

Original Research Article

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Efficiency of Water Hyacinth Biomass on Removal and Recovery of Chromium from Aqueous Solution through Column Study

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ABSTRACT

The global issue associated with the health of environment and human is the quality of water. A serious threat to the aquatic environment through anthropogenic activities is the heavy metal pollution. Therefore, a suitable cleanup technology should be there for making our environment pollution free. This study reports the sorption behaviour of Cr(III) from aqueous solution by water hyacinth biomass through fixed bed column experiment at bed height of 25 cm, initial Cr (III) concentration of 500 mg L⁻¹ and varying flow rates (0.5, 1.0, 1.5 ml minute⁻¹) at optimum pH of 4.0. Greater adsorption capacity of 2.95 mg g⁻¹ was recorded at solute flow rate of 0.5 ml minute⁻¹. On increasing the flow rate, the unit adsorption, percent removal, exhaustion and breakthrough time gets declined. Thomas model was found to highly suitable which gave an idea that internal and external diffusion of solute molecules won't be restricted. The water hyacinth biomass loaded with Cr (III) was desorbed with 0.1 M HCl at the flow rate of 0.5 ml minute⁻¹ and regeneration efficiency of the biomass was examined for about three sorption and desorption cycles. The per cent Cr adsorbed and desorbed was found be 81.7 and 57.3 % respectively in cycle 1 whereas it was declined to 28.0 and 14.5 % in cycle 3. Considering the regeneration efficiency was found to be 62.7 % cycle 2 which was declined to 23.1 % in cycle 3. Thus, it can be concluded that water hyacinth biomass can be effectively utilized for Cr (III) removal in fixed bed column mode and this technology can be upgraded to larger scale.

Keywords

Adsorption, Carbon, Chromium, Recovery, Regeneration

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Introduction

Deterioration of water quality is of global concern today which dragged the people to an appalling situation. A diverse range of toxic heavy metal ions from the industrial discharge is a culprit in contaminating the water. The non- biodegradable and persistence nature of these contaminating metal ions urged the scientific community to work on their removal. Among the industries, tanneries

contribute to chromium (Cr) contamination on a larger scale as only 60-70 per cent of the Cr salts utilized in the tanning process reacts with the hides (Caughlofer, 1986) and the remnant unutilized Cr left in tanning exhaust bath. The foresaid wastewater when allowed for deperation, results in the production of large quantities of sludge with Cr. On an average, the effluent treatment plants of Tamil Nadu alone generate about 100 tonnes of sludge per day (Ahmed and Kashif, 2014).

The disposal of this sludge in soils affects the environmental ambience and nearly 50,000 hectares of agricultural lands in vellore district of Tamil Nadu was severely affected by Cr where 60 per cent of the tanneries in india were located (Mahimairaja *et al.*, 2000). This toxic metal enters the groundwater through leaching during seasonal rains with their concentration exceeding the maximum permissible limits recommended. It has been evident that a single tanning unit is capable of polluting the groundwater for a radius 7-8 kms (Parameswari, 2009; Brindha *et al.*, 2010). To overcome the aforesaid lacuna and to sustain the environment, there is a necessity to remove these hazardous metal ions.

Both batch and column type adsorption experiments were carried out for removing that heavy metal. Adsorption capacity of the adsorbents for various toxic heavy metals at laboratory scale can be determined by batch type adsorption experiments but to know the rate of transport and diffusion of the metal ions in large scale pre-commercial treatment plants, column type of adsorption experiments will be more helpful. Comparing the batch mode experiments, column experiments are more useful as it can treat large quantities of contaminated water with specified adsorbent mass. Though this type of column experiments has greater advantage, only a few studies were reported for the heavy metal removal. The breakthrough curves obtained from the column experiment data can be utilized to study the column dynamics. By predicting this breakthrough point, a column can be designed with some up gradations for an industrial scale. A lot of batch type experiments were carried out to study the heavy metal removal from aqueous system, but no column study has been reported for Cr (III) removal from aqueous system utilizing water hyacinth biomass as adsorbent. To understand the applicability of the adsorbents

in real situations, a series of desorption and degeneration experiments were carried out. Therefore, as an extension of our batch experiment, the present column study was formulated with objective to remove this toxic heavy metal from the aqueous solution by utilizing water hyacinth biomass as adsorbent.

