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Adsorption of Cr (VI) by treated weed *Salvinia cucullata*: kinetics and mechanism

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Abstract In the present study a new low cost, easily available and environmentally friendly adsorbent was used for removal of Cr (VI). The Cr (VI) removal efficiency of the adsorbent was studied as a function of contact time, pH, adsorbent dose, adsorbate concentration, temperature and stirring speed. Different adsorption model equations for kinetics, isotherm and rate mechanism of the process were used to find the best model, which fit well to the experimental data. A full factorial design of n^k type was used to find a mathematical relation between the percentage of adsorption and variables affecting the adsorption process such as time, pH, adsorbate concentration and temperature. Using the Students 't' test, the significance of each term of the derived equation was tested. The insignificant terms were removed from the derived equation. The adequacy of the equation after removing the insignificant terms was tested using the Fisher adequacy test. From the factorial design analysis it is found that pH has the most pronounced effect followed by time, temperature and the adsorbate concentration. A column study was performed using the optimum operating conditions.

Keywords Cr (VI) removal · Waste water treatment · Kinetics · Isotherm · Rate mechanism · Factorial design · Column studies

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1 Introduction

The extensive use of chromium in leather tanning, metallurgy, electroplating and other industries has resulted in higher chromium concentrations in aquatic systems. Generally chromium exhibits two valance states, i.e., Cr (III) and Cr (VI). Cr (III) is essential to animals and human beings. It is recommended that a daily intake of 50 to 120 µg (for adults) is helpful for human beings (Wang and Li 2004). Whereas, Cr (VI) is highly toxic in nature. Cr (VI) causes variety of diseases such as dermatitis, congestion of respiratory tracts and perforations in the nasal septum (Pmila et al. 1991).

The Cr (VI) present in the aqueous solution either in form of dichromate ($Cr_2O_7^-$), hydro chromate ($HCrO_4^-$), or chromate (CrO_4^{2-}). These Cr (VI) anion species are generally poorly adsorbed by the negatively charged soil particles due to the repulsive electrostatic interaction. On the contrary Cr (III), which occur in the form of Cr^{3+}, $Cr(OH)^{2+}$ or $Cr(OH)_2^+$ are adsorbed on the negatively charged soil particles and thus are less mobile (Deng and Bai 2004). In India, the permissible limit of Cr (VI) is 0.1 mg/L for drinking water, but industrial and mining effluents can be discharged with 0.5 mg/L. Before treatment, mining water may contain 2 to 5 mg/L and the effluent from electroplating and leather tanning industries may contain 50 to 100 mg/L of Cr (VI), which are much higher than the permissible limit (Xi and Sun 1996). So removal/reduction of Cr (VI) from mining and industrial effluents is important before discharging them into aquatic environment.

A number of physical and chemical treatment processes like electrolysis, ion exchange, reverse osmosis foam floatation, etc. have been reported. However, these methods are ineffective for Cr (VI) concentrations lower than 100 mg/L and are prohibitively costly (Matheichal et al. 1997). Among other different processes, adsorption is an economically feasible alternative. The utilization of biomaterials even makes adsorption more environmentally friendly, more cost effective, and more technically feasible. A number of adsorbents, such as Casurina leave (Ranganathan 2003), leaf mould (Sarma and Foster 1994), coconut waste (Selvi et al. 2001), rubber wood (Raji and Anirudhan 1997), etc. were used for Cr (VI) abatement. However, some of these adsorbents do not have high adsorption capacity or need long adsorption equilibrium time, while others may have problems in regeneration for reuse (Nakano et al. 2001). Therefore, a new economical, easily available, and effective adsorbent needs to be found.

In the present study, a new waste material, i.e., waste sweet waterweed *Salvinia cucullata* was used for the removal of Cr (VI). It has many specific advantages like low cost, easy availability, and high adsorption capacity. The weed was treated with 1 N acetic acid to improve its physical and chemical characteristics. The removal efficiency of the adsorbent was investigated as a function of pH, contact time, concentration of adsorbate, temperature, agitation speed, and adsorbent dose. Different adsorption isotherms were used to find the best fit to the experimental data by use of the average absolute percentage deviation between the experimental and predicted uptake. The thermodynamics parameters were calculated to find the feasibility of the adsorption process. Desorption studies were also carried out to show its suitability for treating Cr (VI) contaminated water.

2 Experimental

The weed, *Salvinia cucullata* used in this experiment was collected from the lake of Nandankanan that is situated at a distance of 15 km from Bhubaneswar, the capital city of Orissa. The weed was dried at 60 °C for 4 hours and then ground and sieved to different size fraction. 200 g of the smallest size fraction (-75 micron) was mixed with 500 ml of 1 N acetic acid and kept overnight. The treated weed was then washed several times with distilled water to remove excess acid followed by drying the material at 60 °C for 4 hrs. A stock solution of Cr (VI) having a concentration of 5 g/L was prepared by using $K_2Cr_2O_7$ (Analytical grade). Experimental solutions of desired concentrations were obtained by successive dilution. The pH of the solution was maintained by adding dilute HCl or NaOH solution. Batch adsorption studies were carried out in a 500 ml beaker using 250 ml of Cr (VI) solution and stirring was done by a magnetic stirrer. For higher temperatures, the adsorption studies were carried out in a sealed unit to avoid loss due to evaporation. At regular intervals 5 ml samples were withdrawn and filtered. The residual concentration in the solution was estimated colorimetrically with 1,5-diphenyl carbazide as a complexing agent at 540 nm (Chun et al. 2004). All the experiments were performed in triplicate, and the average of the three was taken for subsequent calculations. The equilibrium adsorption capacity was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where q_e is the equilibrium adsorption capacity (mg/g), C_0, C_e are initial and equilibrium concentrations (mg/L) of Cr (VI) in the solution, V is the volume (l) of solution taken, and M is the mass (g) of adsorbent used. To find the possibility of reduction of Cr (VI) to Cr (III) during the adsorption process, the initial and final concentrations of Cr (III) in the solution were estimated. It is found that there is hardly any change in Cr (III) concentration in the solution; hence, no reduction of Cr (VI) takes place. The mechanism of Cr (VI) removal by the acid-treated weed was elucidated on the basis of FT-IR analysis. 2 g of finely ground adsorbent, as well as Cr (VI)-loaded adsorbent, were mixed separately with 400 g of KBr to prepare translucent sample disk. The sample disk was analyzed by a Perkin Elmer model 1600 FT-IR. All the chemicals used in these experiments were of analytical grade.

