

Sequestration of Cr(VI) from water using the agricultural weed – *Acharanthes Aspera*

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Abstract

In the present study, the well known agricultural weed called *Acharanthes aspera* is used to remove chromium(VI) from aqueous solution after treatment with sulphuric acid. The effect of pH, initial concentration of metal ions, contact time, and the effect of adsorbent dose are studied in order to find out the sorption capacity of the activated carbon using batch mode operations. The optimum pH value for Cr(VI) adsorption is determined as 2.0. The experimental results are fitted with the Freundlich, Langmuir and Redlich Peterson models to find out the mechanism behind the adsorption process. The kinetic data are fitted with the Lagergren-first-order, and pseudo-second-order. The Langmuir and Redlich-Peterson isotherm model and the pseudo-second-order kinetic models are found better to describe the experimental data. The maximum adsorption capacity obtained from Langmuir equation is 68.2 mg/g. From the experimental studies the activated carbon developed from *Acharanthes aspera* used as for the removal of Cr(VI) from aqueous solution.

Keywords: Adsorption Isotherms, *Acharanthes aspera*, Langmuir, Redlich-Peterson, Pseudo-Second-Order

1. Introduction

Release of large quantities of heavy metals into the natural environment has resulted in a number of environmental problems [1]. Chromium is one of the most toxic element and its removal has become a serious health concern. It is a naturally occurring element found in rocks, animals, plants, soil and in volcanic dust and gases. An important ore of chromium is chromite. Although many different oxidation states of chromium exist in the environment, only chromium(III) and (VI) are the most stable ones. chromium(III) is an essential dietary nutrient, required to potentiate insulin for normal glucose metabolism and helps the body to use sugar, protein and fat efficiently. chromium(VI) is generally considered thousand times more toxic than chromium(III) [2].

Chromium is used in industries like metallurgical, chemical, refractory, electroplating, leather tanning and textile [3,4]. These industries are the largest source of ambient chromium in surface waters. Leaching from top soil and rocks is the most important natural source of chromium entry into the water bodies. Improper disposal of solid wastes from chromate processing is the main reason for contamination of ground water with chromium. Reports are available to indicate that workers in

tanneries and chrome plating industries are found to suffer from lung cancer. Skin mucous membrane irritation and dermatitis have been observed among chrome workers [5,6]. Many cases of nasal membrane inflammation, nasal septum perforation, and chronic rhinitis have been reported among chrome workers, who are exposed to chromic acid dust and mist. Asthma is often observed among chrome platters. Dermatitis, owing to chromium pollution among the workers causes the hands, arms and face red and also causes swelling with intense itching. The first case of occupational health effects from hexavalent chromium is reported in 1827 by Cumin [7]. The recommended limit of chromium in potable water is 0.05 mg/L [8]. So many methods are used for the removal of toxic metals, that includes reverse osmosis, evaporation, ion exchange and adsorption among which adsorption is the most promising technique for the removal of chromium at ppm level [9-12]. *Acharanthes aspera* is an agricultural waste that is produced considerable quantities every year in India. In the present work, *Acharanthes aspera* was treated with sulfuric acid to produce a dehydrated carbonaceous sorbent. The capability of the produced sorbent to remove Cr(VI) from aqueous solution was tested and removal mechanism was investigated.

2. Materials and Methods

2.1. Preparation and Characterization of Sorbent

Acharanthes aspera, collected from Tiruchirappalli, India, is dried and the stem portions are chopped into small pieces. The chopped pieces are treated with concentrated sulfuric acid (Sp.gr. 1.84) in a weight ratio of 1:0.92 (AA:acid) and the resulting black product is kept in an air oven maintained at $160\pm 5^\circ\text{C}$ for 10 h, followed by washing with distilled water until it is free from excess of acid and dried at $105\pm 5^\circ\text{C}$. The carbon adsorbent obtained is designated as AAC. The carbon is ground and the portion retained between 150 and 170 μm sieves is used for the adsorption studies.