Materials and Methods

Preparation of water hyacinth biomass

Water hyacinth plants were collected from Vaigai dam of Theni district, Tamil Nadu, India. The aquaphytes were washed to remove the sediments and other small floating fresh water aquatic weeds like *Lemna* sp. After washing, the plants were dried, ground with a blender and sieved (desirable size) to obtain powdered biomass as adsorbent.

Experimental setup for column experiment

The experimental design consists of glass column made up of borosilicate with the flow of adsorbate in downward mode as depicted in Fig. 1. The length and internal diameter of the column was about 52.7 and 4.6 cm, respectively. The wire mesh (0.2mm) and muslin cloth were placed at the bottom of each column and sand of 1cm height each in the top and bottom of column were placed to avoid the washing of adsorbents. The column's bottom had a closed end and top of the column was closed with stop cork. The adsorbent [biomass (106g)] of 0.2 mm size was packed in a column with the bed height of 25cm and the resulting bulk density was 0.255 g cm^{-3} . The chromium solution of 500 mg L^{-1} , pH of 4.0 was fed in a downward mode (towards gravity) into the packed bed at varying flow rates of 0.5, 1.0 and 1.5 ml min^{-1} at laboratory conditions. The treated outlet samples were collected at regular time intervals to determine the residual Cr concentration. The column operation was

ceased at a stage where there was no Cr sorption, and the inlet and outlet Cr concentration were equal (known as exhaustion of the column). The treated effluent samples from the column were analyzed using AAS (Perkin Elmer AA400). Break through curves were determined to assess the efficiency of the column adsorption study. Breakthrough curve is obtained by plotting C_t/C_0 against time (t) (where C_0 is the initial concentration of adsorbate in inlet and C_t is the concentration of adsorbate at time, t). Breakthrough point is the point where the ration of C_t to C_0 varies from 0.05 to 0.90. The 50% breakthrough time occurs when C_t/C_0 is 0.50.

Modeling of column data

The sorption capacity of Cr(III) onto water hyacinth biomass at different flow rates can be well explained by using mathematical models like Thomas model. It is explained below.

Thomas model

It is an indispensable model that helps in determining the maximum capacity of the Cr to the biomass in packed column. This model relies on langmuir isotherm and pseudo second order kinetics without any axial dispersion (Thomas, 1944). Thomas model for adsorption in a column is given by eqn. (1) (Chowdhury *et al.*, 2012).

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{K_T q_0 x}{Q} - K_T C_0 t\right)} \longrightarrow (1)$$

Where, C_t is the Cr concentration in outlet at time t (mg L^{-1}), C_0 is the Cr concentration in the inlet (mg L^{-1}), K_T is the kinetic rate constant of thomas model ($\text{ml mg}^{-1} \text{min}^{-1}$), Q is the flow rate (ml minute^{-1}), q_0 is the Cr adsorption capacity to the biomass (mg g^{-1}), x is the mass of the biomass (g), t is the time

(minutes). The constants (K_T and q_0) in thomas model were determined from the slope and intercept of plot between $\ln(C_0/C_t - 1)$ Vs t .

Desorption and regeneration of adsorbent

After the sorption study, the column materials were washed with distilled water to remove the ions which were not bind to the biomass. To assess the Cr recovery from the biomass, a column desorption study was conducted with the metal desorbents. For this, the biomass loaded with Cr ions were desorbed by passing 0.1 M HCl at the flow rate of $0.5 \text{ ml minute}^{-1}$ through the column operated under flow rate of 0.5 ml min^{-1} and Cr concentration of 500 mg L^{-1} in a downward direction. The outlet was collected at regular time intervals (30 minutes) and was analyzed for Cr as explained in previous section. The experiment was continued till there was no prominent Cr concentration in outlet.

After elution, the packed column was washed with distilled water till the pH of the wash effluent became neutral. The regenerated biomass was again utilized in adsorption experiment to study its reusability. The adsorption capacity of the biomass was studied for successive three cycles of sorption and desorption.

