{-1}	Slope $1 / k_1^{-1}$
60	0.06	0.0292	0.3891	0.9806	0.3296	1.9257
	0.08	0.0192	0.3597	0.9743		
	0.1	0.0139	0.3559	0.9681		
	0.12	0.0108	0.3546	0.9619		

Freundlich adsorption isotherm

Attempts were made to fit the adsorption data obtained in this study into Freundlich adsorption isotherm.

The linear form of Freundlich adsorption isotherm is given below,

$$\log x/m = \log k_f + 1/n \log C_e$$

where x is the amount of Cr(VI) adsorbed in mg; m is the weight of the adsorbent (g)

C_e is the amount of Cr(VI) in the bulk solution in mg

K_f and $1/n$ are Freundlich constants related to the adsorption capacity and adsorption intensity respectively.

The linear form of Freundlich adsorption isotherm at room temperature is obtained by plotting $\log x/m$ versus $\log C_e$ for different concentrations of the aqueous solution of Cr(VI) . K_f and $1/n$ are evaluated from the slope and intercept respectively (Table 5).

Table – 5: Interpretation of results of adsorption of Cr(VI) in terms of Freundlich adsorption isotherm for variation of concentration of Cr(VI) solution

Time in minutes	Initial concentration in mg/l	logC _e	logx/m	Intercept	Slope n	1/n
60	0.06	1.5353	0.4099	0.2732	0.0934	10.6100
	0.08	1.7177	0.4440			
	0.1	1.8567	0.4487			
	0.12	1.9628	0.4502			

CONCLUSION

The carbon derived from the *Delonix regia* pods can be used as an efficient adsorbent for the removal of toxic Cr(VI) from aqueous solution. The adsorption of Cr(VI) was found to be concentration dependent. Percentage removal of Cr(VI) increased with decrease in pH and it was found to increase from 36.75% to 90.12% for the variation of pH from 4 to 2. The maximum removal of Cr(VI) was observed at pH 2. Removal of Cr(VI) increased from 70.58% to ~100% with increasing adsorbent dosage from 50 to 200 mg. Langmuir adsorption isotherm plots obtained by plotting $1/C_e$ Vs m/x are linear shows that the adsorption Cr(VI) using activated carbon prepared from the *Delonix regia* pods followed Langmuir adsorption isotherm. The favourable value of R_L showed the feasibility of the process at all initial concentrations (0.06 to 0.12 mg/l) of Cr(VI) solution used in this study. The Cr(VI) adsorption followed Freundlich adsorption isotherm also.

Thus it can be concluded that the activated carbon prepared from the *Delonix regia* pods, an inexpensive plant material and use of the same provides an effective solution for treatment of effluents containing hexavalent chromium. Hence the use of low cost carbon prepared and used as an adsorbent for Cr(VI) removal in this study, is of practical importance and is expected to be economical.

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