2.2. Adsorption Studies

Batch experiments was carried out by agitating the carbon with 100 ml of Cr(VI) solution (prepared from $\text{K}_2\text{Cr}_2\text{O}_7$) of desired concentration at pH 2.0 and at room temperature ($32\pm 1^\circ\text{C}$) in an orbital shaker (300 rpm). After equilibrium was achieved, samples were withdrawn from the shaker, centrifuged and the supernatant solutions was analysed for residual Cr(VI) concentration. The total Cr(VI) concentration was determined by oxidizing Cr(III) to Cr(VI) using KMnO_4 and determining final Cr(VI) content in the sample [13]. The residual chromium concentration was determined by UV (Perkin Elmer EZ301) spectrophotometer at 540 nm, using the diphenyl carbazide reagent. A calibration plots for Cr(VI) were drawn. Runs were made in triplicate.

The effect of pH on Cr(VI) removal was established by adjusting 60 mg/L of Cr(VI) solutions to different pH values using dilute HCl or NaOH and agitating each with 1.0 g/L of AAC dose for 3 h. For the initial metal concentration study, a concentration range of 10 – 80 mg/L of Cr(VI) was agitated with 1.0 g/L of AAC at pH 2.0 for 3 h. The kinetics of Cr(VI) adsorption was followed with three different initial metal concentrations of 10, 20, and 30 mg/L, each agitated separately with a fixed AAC dose of 1.0 g/L for predetermined intervals of time at pH 2.0. The effect of adsorbent concentration was studied by agitating 60 mg/L of Cr(VI) solutions with a range of AAC dose, 0.1 to 1.5 g/L, after adjusting to pH 2.0 for 3 h.

The amount of metal sorbed at time t , q_t and at equilibrium, q_e was calculated from the mass balance equation:

$$q_t = (C_0 - C_t) \frac{V}{m} \quad (1)$$

where C_0 and C_t are the initial and final metal concentrations (mg/L), respectively, V is the volume of metal solution and m is the mass of the sorbent. When t is equal to the equilibrium contact time, $C_t = C_e$, $q_t = q_e$, the amount of metal adsorbed at equilibrium, q_e is calculated using Eq. (1). Calculation and graphical representations were performed in the Microsoft Excel™ software package. In this study, a trial-and-error procedure, which is applicable to computer operation, is used to compare the best-fitting isotherms using an optimization routine to maximize the coefficient of determination between the experimental data and isotherms in the *solver* add-in in Microsoft Excel [14].

3. Results and Discussions

3.1. Characterization of the Adsorbent

The physico-chemical characteristics of AAC are summarized in Table 1. FT-IR (Perkin Elmer Spectrum One model) spectrum for AAC is shown in Fig. 1. The intense and broad absorption band around 3409 cm^{-1} is assignable to O–H stretching of hydroxyl group. As the frequency of free OH groups is sharp and is located above 3500 cm^{-1} , these vibrations are associated with hydrogen bonds between the surface O–H groups and the water molecules adsorbed by the carbon sample [15]. The band at 2924 cm^{-1} denotes the presence of stretching C–H vibrations in CH_2 or C=C–H group. The peak at 1695 cm^{-1} suggests the presence of stretching of C=O vibrations arising from groups such as lactone, quinone and carboxylic acids. The band at 1614 cm^{-1} may be due to the asymmetric and symmetric stretching COO^- vibrations or to skeletal C=C aromatic vibrations. The band appearing around 1384 cm^{-1} is due to C = S stretching vibration. The bands appearing at 1039 and 623 cm^{-1} are compatible with absorptions due to S=O and S–O stretching in species such as HSO_4^- and SO_4^{2-} . The scanning electron micrographs with 1000X magnification revealed the surface texture and morphology of the sorbent in Fig. 2. SEM is widely used to study the morphological features

and surface characteristics of the adsorbent materials.