Continuous adsorption studies were carried out in a perspex column. The ID and height of the column were 5 cm and 30 cm, respectively. The Cr (VI) solution was pumped through a metering pump (Watson Marlow make) at the bottom of the column and the effluent was collected from the top. Samples were collected at regular intervals for analysis. The flow rate of solution was checked regularly. The pressure drop was measured through a manometer. The initial Cr (VI) concentration and flow rate were 500 mg/L and 60 ml/min, respectively. The adsorption studies continued till there was no difference between inlet and outlet solution.

3 Result and discussion

3.1 Effect of contact time

In order to find the equilibrium contact time, adsorption experiments were carried out by varying the contact time up to 15 hrs. From the experimental data, it is observed that percentage adsorption increased with increasing contact time up to 12 hrs and beyond that duration, little further increase was observed. From Fig. 1 it is observed that initially the adsorption rate was fast followed by slower rate. As equilibrium was observed to be reached in 12 hrs, hence rest of the experiments were carried out for 12 hrs.

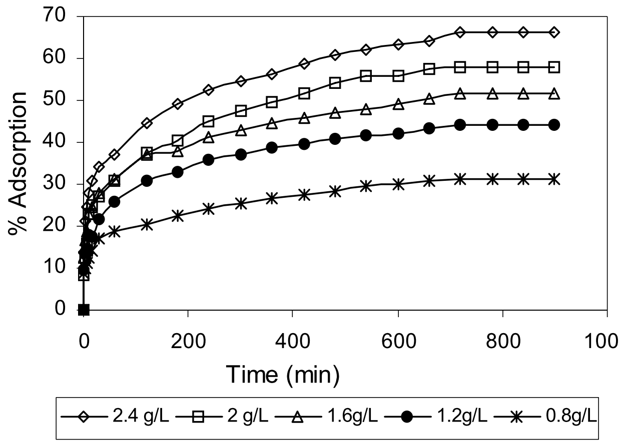

Fig. 1 Effect of contact of time. (Conditions: pH 1.7, adsorbate concentration 500 mg/L, adsorbent dose 2 g/l, stirring speed 600 rpm, temperature 30 °C)

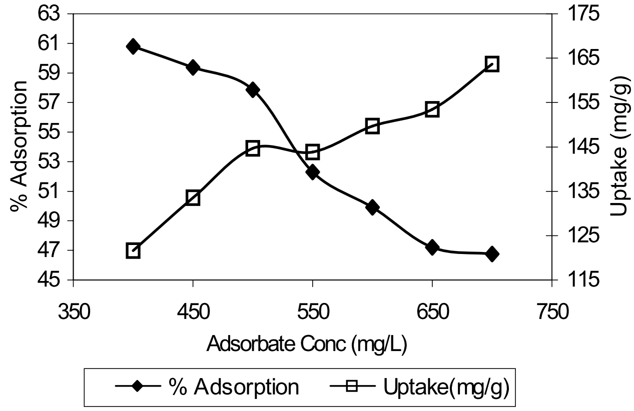

Fig. 2 Effect of adsorbate concentration. (Conditions: time 720 min, pH 1.7, adsorbent dose 2 g/l, stirring speed 600 rpm, temperature 30 °C)

3.2 Effect of adsorbate concentration

The effect of initial Cr (VI) concentration on the extent of uptake was studied by varying the initial Cr (VI) concentration from 400 mg/L to 700 mg/L. It is observed that the % adsorption increased from 46.8 to 60.8 and the uptake decreased from 163.7 to 121.6 when the concentration decreased from 700 to 400 mg/L (Fig. 2). The increase in uptake of Cr (VI) may be due to the competition between the adsorbate ions for limited adsorbent surface.

3.3 Effects of adsorbent dose

Batch experiments were carried out by varying the adsorbent dose from 0.8 to 2.4 g/l. The % of adsorption increases from 31.5 to 66% and the uptake decreases from 196.5 to 137 mg/g when the adsorbent dose increases from 0.8 to 2.4 g/l (Fig. 3). The increase in % adsorption is due to the increase in amount of free surface available. The decrease in uptake is on account of the favorable isotherm and mass balance constraints.