The amount of Cr recovered from the biomass was calculated through eqn. (4)

$$\text{Cr desorbed (\%)} = \frac{q_d}{q_a} \times 100 \longrightarrow (4)$$

Where q_a is the amount of Cr adsorbed (mg), q_d is the amount of Cr desorbed by 0.1 M HCl (mg)

The regeneration efficiency of the biomass was calculated through eqn. (5)

$$\text{Recovery efficiency (\%)} = \frac{q_r}{q_o} \times 100 \rightarrow 5$$

Where q_o is the Cr adsorption capacity of the biomass originally (mg g^{-1}), q_r is the Cr adsorption capacity of the regenerated biomass in successive regeneration cycles (mg g^{-1})

Results and Discussion

Effect of solute flow rate on Cr(III) adsorption by water hyacinth biomass

The efficiency of the water hyacinth biomass packed in the column against varying flow rate of Cr (III) can be evaluated by the unit adsorption, time required for the breakthrough and shape of the breakthrough curve. Flow rate of the solute has a profound influence on the unit adsorption and percent removal of Cr. The upshot of varying flow rates (0.5, 1.0, 1.5 ml minute^{-1}) with constant conditions of bed height (25 cm), Cr (III) concentration (500 mg L^{-1}) and solution pH (4.0) is depicted in Fig.2.

The experimental results revealed that unit adsorption of 2.95, 1.12 and 0.82 mg Cr (III) per gram of biomass at solute flow rates of 0.5, 1.0 and 1.5 ml minute^{-1} respectively (Table1). Higher unit adsorption of Cr (III) and per cent adsorption at lower flow rate of 0.5 ml minute^{-1} might be due to the availability of the sufficient residence or retention time for the solute molecule to make contact with adsorbent causing complete diffusion of solute molecules into the sorption sites (Muthusamy and Venkatachalam, 2015; Premalatha *et al.*, 2018).

At higher flow rate (1.5 ml minute^{-1}), shorter contact time was needed to attain a exhaustion point whereas it was longer in case of lower solute flow rates (0.5 ml minute^{-1}). Similar tendency was observed by Chowdhury and his co-workers in lignocellulose wastes

(Chowdhury *et al.*, 2014). For adsorption of Cr (III) onto biomass, 50% breakthrough time and exhaustion time was 21 hrs and 25 hrs 30 minutes respectively at solute flow rate of 0.5 ml minute^{-1} . On increasing the flow rate, the exhaustion and breakthrough time gets declined i.e., at the flow rate of 1.0 ml minute^{-1} , the 50% breakthrough and exhaustion time was 4 hrs and 8 hrs respectively. With the consideration of unit adsorption, percent removal, solute flow rate of 0.5 ml minute^{-1} was found be optimum. It was obvious from the figure that, increasing the flow rate of the Cr (III) makes sharper and steeper breakthrough curves whereas it was very gentle in case of lower flow rate of 0.5 ml minute^{-1} . The prominent S- shaped breakthrough curve was noticed in the present study at solute flow rate of 0.5 ml minute^{-1} .

Considering the Cr adsorption capacity, the present column experiment recorded a very low unit Cr adsorption compared to batch studies (76.9 mg g^{-1}). Higher unit Cr adsorption in batch experiment might be due to continuous shaking of the adsorbent in the orbital shaker for a predetermined time which provoked the percent Cr adsorption leaving lesser quantities in the liquid phase.

Lower Cr adsorption capacity in the column mode might be the fact that, the concentration of the adsorbate molecules are increased continuously making the sorption, an irreversible process (Jain *et al.*, 2015). Similarly, Setshedi and his co-workers reported a huge reduction in unit adsorption of Cr(VI) by adsorbent like carbon from stem wastes of sunflower plants and calcium alginate beads in column mode of experiment compared to batch studies (Setshedi *et al.*, 2015). Apart from this, the possible reasons for reduced adsorption capacity are non static nature of adsorbate, tight packing and lack of stirring action in column mode of experiment (Goel *et al.*, 2005).

Mathematical modeling

The adsorption of Cr (III) onto biomass in a column study undergoes a dynamic equilibrium which can be better explained through mathematical models. In the present investigation, the data obtained from the above column study to assess the influence of solute flow rate on Cr (III) adsorption was fitted to models like Thomas models and the parameters determined from the above model was represented in Table 2.

