Chromium (VI) removal from aqueous solutions using *Eichhornia* as an adsorbent

Neetu Rani, Bhupender Singh and Tuisem Shimrah

ABSTRACT

The study was carried out to check the potential of water hyacinth, *Eichhornia crassipes,* to remove chromium (VI) in batch process. Powder was prepared from dried *Eichhornia* (particle size 0.3 mm and 1.0 mm). The influence of various parameters on adsorption (pH, dose, contact time, temperature) was studied. The Cr(VI) removal was 60.9% and 79.2% for 1.00 mm and 0.3 mm particles of *Eichhornia* treated (ET) after 30 min contact time and 52.7% and 53.4% for 1.00 mm and 0.3 mm particles of *Eichhornia* untreated (EU) after 75 min contact time respectively. The optimum pH for both adsorbents was found to be 2.0 and optimum dose was found to be 0.4 g 100 ml^{-1} for ET and 0.6 g 100 ml^{-1} for EU. Maximum adsorption occurred at room temperature (26 ± 1 °C) in case of both ET and EU, respectively. The adsorption process followed the first order mechanism as well as the Langmuir isotherm. Finally, it was concluded that the adsorbent prepared from *Eichhornia* is very effective in removing Cr(VI) and it can be used for industrial wastewater treatment.

Key words | adsorption, adsorption isotherm, *Eichhornia*, intraparticle diffusion, spectrophotometer

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INTRODUCTION

The discharge of heavy metals into aquatic ecosystems has become a matter of concern over the last few decades. The major sources of heavy metal contamination are the industrial effluents that adversely affect water resources, soil fertility, aquatic organisms and ecosystem integrity. Metal ions in wastewater can cause serious toxicological problems and thus are dangerous to the environment and human beings (Yu *et al.* 2011; Kargar *et al.* 2012). Hexavalent chromium (Cr(VI)) is highly toxic and carcinogenic. Waste containing Cr(VI) in solution may result from a variety of operations like steel manufacture, paint and pigment production, electroplating, leather tanning and chemical manufacturing (Sharma 2001; Hu *et al.* 2003). Hence the element has become a significant constituent of sewage and soil and is a potentially serious pollutant. The permissible limit of Cr(VI) for potable water is 0.05 mg/L, and 0.1 mg/L for discharge to inland surface water. Human health is highly affected when exposed to Cr(VI) in excess of the permissible limit. It affects the lungs, liver, nervous system and kidneys in mammals. Therefore, it is imperative to remove chromium from industrial effluent before discharging it into the water. Reduction-precipitation, coagulation, reverse osmosis and ion exchange are widely practiced techniques for Cr(VI) removal (Iqbal *et al.* 2002; Ali 2010). These conventional methods cannot completely remove toxic metals and moreover these techniques are expensive (Ali *et al.* 2012; Khan *et al.* 2013). Removal of the Cr(VI) from industrial wastewater through adsorption is an effective alternative due to its easy operation and economic viability. Materials already used for removal of hexavalent chromium include activated carbon prepared from ground nut husk, coconut sawdust, *Hevea brasiliensis* sawdust and rice husk ash (Periyasamy *et al.* 1991; Selvi *et al.* 2001; Karthikeyan *et al.* 2005; Singh &

Singh 2012), as well as clay, pine needle powder and guar gum–nano zinc oxide biocomposite (Bhattacharya & Gupta 2006; Hadjmohammadi *et al.* 2011; Khan *et al.* 2013). However, there is some need to develop more efficient and locally available cheap adsorbents for the removal of Cr(VI).