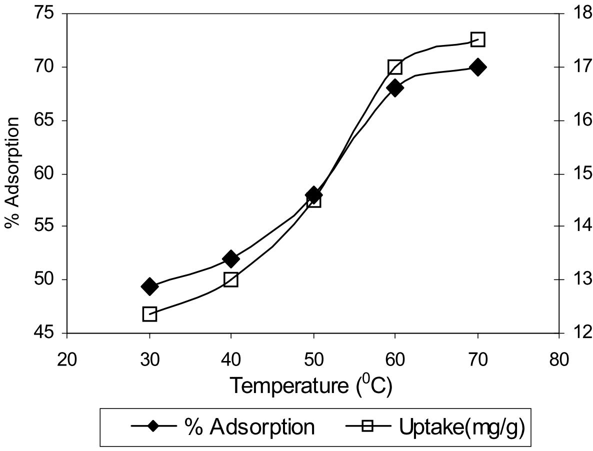

Fig. 3 Effect of adsorbent dose. (Conditions: time 720 min, adsorbate concentration 500 mg/L, pH 1.7, stirring speed 600 rpm, temperature 30 °C)

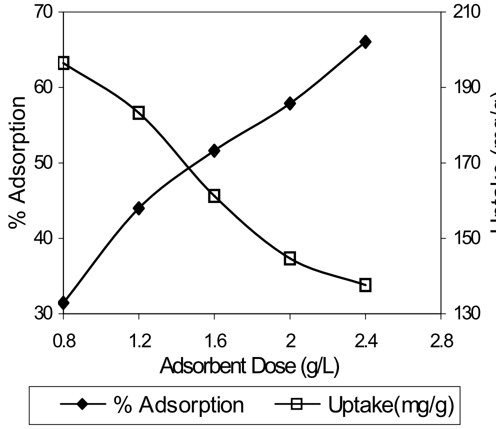

Fig. 4 Effect of temperature (Conditions: time 720 min, adsorbate concentration 500 mg/L, adsorbent dose 2 g/l, stirring speed 600 rpm, pH 1.7)

3.4 Effect of temperature

Experiments were performed at different temperatures, from 30 to 70 °C. The % of adsorption and uptake of Cr (VI) increased from 49.4 to 70 and 123.5 to 175 mg/g respectively when the temperature increased from 30 to 70 °C (Fig. 4). The increase in % adsorption and uptake showed the endothermic nature of the process. Apart from the apparent endothermic nature, the adsorption mechanism may be controlled by diffusion, as the adsorbent is apparently porous in nature. The increase in temperature favors adsorbate transport within the pores of the adsorbent. The increase in adsorption with temperature may also be attributed to the increase in the number of adsorption sites generated due to

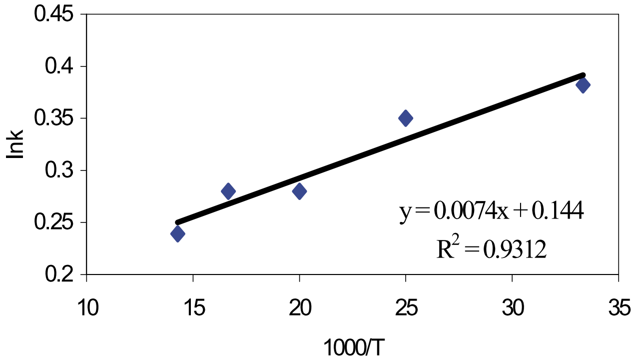

Fig. 5 Evaluation of activation energy

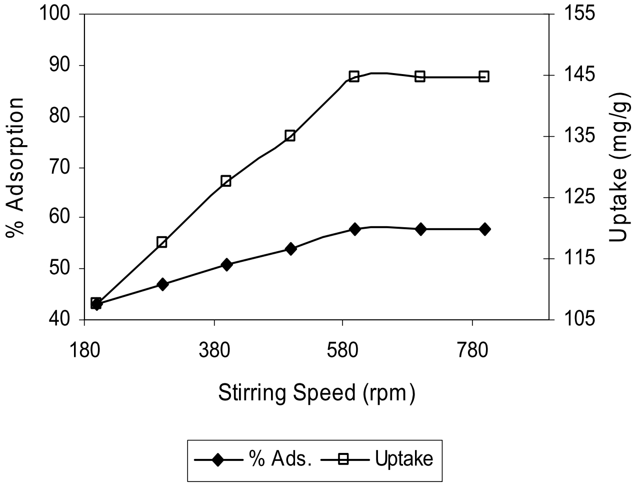

Fig. 6 Effect of stirring speed. (Conditions: time 720 min, adsorbate concentration 500 mg/L, adsorbent dose 2 g/l, pH 1.7, temperature 30 °C)

breaking of some initial bonds near the edge of the active surface site of the adsorbent (Sing et al. 2005).

3.5 Effect of stirring speed

The % of adsorption and uptake increased from 43 to 57.9 and 107.5 to 144.7 mg/g when the stirring speed increased from 200 to 600 rpm, respectively (see Fig. 6). The increase in stirring speed may have reduced the film resistance to the adsorbent, and may have slightly distorted the adsorbent structure, which causes increase in % adsorption. Beyond 600 rpm there is no further increase in adsorption, which may be due to the complete removal of film diffusion barrier.

3.6 Effect of pH

Adsorption experiments were performed over a range of pH (1.7, 2.0, 2.5, 3.5, and 4.5). From Fig. 7 it is observed that the percentage of adsorption and uptake increase from 6.2 to 57.9 and 15.5 to 144.7 when the initial pH of the solution decreased from 4.5 to 1.7. The increase in the percentage adsorbed, as well uptake, at lower pH could be well explained by protonation properties of the adsorbent. At low pH, i.e., higher hydrogen ion concentration, the negative charges at the surface of internal pores are neutralized and some more new adsorption sites were developed as a result the surface provided a positive charge for anionic Cr (VI) complex to get adsorbed. Again it is observed that the final pH of the solution is always greater than the initial pH of the solution, which confirms the Brønsted–Lowry basicity of the negative charges at the surface. As a result the concentration of H^+ ion decreases in the solution, and hence the pH of the solution increased. Many authors also showed similar results (Yu et al. 2003).