Table 1. Characteristics of *Acharanthes aspera* (AAC) adsorbent

Characteristics	Values	Characteristics	Values
Moisture content (%)	17.85	pH	5.6
Ash content (%)	6.84	Decolorising power (mg/g)	55.2
Water soluble matter (%)	1.1	BET surface area (m ² /g)	150.61
Fixed carbon (%)	26.75	Bulk density (g/cm ³)	0.562

Figure 1. FT-IR Spectrum of AAC

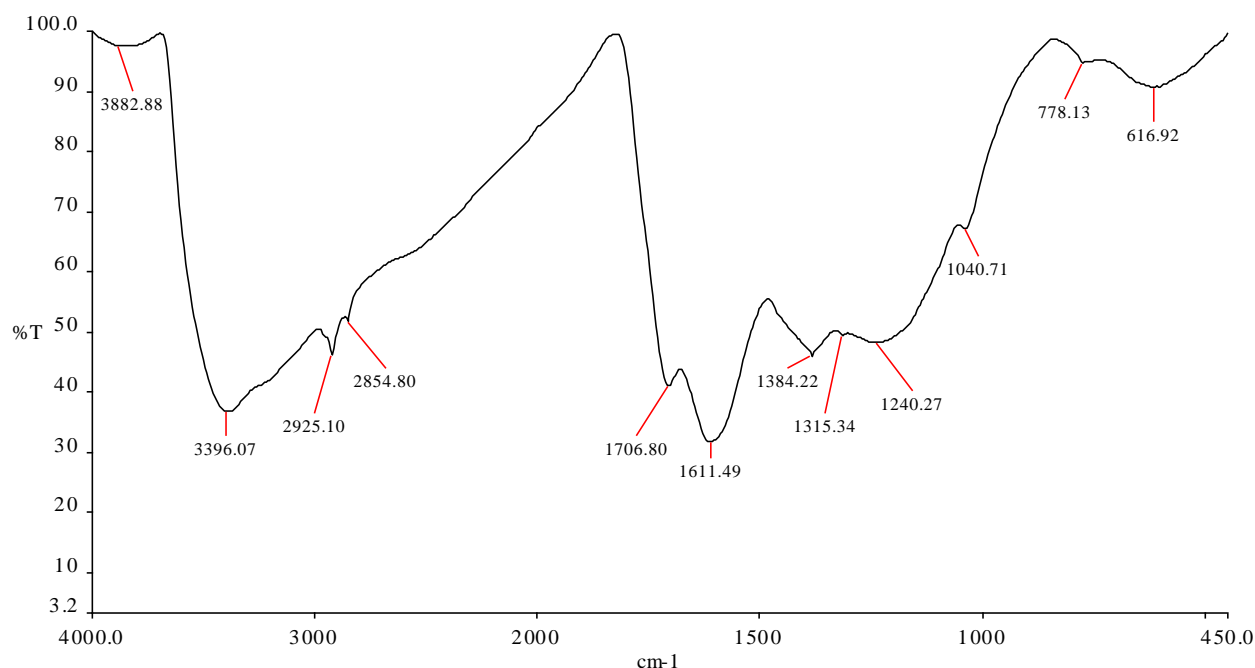
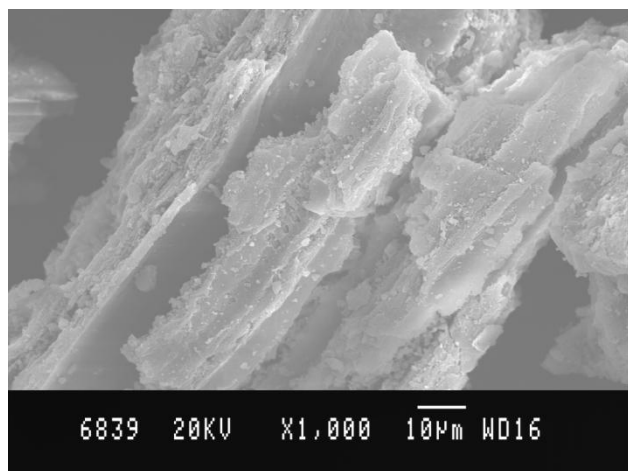