Water hyacinth, *Eichhornia crassipes*, is a floating macrophyte whose requirement for nutrients and explosive growth rate has been put to use in cleaning up municipal and agriculture wastewater. It has been discovered that *Eichhornia*'s uptake of nutrients can be turned in a more useful direction. Its enormous biomass production rate, high tolerance to pollution and heavy metal and nutrient absorption capacities qualify it for use in wastewater treatment (Ingole & Bhole 2003; Singhal & Rai 2003; Liao & Chang 2004). The plant has been shown to accumulate trace elements such as Cu, Fe, Cr, Pb, Cd and Zn from textile effluent (Priya & Selvan 2014). Considering the applications and utilization of *Eichhornia* in the above-mentioned examples, we have tested its capability to remove Cr(VI) from aqueous solutions in the present study.

MATERIALS AND METHODS

Preparation and characterization of adsorbent

Eichornia utilized for the preparation of adsorbents was procured from the local fields in Delhi. It was washed with distilled water several times and kept in an oven overnight at 120 °C for thermal activation, and was then ground to fine powder and sieved through a standard sieve (Sonar GSMS, Mumbai, India) to obtain particles of size up to 0.3 and 1.0 mm. This was termed untreated *Eichhornia* (EU). The prepared *Eichhornia* was treated with 1% formaldehyde solution to remove the color and then with distilled water to remove impurities and excess formaldehyde and oven-dried at 105 °C for 12 hours to prepare *Eichhornia*-treated (ET) adsorbent. The various physico-chemical characteristics of *Eichhornia* (treated and untreated) are presented in Table 1.

Reagent preparation

All the chemicals used for preparation of reagents were of AR grade. Potassium dichromate, sodium thiosulfate,

Table 1 | Characteristics of adsorbents

Parameter	ET (0.3 mm)	EU (0.3 mm)
pH	7.2	7.2
Conductivity ($\mu S\ cm^{-1}$)	2.3	2.3
Bulk density ($g\ cc^{-1}$)	0.80	0.75
Moisture (%)	10	8.69
Volatile matter (%)	26.50	26.50
Solubility in water (%)	1.35	1.39
Solubility in acid (%, 0.25 M HCl)	1.01	1.02
Surface area ($m^2\ g^{-1}$)	327	215
Loss on ignition (%)	51.5	52
Porosity (%)	14.89	15.72
Particle density ($g\ cm^{-2}$)	0.94	0.89

Note: pH and conductivity were measured in the suspension phase using pH and EC meters, respectively.

sodium hydroxide, potassium iodide (all Merck, India) and hydrochloric acid (Qualigens, India) were used for preparation of reagents. The stock solution of Cr(VI) was prepared by dissolving a known quantity of potassium dichromate ($K_2Cr_2O_7$) in de-ionized water, and then diluting to desired concentrations.

Adsorption experiments

All the studies were carried out at fixed agitation speed at room temperature (26 ± 1 °C) in a batch mode process. For this, 100 mL test solution of known concentration was added to known amount of adsorbent in a conical flask. The mixture was stirred on a mechanical shaker at constant speed for the desired contact time. The conical flask was allowed to stand for 2 min for settling of adsorbent. The residual concentration of Cr(VI) ions in the supernatant was determined spectrophotometrically and described in standard methods using sodium 1,5-diphenylcarbazide at 540 nm wavelength (APHA 1985). The batch study was conducted to study the effect of pH (2–10), amount of adsorbent (0.1–1.0 g 100 ml^{-1}) and contact time (15–90 min) on the removal of Cr(VI).

RESULTS AND DISCUSSION

Finding the optimum pH, dose and contact time is very important for determining the maximum possible adsorbate

removal. For this purpose, 100 mL of test solution of known concentration was added to each conical flask and equilibrated with an adsorbent dose of 0.5 g while varying pH.