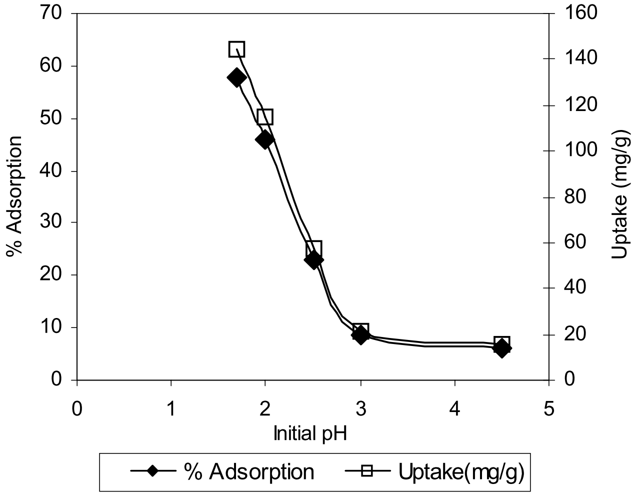

Fig. 7 Effect of pH. (Conditions: time 720 min, adsorbate concentration 500 mg/L, adsorbent dose 2 g/l, stirring speed 600 rpm, temperature 30 °C)

3.7 FT-IR analysis

Apart from electrostatic force, the adsorption may be due to formation of complex with the ligands (Lewis bases) available in the adsorbents. The adsorbent as such showed peaks at 3450, 3330, 2920, 1670, 1363 and 1035 which corresponds to bonded OH group, NH stretching, aliphatic C–H group, C=O stretching, C–O stretching and C–C stretching respectively. The Cr (VI) loaded adsorbent showed either shift or reduction in adsorption peaks suggesting the vital role played by the functional group. Therefore FT-IR studies showed the vital role-played due to chelation. The formation of chelates may be favoured at lower pH and the adsorption efficiency was higher.

4 Adsorption kinetic studies

In many cases, the kinetics of adsorption by biological materials has been tested for pseudo 1^{st} order dependence. However, it has also been shown that pseudo 2^{nd} order and the Ritchie 2^{nd} order equation can sometimes provide a better description of the adsorption kinetics. So, in the present studies, pseudo 1^{st} order, pseudo 2^{nd} order and the Ritchie 2^{nd} order equations have been used for modeling the kinetics of Cr (VI) sorption. The pseudo 1^{st} order rate equation is expressed as

$$\log(q_e - q) = \log qe - \frac{k_1'}{2.303}t \tag{2}$$

where q and q_e are the uptake at time, t, and at equilibrium, respectively, and k_1' is the rate constant (Cemioglu 2005). The values of k_1' at different adsorption parameters were calculated from the plots of $\log(q_e - q)$ vs. t.

The pseudo 2^{nd} order rate equation is expressed as (Loukidous et al. 2004),

$$\frac{t}{q_t} = \frac{1}{(q_{eq})^2 k_2} + \frac{t}{q_{eq}} \tag{3}$$

where k_2 is the rate constant, q_t and q_{eq} are the uptake at time t and at equilibrium, respectively. The values of k_2 were calculated from the plots of t/q_t vs. t/q_e.

Similarly, the Ritchie 2^{nd} order rate equation can be expressed as (Cheung et al. 2001)

$$\frac{q_e}{q_e - q_t} = 1 + k_2 t \tag{4}$$

where q_t, q_e and k_2 are their usual meanings. The values of k_2 were calculated from the plots of $q_e/(q_e - q_t)$ vs. t.

The estimated values of kinetic model parameters were reported along with other statistical parameters such as the correlation coefficient, R^2, and the average absolute percentage deviation (% Desv) between $q_{e(cal)}$ and $q_{(exp)}$. The latter values were calculated by using the following equation;

$$\%Desv = 100 \times \frac{1}{N} \sum_{i=1}^{N} \left| \frac{(q_e)_{\exp} - (q_e)_{pred}}{(q_e)_{\exp}} \right|_i \tag{5}$$

From the parameters listed in Table 1, it can be concluded that the kinetics followed pseudo 2^{nd} order model.

5 Equilibrium isotherm studies

Analysis of equilibrium data is important for developing an equation that can be used for design purposes. Here, an attempt has made to find the adsorption isotherm, which best fit the experimental data. Three adsorption isotherms were considered such as Langmuir, Freundlich and Temkin isotherm.

The Langmuir adsorption isotherm, which is based on the monolayer adsorption of Cr (VI) ion of the surface of adsorbent, can be expressed in linearized form as Hamid et al. (2001)

$$\frac{1}{q_e} = \frac{1}{Q_0 b}\left(\frac{1}{C_e}\right) + \frac{1}{Q_0} \tag{6}$$

where C_e is the equilibrium concentration and q_e is the amount adsorbed at equilibrium. The Langmuir constant, Q_0 (mg/g), represents the monolayer adsorption capacity and the parameter, b, is related to the equilibrium constant of adsorption.

The Freundlich adsorption isotherm which describes the heterogeneous surface can be written in linear form as (Tiwari et al. 2005),

$$\ln q_e = \ln h_f + b_f \ln C_e \tag{7}$$

where k_f indicates adsorption capacity and b_f is an empirical parameter related to the heterogeneity of the adsorbent. For values in the range of $0.0 < b_f < 1$ adsorption is favorable (Raji and Anirudhan 1998). The smaller the value of b_f the greater is the favorability of adsorption.

Temkin and Pyzhev suggest that, due to indirect adsorbate/adsorbent interactions, the heat of adsorption of all the molecules in the layer would decrease linearly with coverage (Karthikeyen et al. 2005). The linear form of the Temkin isotherm equation can be written as,

$$q_{eq} = B \ln A + B \ln C_{eq} \tag{8}$$

where $B = RT/b$, T is absolute temperature in K and R is the universal gas constant. The constant b is related to the heat of adsorption.