Figure 2. SEM Image of bare AAC

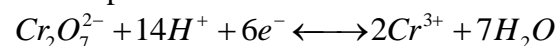


3.2. Effect of pH

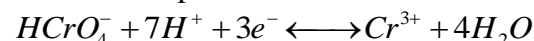
The pH of the solutions has been identified as the most important variable governing metal ion sorption. The effect of pH on sorption efficiency of Cr(VI) is maximum at pH 2.0. On increasing the pH beyond 2.0, there is a progressive decrease in the Cr(VI) adsorption by AAC. The high chromium(VI) removal at low pH values is probably due to reduction of

chromium(VI) to chromium(III) in accordance with the following reactions taking place at low and moderate pH values [16-18].

At low pH



At moderate pH



The predominant anionic forms at low pH values are $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- which have the tendency to oxidize the adsorbent surface thereby getting itself reduced and remains in solution as Cr(III). Therefore it is envisaged that the removal of Cr(VI) is governed by both chemical reduction [Cr(VI) to Cr(III)] and physico-chemical adsorption [mainly Cr(VI)]. It is reported that Cr(III) adsorption is not favored at low pH values due to larger coordination sphere with water [19]. The tendency of the adsorbent surface to reduce Cr(VI) to Cr(III) and the unfavourability of Cr(III) adsorption at low pH values explains the higher Cr(VI) removal observed where the Cr(VI) reduced to Cr(III) is not accounted. Therefore in order to

find out the amount of Cr(VI) that has been reduced to Cr(III), after performing the adsorption experiments, one portion of the solution is analysed for residual Cr(VI) present in solution. This corresponds to chromium present as Cr(VI) in solution. Another portion was oxidized using KMnO_4 and this gives the amount of total chromium present in solution. On subtracting these two, the amount of Cr(VI) that has been reduced to Cr(III) can be obtained.

3.3. Adsorption Isotherms

The distribution of solute between the liquid phase and the sorbent is a measure of the position of equilibrium in the sorption process and can be generally expressed by two of the most popular isotherm models, namely, Freundlich [20] and Langmuir [21] isotherms represented as Eqs. (2) and (3), in their nonlinear forms.

$$q_e = K_F C_e^{1/n} \quad (2)$$

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (3)$$

where, K_F and n are the Freundlich constants. and q_m and K_a are the Langmuir constants representing sorption capacity (mg/g) and energy of sorption (L/mg), respectively.

For practical design purposes in a system operating over a wide range of concentration an intermediate isotherm is often a more realistic representation of the system. Therefore, in addition to the above isotherms, one more isotherm that combine the features of Freundlich and Langmuir isotherms was considered. That is: Redlich-Peterson [22] isotherm model represented as:

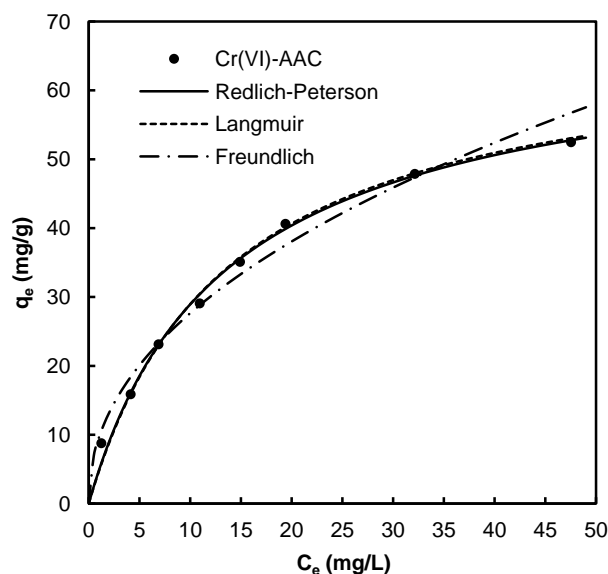
$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (4)$$