Effect of pH

pH is an important factor that controls the adsorption process. The effect of pH on removal of Cr(VI) was studied at pH 2.0 to 10.0. Results are shown in Figure 1. The maximum removal of Cr(VI) was found to be 53.6% and 67.8% for 1.0 mm and 0.3 mm ET; and 43.6% and 44.9% for 1 mm and 0.3 mm EU, respectively, at pH 2. Thus, high adsorption of Cr(VI) was observed at low pH and the removal decreased with increase in pH. *Eichhornia* contains many functional groups. The variation in adsorption may be due to the type and ionic state of these functional groups and metal chemistry in solution (Matheickal *et al.* 1999). At acidic pH, the predominant species of Cr(VI) were Cr_2O7^{2-}, $HCr_2O_7^-$ and CrO_4^{2-}. The hexavalent species exist primarily as chromic acid (H_2CrO_4) and its salts depending on the pH. The predominant species present, as a function of pH, are H_2CrO_4 at pH less than or about 1, $HCrO_4^-$ at pH between 1 and 6 and CrO_4^{2-} at pH 6 or above. It can be said that the removal of Cr(VI) at low pH is due to the electrostatic attraction of positively charged surface functional groups with $HCrO_4^-$ species. At low pH, the functional group carries positive charge and as the pH increases the adsorbent surface possesses more functional group carrying a net negative charge which tends to repulse the anions (Gupta *et al.* 2001; Sharma 2001).

Effect of dose and contact time

Determining the adsorbent dose is the another important step in finding the maximum possible Cr(VI) removal. For this purpose, a series of 100 mL of test solutions were shaken at optimum pH with varying adsorbent doses of 0.1 g to 1 g. The removal of Cr(VI) increased from 38.8% to 90.7% for 1.0 mm ET and 47.1 to 93.0% for 0.3 mm ET as dosage increased from 0.1 g 100 ml^{-1} to 1 g 100 ml^{-1}. Similarly, the removal increased from 11.7% to 61.0% for 1.0 mm EU and 13.8% to 62.2% for 0.3 mm EU as dosage increased from 0.1 g 100 ml^{-1} to 1 g 100 ml^{-1}. The percent uptake of Cr(VI) ions with varying doses of ET and EU is shown in Figure 2. It can be seen that no considerable increase in percent removal of Cr(VI) occurred above a certain dose. The optimum dose was considered to be 0.4 g for ET and 0.6 g for EU 100 ml^{-1}. The increase in percentage removal of adsorbate ions with increase in the adsorbent dose could be attributed to greater availability of adsorption sites. Above the optimum dose, the percentage removal became constant probably because of saturation of the available adsorption sites (Khan *et al.* 2013).

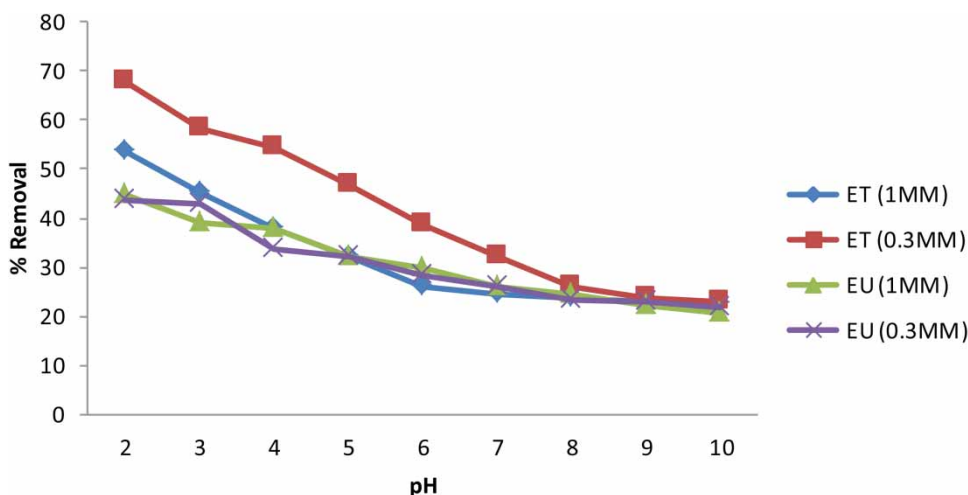The effect of varying contact times was studied at optimum adsorbent dose and pH. The results are