The Langmuir constants, Q_0 and b, the Freundlich constants, h_f and b_f, and the Temkin constants, A and B, were calculated from plots of C_e/q_e vs. C_e, $\ln q_e$ vs. $\ln C_e$ and q_e vs. C_e, respectively. In Table 2, the estimated values of the model parameters are reported along with other statistical parameters, such as the respective correlation coefficients, R^2, and the average absolute % deviations between $q_{e(cal)}$ and $q_{e(exp)}$. From those parameters listed in Table 2, it can be concluded that the experimental data were well fitted by both the Langmuir and Freundlich adsorption isotherm models. Almost all b_f values were in the range of 0.0 to 1 indicating the adsorption to be favorable (Raji and Anirudhan 1998).

6 Adsorption mechanism

The adsorption process for porous solid can be separated into 3 stages i.e. (a) mass transfer (boundary layer/film diffusion), (b) intra-particle diffusion, and (c) sorption of

Table 1 Adsorption kinetic model parameters

Pseudo 1st order kinetics						Ritchie 2nd order kinetics				Pseudo 2nd order kinetics			
	k'_1	R^2	q_{ecalc}	q_{eExp}	% Desv	k_m	R^2	q_{ecalc}	% Desv	k_m	R^2	q_{ecalc}	% Desv
pH													
1.7	0.003	0.94	111	144.7		0.223	0.88	105.3		0.00016	0.99	149.3	
2	0.002	0.98	69.2	114.8		0.288	0.9	90.91		0.00029	1	117.6	
2.5	0.003	0.92	35.4	57.8	28.9	0.107	1	52.63	22.82	0.00062	1	58.82	3.23
3	0.002	0.97	17.4	21.64		0.147	0.96	16.34		0.00081	0.99	22.68	
4.5	0.002	0.99	11.8	15.41		0.16	0.89	10.4		0.00125	0.99	16.03	
Adsorbent dose (mg/L)													
2.4	0.002	0.99	86.6	137.6		0.342	0.84	104.2		0.00019	0.99	140.8	
2	0.003	0.94	111	144.7		0.223	0.88	105.3		0.00016	0.99	149.3	
1.6	0.002	0.97	97.5	161.2	34	0.4	0.78	122	25.89	0.00018	0.99	163.9	2.39
1.2	0.002	0.97	121	183.2		0.354	0.77	135.1		0.00015	1	188.7	
0.8	0.002	0.97	127	196.5		0.5	0.63	142.9		0.00013	0.99	200	
Adsorbate concentration (mg/L)													
400	0.002	0.9	96.8	121.6		0.404	0.66	83.33		0.00016	0.99	126.6	
450	0.002	0.94	105	133.6		0.306	0.77	92.59		0.00015	0.99	138.9	
500	0.003	0.94	111	144.7		0.223	0.88	105.3		0.00016	0.99	149.3	
550	0.002	0.95	108	143.8	25.1	2.798	0.72	36.1	35.39	0.00016	0.99	149.3	3.77
600	0.002	0.96	116	149.7		0.448	0.56	100		0.00014	0.99	156.3	
650	0.002	0.98	107	153.5		0.367	0.76	111.1		0.00014	0.99	158.7	
700	0.003	1	110	163.7		0.38	0.75	126.6		0.00024	1	169.5	
Stirring rate (rpm)													
200	0.002	0.98	84.8	107.5		0.208	0.87	72.46		0.00016	0.99	112.4	
300	0.002	0.94	95.3	117.5		0.2	0.88	78.74		0.00014	0.99	123.5	
400	0.002	0.95	101	127.5	30.28	0.185	0.9	87.72	30.28	0.00013	0.99	133.3	4.33
500	0.002	0.95	104	135		0.19	0.91	98.04		0.00015	0.99	140.8	
600	0.003	0.94	111	144.7		0.223	0.88	105.3		0.00016	0.99	149.3	
Temp. (°C)													
30	0.002	0.97	98.3	123.5		0.382	0.7	86.96		0.00017	0.99	128.2	
40	0.002	0.94	105	130		0.401	0.72	95.24		0.00019	0.99	135.1	
50	0.002	0.99	111	145	19.9	0.221	0.93	112.4	26.21	0.00017	1	149.3	3.56
60	0.002	0.97	141	170		0.352	0.72	123.5		0.00016	1	175.4	
70	0.002	0.98	141	175		0.239	0.88	131.6		0.00016	1	181.8	

Table 2 Adsorption isotherm parameters

Langmuir isotherm							Freundlich adsorption isotherm					Temkin adsorption isotherm				
Adsorbate conc. (mg/l)	q_{ecalc}	q_{eExp}	% Desv	Q_0	b	R^2	q_{ecalc}	% Desv	b_f	k_f	R^2	q_{ecalc}	% Desv	b	A	R^2
400	124.27	122	2.39	200	0.0105	0.92	126.1	2.437	0.28	30.49	0.9	126	2.435	62.69	0.151	0.91
450	131.35	134					131.7					132				
500	137.58	145					137.1					138				
550	146.60	144					145.8					146				
600	151.75	150					151.4					152				
650	156.43	153					157.2					157				
700	159.18	164					160.9					160				