It has three isotherm constants, namely, A (L/g), B (L/mg) and g , which characterize the isotherm. In the above equation, constant g is the exponent, which lies between 0 and 1. If constant g is equal to one, the equation modifies to the Langmuir model. If constant g is equal to zero, then the equation changes to Henry's law equation. In addition, Freundlich is a special case of the Redlich-Peterson isotherm when constants A and B were much bigger than one [23].

The results derived from the equilibrium initial metal concentration study were modeled

with the isotherms discussed above. Fitted curves of the each isotherm model with the experimental data are shown in Fig. 3 and the fitting sorption parameters derived for the models are presented in Table 2. It is clear from the Table 2 that the Langmuir and Redlich-Peterson isotherm model gives a better fit of the experimental data as evident from the higher r^2 values obtained compared to other model.

Figure 3. Fitted Isotherm models for Cr(VI) adsorption on AAC



The Freundlich constant, n value obtained is in between 1 to 10 (2.17) which indicates the favourable adsorption of Cr(VI) on AAC [24]. The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant separation factor called equilibrium parameter R_L [25], which is defined as, $R_L = 1/(1 + K_a C_0)$ where K_a is the Langmuir constant and C_0 is the initial concentration. The R_L value, indicates the type of isotherm and the values obtained are in the range of 0.103 – 0.535, which indicate that the adsorption of Cr(VI) on AAC is favourable for the concentration range studied.

3.4. Sorption Kinetics

The agitation time experimental results showed a progressive increase in Cr(VI) uptake with time for all the initial concentrations studied. With increase in Cr(VI) concentration from 10 to 30 mg/L, the amount of Cr(VI) adsorbed at equilibrium time increased from 10.0 to 28.7 mg/g, indicating that the Cr(VI) removal by adsorption on AAC is concentration dependent. This is obvious because more efficient utilization of the adsorption capacities

of the adsorbent is expected due to a greater driving force by a higher concentration gradient pressure.

Table 2. Parameters for the fitted isotherm models for the AAC-Cr(VI) system

Isotherm	Parameters	
Langmuir	q_m (mg/g)	68.2
	K_a (L/mg)	0.074
	r^2	0.993
Freundlich	$1/n$	0.461
	K_F (L/g)	9.55
	r^2	0.975
Redlich-Peterson	g	0.981
	B (L/mg)	0.08
	A (L/g)	5.2
	r^2	0.993

The kinetic experimental results were fitted with various kinetic model equations namely, Lagergren's pseudo-first-order and pseudo-second-order to find out which of these models best define the experimental data points. Lagergren pseudo-first-order [26,27] equation which is expressed as:

$$q_t = q_e [1 - \exp(-k_1 t)] \tag{5}$$

Where q_e and q_t are the amounts of Cr(VI) adsorbed at equilibrium and at time t in mg/g, respectively, and k_1 is the pseudo-first order rate constant (min^{-1}).