Figure 1 │ Effect of pH on Cr(VI) removal (initial Cr conc.: 20 ppm; contact time: 1 h; dose: 0.5 g 100 ml^{-1}).
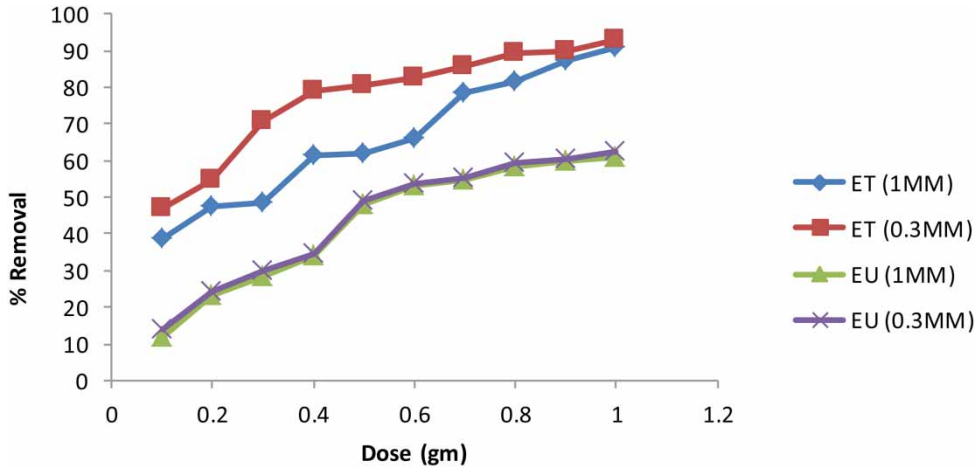
Figure 2 | Effect of dose on Cr(VI) removal (initial Cr conc.: 20 ppm; contact time: 1 h; pH: 2).

shown in Figure 3. It was observed that removal of Cr(VI) by ET and EU increased initially. This is unsurprising as a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time the remaining vacant surface sites are difficult to occupy due to repulsive forces between the solute molecules on the solid and bulk phases (Mall *et al.* 2006). The Cr(VI) removal was 60.9% and 79.2% for 1.00 mm and 0.3 mm for ET in 30 min contact time and 52.7% and 53.4% for 1.00 mm and 0.3 mm for EU in 75 min contact time. There was no significant increase in percentage removal of Cr(VI) thereafter.

Kinetics of adsorption

The effect of initial Cr(VI) concentration on the kinetics of Cr(VI) adsorption was studied. It was shown that equilibrium had been achieved. The plot of $Log(q_e - q)$ versus time is a straight line indicating the applicability of Lagergren equation. The kinetics of Cr(VI) adsorption on the adsorbent was found to follow the first-order rate law derived by following the Lagergren equation. The values of K_{ad} and regression coefficients (R^2) for ET and EU were calculated and are shown in Table 2.