Table 3 Adsorption rate controlling mechanism

	k_{id}	R^2	$D_1 \times 10^{-12}$	R^2	$D_2 \times 10^{-12}$	R^2
pH						
1.7	3.552	0.981	0.492	0.923	17.486	0.912
2	2.078	0.987	0.537	0.873	13.473	0.987
2.5	0.813	0.966	0.965	0.964	15.479	0.849
3	0.631	0.980	0.335	0.791	16.626	0.962
4.5	0.387	0.980	0.378	0.986	13.473	0.974
Adsorbent dose (mg/l)						
2.4	2.994	0.979	0.284	0.906	12.613	0.984
2	3.552	0.981	0.365	0.908	17.486	0.911
1.6	3.161	0.986	0.274	0.954	12.039	0.953
1.2	3.755	0.975	0.200	0.929	14.046	0.938
0.8	4.275	0.996	0.209	0.992	13.186	0.944
Adsorbate concentration (mg/l)						
400	3.081	0.993	0.105	0.929	17.772	0.854
450	3.277	0.987	0.236	0.982	17.486	0.909
500	3.552	0.981	0.365	0.908	17.486	0.911
550	3.495	0.979	0.213	0.975	16.913	0.915
600	3.863	0.970	0.068	0.978	16.913	0.923
650	3.733	0.993	0.172	0.829	14.333	0.962
700	3.126	0.883	0.238	0.958	21.499	0.996
Stirring rate (rpm)						
200	3.113	0.984	0.266	0.923	14.619	0.979
300	3.432	0.993	0.294	0.965	15.193	0.901
400	3.530	0.997	0.412	0.977	14.333	0.925
500	3.445	0.989	0.425	0.939	16.626	0.924
600	3.552	0.981	0.365	0.908	17.486	0.911
Temp. °C						
30	2.932	0.977	0.119	0.908	16.626	0.898
40	3.055	0.974	0.115	0.673	19.492	0.917
50	3.336	0.961	0.254	0.800	17.486	0.891
60	3.713	0.968	0.188	0.971	20.066	0.937
70	3.494	0.978	0.296	0.952	18.059	0.950

ions at sites. In many cases there is a possibility that intraparticle diffusion will be the rate-limiting step and is given by Karthikeyen et al. (2005);

$$q_t = k_{id} t^{1/2} \tag{9}$$

Regressing q vs. $t^{1/2}$ gives the values of k_{id} for different adsorption experiments. The plots were not linear over the entire time range indicating that more than one mechanism affects adsorption. As an approximation, the adsorption path can be divided into two parts, the initial curved portion relates to film diffusion (D_1) and the later linear portion relates to the diffusion within the adsorbent. The equation for D_1 and D_2 are given by;

$$\frac{q_t}{q_e} = 6\left(\frac{D_1}{\pi a^2}\right)^{\frac{1}{2}} t^{\frac{1}{2}} \tag{10}$$

$$\ln\left(1 - \frac{q_t}{q_e}\right) = \ln\left(\frac{6}{\pi^2}\right) - \left(\frac{D_2 \pi^2 t}{a^2}\right) \tag{11}$$

D_1 can be calculated from the slope of the plot between q_t/q_e vs. $t^{1/2}$ for the initial curved portion. D_2 can be calculated from the slope of the curve between $\ln(1 - q_t/q_e)$ vs. t. The values of D_1, D_2 and k_{id} along with R^2 values for different adsorption experiments are shown in Table 3.

7 Determination of number of stages

The number of stages/batch contactors required for removal of Cr (VI) was calculated from equilibrium curve (Aksu and Kutsal 1991) obtained from the plot between predicted C_e and q_e values from Langmuir adsorption isotherm at 35 °C and pH-1.7. The operating line was drawn such that it passed through the point ($C_o = 500$ mg/L, $q_0 = 0.0$ mg/g) and having slope V_0/X_0 is $-1/2$ where V_0 and X_0 are expressed in dm^3 and g, respectively. Figure 8 shows the adsorption isotherm. From Fig. 8 it can be concluded that the Cr (VI) concentration can be reduced from 500 to <1 mg/L in 3 stages.

8 Factorial design and optimization of parameters

Since multiple variables were considered together, a full factorial design of type n^k ($n = 2$ and $k = 4$) has been used to find out the optimum conditions for the adsorption process where n is the number of levels and k is the number of factors examined. Thus the total number of trial experiments needed for an investigation is 2^4. The regression equation with four parameters and their interaction with each other is given by Akhnazarova and Katarov (1982);

$$\begin{aligned} Y = {} & b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_3 \\ & + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4 \\ & + b_{123}x_1x_2x_3 + b_{124}x_1x_2x_4 + b_{234}x_2x_3x_4 \\ & + b_{134}x_1x_3x_4 + b_{1234}x_1x_2x_3x_4 \end{aligned} \tag{12}$$

where b_1, b_2, b_3 and b_4 are the regression interaction coefficient of the concern variables and x_1, x_2, x_3 and x_4 are the variable affecting the process.

The experiments were designed and adsorption experiments were carried out using a design matrix. The variable parameters and their coded values are given in Table 4. The