The pseudo-second-order kinetic model [28,29] is expressed as:

Table 3. Parameters for the fitted kinetic models for the AAC-Cr(VI) system

C_0 mg/L	Pseudo-first order			Pseudo-second order			
	q_1 mg/g	k_1 min^{-1}	r^2	q_e mg/g	k_2 g/mg min	h mg/g min	r^2
10	8.67	0.0238	0.987	11.7	0.00175	0.238	0.992
20	15.9	0.0318	0.990	19.6	0.00165	0.634	0.993
30	20.6	0.0259	0.987	25.7	0.00101	0.667	0.998

3.5. Effect of Carbon Concentration

Effect of AAC dose on Cr(VI) sorption was studied by varying the dose from 0.1 to 1.5 g/L, taking 60 mg/L as initial metal concentration. The amount of Cr(VI) sorption increased with increase in carbon dose and reached a maximum value after a particular dose. It is apparent that maximum removal from 60 mg/L of Cr(VI) solution was achieved at an optimum carbon dose of 1.0 g/L. While increasing the carbon

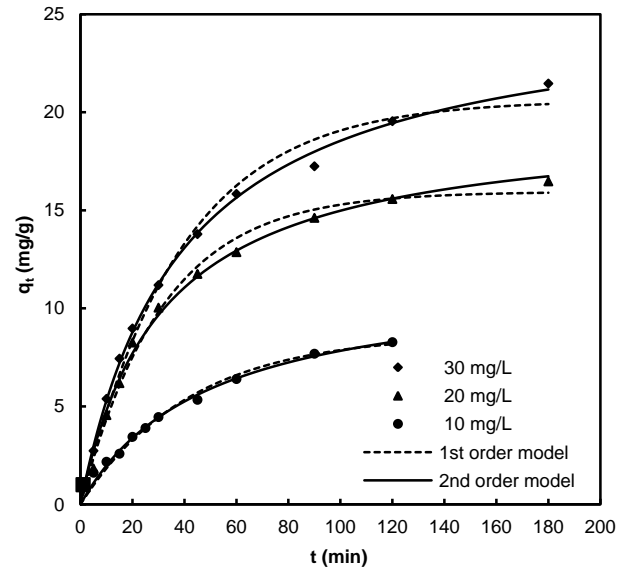
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

The initial adsorption rate is $h = k_2 q_e^2$, then the Eq. (6) becomes [28,29]:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \tag{7}$$

where the initial adsorption rate (h), the equilibrium adsorption capacity (q_e), and the second order constants k_2 (g/mg min). The fitted curves of these kinetic models along with the experimental data are illustrated in Fig. 4 and the fitted parameters of the models are presented in Table 3.

Figure 4. Fitted kinetic model for Cr(VI) on AAC system



dose from 0.1 to 1.5 g/L, the sorption of metal ions per unit weight of carbon decreased from 142.85 to 32.27 mg/g. There are many factors that can contribute to this sorbent concentration effect. The first and most important factor is that sorption sites remain unsaturated during the sorption reaction. This is due to the fact that as the dose of carbon is increased, there is less commensurate increase in sorption resulting from the lower sorptive capacity utilization of the carbon [30]. The second cause may be the

aggregation/agglomeration of carbon particles at higher concentrations, which would lead to a decrease in the surface area and an increase in the diffusion path length [31]. The particle interaction at higher carbon concentration may also help to desorb some of the loosely bound metal ions from the sorbent surface.

3.6. Desorption Studies

Desorption studies were carried to recover the Cr(VI) adsorbed onto adsorbent which would help to regenerate and recycle the spent adsorbent. After performing adsorption experiment with 10 mg/L of Cr(VI) solution and 1 g/L of sorbent at the optimum pH of the system, the spent adsorbent were washed with distilled water to remove any unadsorbed metal ion. The metal loaded adsorbents were then agitated with 100 mL of 0.1 M NaOH for 1 h. About 70 % of Cr(VI) was recovered from the spent AAC.

4. Conclusion

The adsorption kinetics and isotherm of Cr(VI) removal using AAC was carried out in batch experimental system. The following conclusions can be drawn based on the above study. The adsorption strongly depends on the parameters such as initial concentration of Cr(VI), pH, carbon dose and contact time. The rate of adsorption follows pseudo-second-order rate equation. The spent carbon can be reused. The Proposed sorbent is an efficient, environment friendly and can reduce the amount of toxic chromium ions discharged by the industries.

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