$$Log(q_e - q) = \frac{\log q_e - k_{ad}t}{2.303}$$

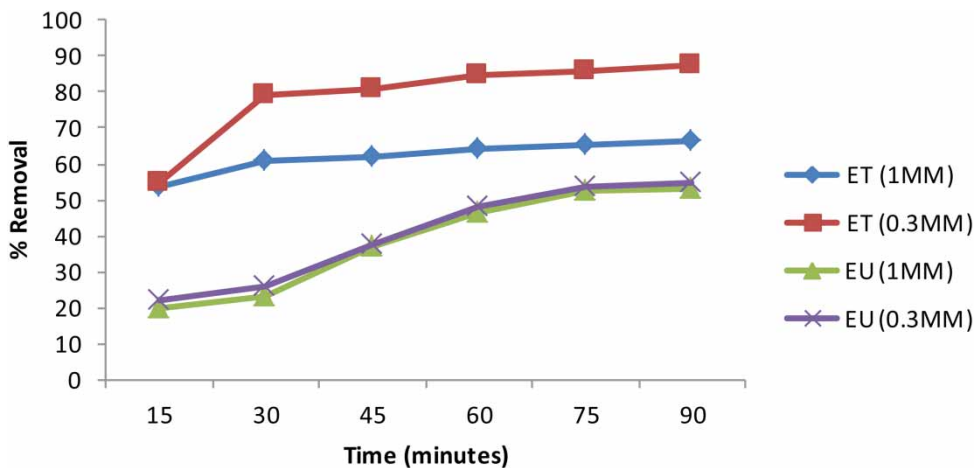**Figure 3** | Effect of time on Cr(VI) removal (initial Cr conc.: 20 ppm, dose: 0.4 g 100 ml^{-1} for ET and 0.6 g 100 ml^{-1} for EU, pH: 2).

Table 2 │ Rate constant of adsorption (K_{ad}) and intraparticle diffusion constant for Cr(VI) removal

Adsorbent	Rate constant	R^2	Intraparticle diffusion constant k_i (mg/g min$^{0.5}$)	R^2
ET (0.3 mm)	2.1×10^{-2}	0.99	5.636	0.87
ET (1 mm)	1.6×10^{-2}	0.98	2.092	0.90
EU (0.3 mm)	2.5×10^{-2}	0.99	6.448	0.98
EU (1 mm)	2.2×10^{-2}	0.99	6.018	0.97

where q_e and q are the amount of Cr(VI) adsorbed at equilibrium and at any time in mg/g.

Adsorption isotherm

The equilibrium data for adsorption of Cr(VI) at fixed dose and temperature was fitted into the Langmuir isotherm model. The corresponding isotherm pattern and regression coefficients (R^2) are given in Table 3.

Table 3 │ Langmuir constant for Cr(VI) removal

| Adsorbents	Langmuir constant		
	K_L	b	R^2
ET (0.3 mm)	0.086	0.002	0.99
ET (1 mm)	0.090	0.003	0.99
EU (0.3 mm)	0.273	0.123	0.99
EU (1 mm)	0.320	0.018	0.99

The linearized Langmuir adsorption isotherm is expressed as:

$$\frac{Ce}{q_e} = \frac{1}{KL.b} + \frac{Ce}{b}$$

where Ce is the equilibrium concentration (mg/L) and q_e is the amount of Cr(VI) adsorbed at equilibrium (mg/g); K_L and b are the Langmuir constants related to adsorption capacity and energy of adsorption. The linear plot of Ce/q_e vs Ce suggests the applicability of Langmuir isotherm (Figure 4(a)–4(d)). Values of K_L and b were determined from the slope and intercept of the plots.