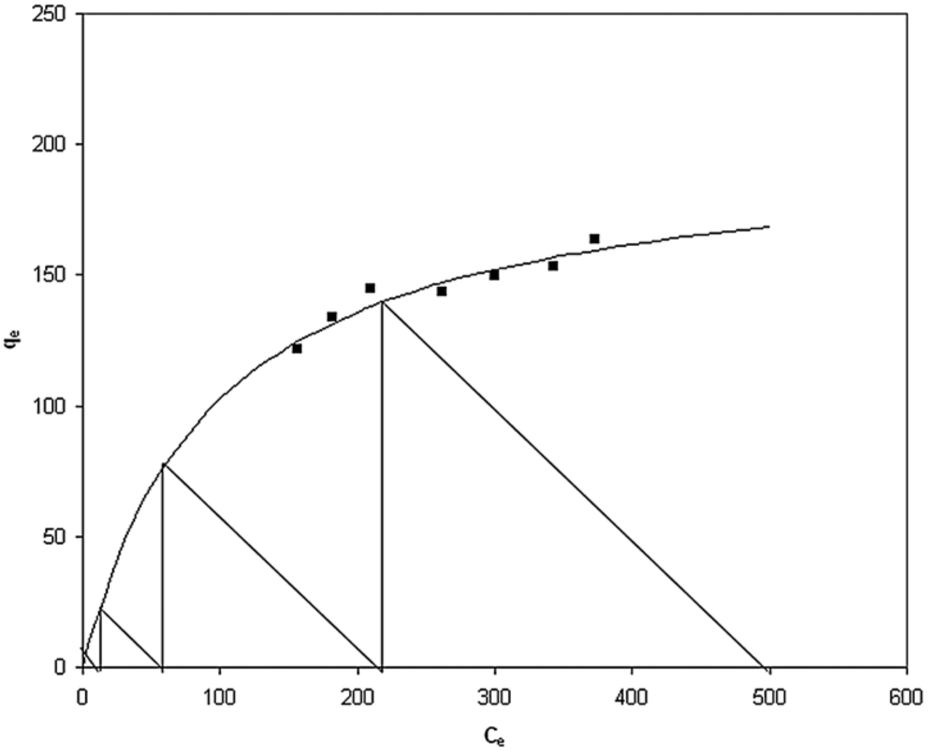

Fig. 8 Determination of number of stages using adsorption isotherm

Table 4 Factorial levels and variation intervals

Factors	−1	0	1	Variation interval
x_1	60	120	180	60
x_2	1.6	1.7	1.8	0.1
x_3	450	500	550	50
x_4	30	35	40	5

x_1 = time in min, x_2 = pH, x_3 = temperature in °C, x_4 = adsorbate concentration (mg/L)

higher, lower and base parameters were designated as +, − and 0, respectively. Sixteen designed trial experiments were carried out together with three base level experiments to estimate error and standard deviation. The regression interaction coefficients were calculated using following formula;

$$b_j = \left\{\sum x_{ij} Y_i\right\}/N \quad \text{where } j = 1, 2, 3, 4, \ldots, n \tag{13}$$

where i and j are the number of row and column, respectively. The results obtained from trial runs are incorporated in the regression equation, and thus the equation becomes

$$\begin{aligned} Y = {} & 37.128 + 3.178x_1 - 3.711x_2 - 2.399x_3 + 2.803x_4 \\ & - 0.534x_1x_2 - 0.306x_1x_3 - 0.123 - 0.575x_2x_3 \\ & - 0.064x_2x_4 + 0.311x_3x_4 + 0.04x_1x_2x_3 \\ & + 0.204x_1x_2x_4 - 0.308x_2x_3x_4 - 0.236x_1x_3x_4 \\ & + 3.178x_1x_2x_3x_4 \end{aligned} \tag{14}$$

The significance of each coefficient was assessed using the Student’s ‘t’ method at 5% significance level (Akhnazarova and Katarov 1982) and insignificant terms were neglected from (14). The regression equation was tested to see how it fitted with the observation using Fisher’s adequacy test (Akhnazarova and Katarov 1982) at the 95% significance level and it is observed that the following equation is adequate.

$$\begin{aligned} Y = {} & 37.128 + 3.178x_1 - 3.711x_2 - 2.399x_3 + 2.803x_4 \\ & - 0.534x_1x_2 - 0.575x_2x_3 + 3.178x_1x_2x_3x_4 \end{aligned} \tag{15}$$

The adsorption efficiency calculated by (15) matches well with the experimental values.

9 Column studies

Up-flow column studies were conducted at optimum parameter such as retention time = 10 min, pH = 1.7, temperature = 35 °C obtained form the factorial design method to evaluate Cr (VI) removal from the solution using the prepared adsorbent. The column contains 50 g of adsorbent material. The lower breakthrough point was obtained at an effluent concentration of 0.1 mg/L (Cr (VI)), as it is the permissible limit for potable water (Devy and Bai 2004). The higher breakthrough point relates to complete saturation of the adsorbent material. The lower and higher breakthrough

Table 5 Design of trial runs (in coded form) for adsorption of Cr (VI)

Trial No	x_1	x_2	x_3	x_4	x_1x_2	x_1x_3	x_1x_4	x_2x_3	x_2x_4	x_3x_4	$x_1x_2x_3$	$x_1x_2x_4$	$x_1x_3x_4$	$x_2x_3x_4$	$x_1x_2x_3x_4$	Y
1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	35.75
2	+	+	+	−	+	+	−	+	−	−	+	−	−	−	−	29.89
3	+	+	−	+	+	−	+	−	+	−	−	+	−	−	−	42.5
4	+	−	+	+	−	+	+	−	−	+	−	−	+	−	−	45.45
5	−	+	+	+	−	−	−	+	+	+	−	−	−	+	−	30.62
6	+	+	−	−	+	−	−	−	−	+	−	−	+	+	+	36.1
7	+	−	−	+	−	−	+	+	−	−	+	−	−	+	+	49.22
8	+	−	+	−	−	+	−	−	+	−	−	+	−	+	+	39.31
9	−	+	+	−	−	−	+	+	−	−	−	+	+	−	+	25.51
10	−	+	−	+	−	+	−	−	+	−	+	−	+	−	+	35.75
11	−	−	+	+	+	−	−	−	−	+	+	+	−	−	+	39.55
12	+	−	−	−	−	−	−	+	+	+	+	+	+	−	−	44.22
13	−	+	−	−	−	+	+	−	−	+	+	+	−	+	−	31.21
14	−	−	+	−	+	−	+	−	+	−	+	−	+	+	−	31.75
15	−	−	−	+	+	+	−	+	−	−	−	+	+	+	−	40.6
16	−	−	−	−	+	+	+	+	+	+	−	−	−	−	+	36.61
17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	37.65
18	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	36.81
19	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	37.5
20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	38