The constant, K_T of Thomas model for adsorption of Cr (III) onto biomass was 40×10^{-4} , 40×10^{-4} and $42 \times 10^{-4} \text{L mg}^{-1} \text{min}^{-1}$ for flow rates of 0.5, 1.0 and 1.5ml minute^{-1}

respectively. The Cr (III) sorption capacity (q_0) was found to be 3043.6, 1197.9 and $874.7 \mu\text{g g}^{-1}$ at flow rates of 0.5, 1.0 and 1.5ml minute^{-1} respectively in biomass. The q_0 had good agreement with experimental q_0 ($q_{0\text{exp}}$). i.e., the q_0 for the adsorption for Cr (III) onto biomass predicted from the model was 3.04mg g^{-1} which was close to 2.95mg g^{-1} recorded in the experiment. In Thomas model, on increasing the flow rate of the adsorbate, the values of K_T increased but q_0 decreased. This is in harmony with the research findings of Baral *et al.*, (2009) for adsorption of Cr (VI) onto *Salvinia*. The suitability of Thomas model gives an idea that internal and external diffusion of solute molecules won't be restricted (Aksu and Gonen, 2004).

Table.1 Optimization of flow rate for adsorption of Cr (III) onto adsorbent

Flow rate (ml minute^{-1})	Metal adsorbed (mg g^{-1})	$t_{0.5b}$ (hrs)	t_e (hrs)	% Adsorbed
0.5	2.95	21.0	25.5	81.7
1.0	1.12	4.0	8.0	49.3
1.5	0.82	2.0	6.0	32.1

* C_0 - Initial concentration of metal (mg L^{-1}), $t_{0.5b}$ - time taken for 50% breakthrough (hrs), t_e - time taken for exhaustion (hrs)

Table.2 Thomas model constants at different flow rates

Constants	FR- 0.5ml minute^{-1}	FR- 1.0ml minute^{-1}	FR- 1.5ml minute^{-1}
Thomas model			
K_T ($\text{L mg}^{-1} \text{min}^{-1}$)	40×10^{-4}	40×10^{-4}	42×10^{-4}
q_0 ($\mu\text{g g}^{-1}$)	3043.6	1197.9	874.7
$q_{0\text{exp}}$ ($\mu\text{g g}^{-1}$)	2947.9	1115.3	816.5
R^2	0.972	0.993	0.877

Table.3 Adsorption of Cr onto adsorbent and desorption with 0.1 M HCl in 3 consecutive cycles

Cycle	$t_{0.5b}$ (hrs)	t_e (hrs)	Adsorption capacity (mg g^{-1})	% Adsorption	% Desorption	Regeneration efficiency (%)
1	21.0	25.5	2.95	81.7	57.3	-
2	12.5	15.0	1.85	55.5	30.4	62.7
3	3.0	8.5	0.42	28.0	14.5	23.1

* $t_{0.5b}$ - time taken for 50% breakthrough (hrs), t_e - time taken for exhaustion (hrs), Bed height- 25 cm, flow rate- 0.5 ml minute⁻¹