Intraparticle diffusion study

The results obtained from the experiments were used to study the rate-limiting step in the adsorption process. Adsorption is considered to be a three-step process. The first step involves transport of the adsorbate molecules from the aqueous phase to the film surrounding the adsorbent. In the second step, diffusion of the solute molecules from the film to the adsorbent surface occurs. In the third step the adsorbate molecules diffuse into the pore interiors. The first step is bulk diffusion, the second external mass transfer resistance and the third intraparticle mass transfer resistance. When the intraparticle mass transfer resistance is the rate-limiting step, then the adsorption process is
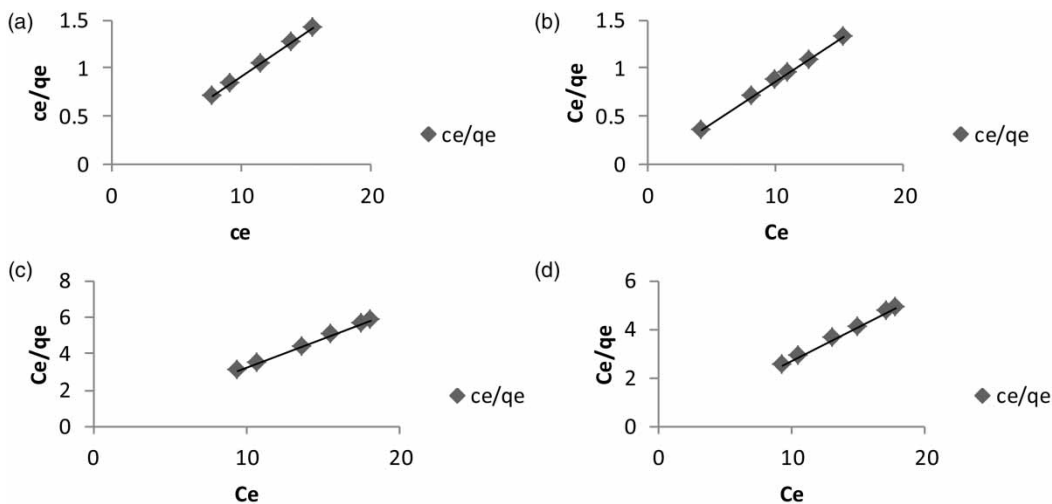
Figure 4 │ Langmuir isotherm: (a) ET 1 mm dose, 0.4 g 100 ml^{-1}; (b) ET 0.3 mm dose, 0.4 g 100 ml^{-1}; (c) EU 1 mm dose, 0.6 g/100 ml^{-1}; (d) EU 0.3 mm dose, 0.6 g/100 ml^{-1}.

described as being intraparticle-diffusion controlled (Khan et al. 2013). The intraparticle diffusion was determined by plotting the amount of Cr(VI) adsorbed at time t versus the square root of time, $t^{0.5}$ (Figure 5). The plots were linear which indicates that intraparticle diffusion controls the adsorption process. The linear portions of the curve do not pass the origin in the figure. This indicates that the mechanism of Cr(VI) adsorption on adsorbents is complex and both the surface adsorption as well as intraparticle diffusion contribute to rate-determining steps (El-Ashtoukhy et al. 2008).

CONCLUSION

The results obtained shows that Eichhornia can be used for the removal of Cr(VI) from the aqueous solutions. Kinetic data was tested using the Lagergren equation and intraparticle diffusion kinetics model. The kinetics of Cr(VI) adsorption on the adsorbent was found to follow the first-order rate law derived by following the Lagergren equation. The plots for intraparticle diffusion were linear contributing to the adsorption process. The equilibrium data were fitted to Langmuir model, and the adsorption equilibrium can be best represented by the Langmuir isotherm model. The Eichhornia adsorbent used in the study is freely and abundantly available and has high adsorption capacity for Cr(VI). Therefore, the use of Eichhornia as an adsorbent is very promising for removal of Cr(VI) from aqueous solutions.
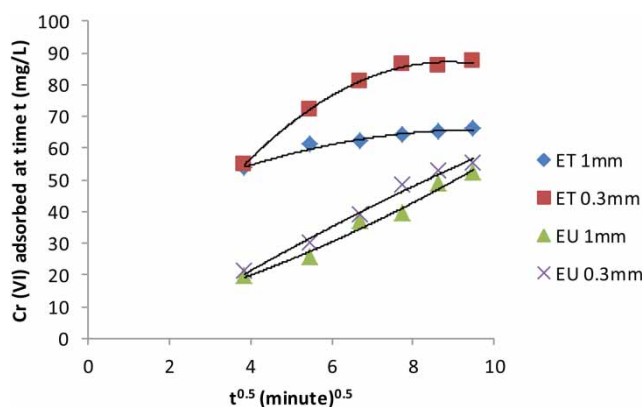
Figure 5 | Plot of Cr(VI) adsorbed vs $t^{0.5}$ for intraparticle diffusion study.

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