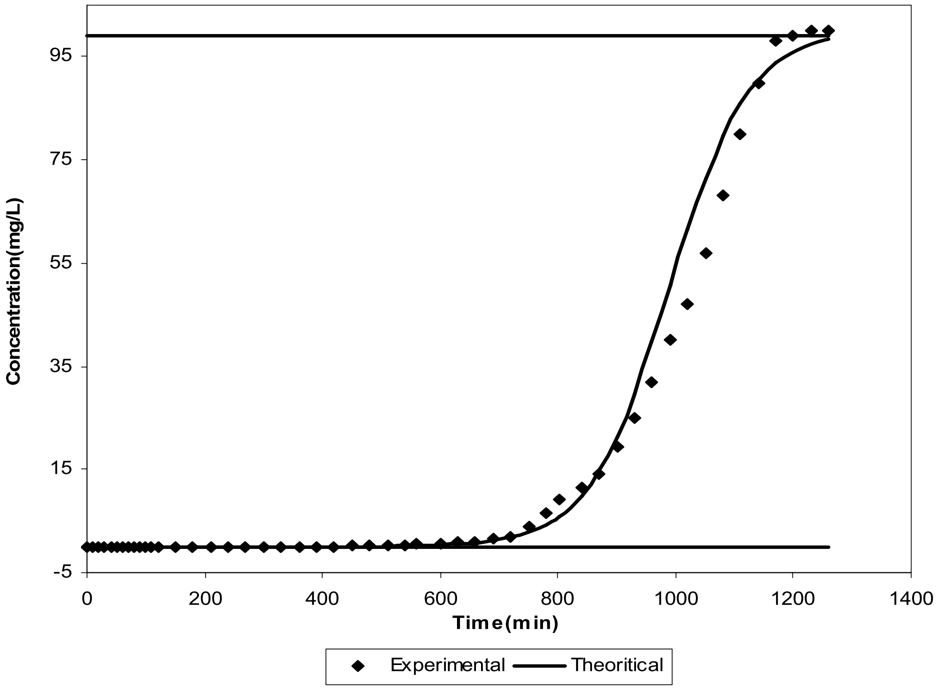

Fig. 9 Breakthrough curve

points were observed to be 420 and 1230 bed volumes for an initial Cr (VI) concentration of 100 mg/L at an initial pH of 1.7 (Fig. 9). The value of 420 bed volumes at the lower breakthrough point indicates that the material is suitable to treat Cr (VI) contaminated water. The stoichiometric breakthrough point was observed to be 1230 bed volumes, which indicates the maximum uptake value to be 98.75 mg/g of adsorbate.

In many cases, kinetics of adsorption in column has been tested using the Bohart-Adams model. So in the present study, the experimental data were fitted to the Bohart-Adams model. Bohart-Adams model is based on surface reaction theory and it assumes that equilibrium is not instantaneous. Therefore the rate of adsorption is proportional to the fraction of sorption capacity still remaining on the sorbent (Goel et al. 2005; Malc et al. 2006). The Bohart-Adams model is used for the initial part of the breakthrough curve (Aksu and Gonen 2004; Liao et al. 2004). The equation is given below:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = k_{AB} C_0 t - k_{AB} N_0 \frac{z}{U_0}$$

where C_0 and C_t are the inlet and outlet Cr(VI) concentration, respectively, z (cm) is the bed height, U_0 is the superficial velocity (cm/min), N_0 is the saturation concentration (mg/L) and k_{AB} is the mass transfer coefficient (l/mg min). In the present study the range of time was considered from the beginning to the end of the breakthrough curve. The mass transfer coefficient k_{AB} and saturation concentration N_0 values were calculated from the slope and intercept of the plot between $\ln(C_t/C_0 - 1)$ versus t. The values of k_{AB}, N_0, and regression coefficient, R^2, were found to be 0.149 (ml/mg min), 98.8 (mg/g) and 0.94, respectively. The predicted breakthrough curve from Bohart-Adams model along with the experimental breakthrough curve is shown in Fig. 9. From the R^2 it can be concluded that the experimental data fit well to the Bohart-Adams model.

From the column study, the maximum adsorption capacity of the adsorbent was found to be 98.8 mg/g at an adsorbate concentration of 100 mg/l. But in case of batch study the adsorbate concentration was varied from 400 to 700 mg/l. Therefore to compare the adsorption capacity in batch and column, uptake capacity of the adsorbent in a batch study at an adsorbate concentration of 100 mg/l was calculated using Langmuir adsorption isotherm. From the Langmuir adsorption isotherm it was observed that the maximum uptake capacity of the adsorbent in batch for adsorbate concentration of 100 mg/l is 103.2 mg/g. From the above discussion, it was concluded that the uptake capacity in both the cases matches well with ~4.3% deviation.

10 Conclusion

The acid treated weed *Salvinia cucullata,* used in this experiment was found to be a good adsorbent for the removal of Cr (VI). The Cr (VI) removal efficiency of the adsorbent is found to be increase with the increase in time, temperature adsorbate concentration, stirring speed and decrease with increase in pH and adsorbent dose. The average absolute percentage deviations (% Desv) between the experimental and calculated equilibrium uptake for each of the three-adsorption isotherm equations studied varied between 3 to 0.4%. So, experimental values were well fitted to the all three isotherm equations. The adsorption kinetics followed a pseudo 2nd order rate equation. Among film diffusion and intra-particle diffusion, film diffusion is found to be the rate controlling mechanism because of its lower diffusion coefficients. The percentage adsorption increases with increasing temperature, which indicates that, the adsorption mechanism is endothermic. Statistical design of experiments for the adsorption of Cr (VI) is used to quantify the effect of variable parameters such as time, pH, adsorbate concentration, and temperature. From the factorial design analysis it is found that pH has the most pronounced effect in increasing the percentage adsorption of Cr (VI), followed by time, temperature and the adsorbate concentration has the least effect. Column studies were carried out at the optimum operating conditions and the maximum uptake is found to be 98.75 mg/g. The Bohart-Adams model was found to be fit well to the adsorption data from the column studies.

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