Fig.1 Experimental setup of column experiment

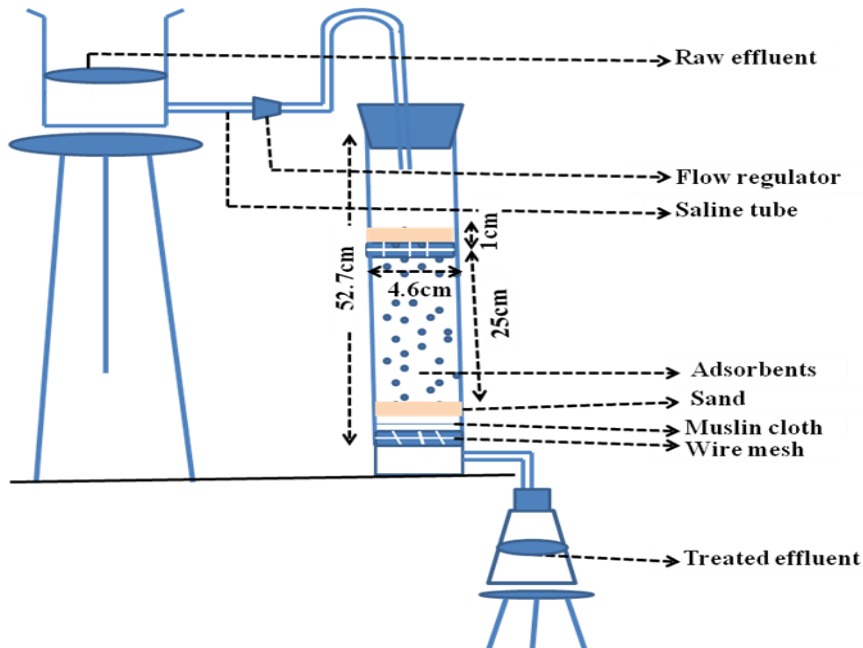
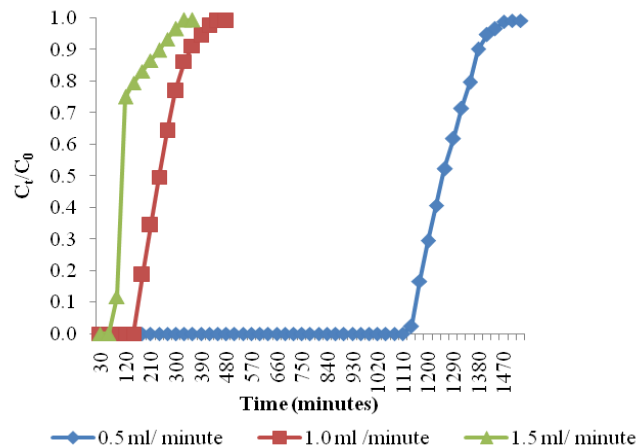


Fig.2 Breakthrough curve for varying solute flow rates at initial Cr(III) concentration of 500mg L^{-1} and bed height of 25cm



Desorption and degeneration of biomass

For a biosorption experiment, regeneration of the adsorbents for the successive reuse should be considered. As the regeneration cycle proceeds, the per cent sorption of Cr onto biomass gets declined which might be due to the reduced per cent desorption of Cr from the adsorbate sorbed biomass. From the experiment, it was clear that as regeneration cycle proceeds, the percent Cr adsorption, breakthrough and exhaustion time gets reduced. Similar findings were reported by Sivaprakash and his co-workers in their study on biosorption of Cu (II) from aqueous solution (Sivaprakash *et al.*, 2010). This decline in the percent sorption in subsequent sorption cycles might be due to the structural cell wall breakdown or damage to binding sites aggravated by desorbing agents or blockage of the binding sites or due to the lack of the eluant's suitability reducing the number of sites available for successive sorption (Lezcano *et al.*, 2011). Considering the regeneration capacity, the sorption and desorption experiment was continued for 3 cycles.

A lot of desorption experiments has been carried in past utilizing acids, base and complexing agents but acids were found be better performing with higher per cent desorption of cationic heavy metals (Stirk and Van Staden, 2002). Hence in the present investigation, the mineral acids were utilized as the desorbing agents. The breakthrough time, exhaustion time, Cr adsorption capacity, % Cr adsorption, % Cr desorption and regeneration efficiency calculated for three cycles is given in Table3. The per cent Cr adsorbed and desorbed was found be 81.7 and 57.3 % respectively in cycle1 whereas it was declined to 28.0 and 14.5 % in cycle 3. The regeneration efficiency was found to be 62.7 % cycle 2 which was declined to 23.1 % in cycle 3. The parameters like breakthrough

time, Cr adsorption capacity and % Cr adsorption declined on increasing the regeneration cycles which shows the deterioration of the sorption sites present in the biomass. The decline Cr adsorption capacity and per cent adsorption might be due to the reduction in the per cent Cr desorption from biomass.

In conclusion, the water hyacinth biomass was utilized in a column experiment for Cr (III) removal. The solute flow rate of 0.5 ml minute⁻¹ was found to be optimum in fixed bed column experiment. Thomas model was found to highly suitable which gave an idea that internal and external diffusion of solute molecules won't be restricted. From the regeneration studies, it was evident that 0.1 M HCl had greater tendency to desorb Cr level. Thus, it can be concluded that water hyacinth biomass can be effectively utilized for Cr (III) removal in fixed bed column mode and this technology can be upgraded to larger scale.

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