OPEN ACCESS JOURNAL

BIOINTERFACE RESEARCH IN APPLIED CHEMISTRY

ORIGINAL ARTICLE

www.BiointerfaceResearch.com

ISSN 2069-5837

Volume 2, Issue 2, 2012, 284-290

Received: 18.01.2012 / Accepted: 02.03.2012 / Published on-line: 04.03.2012

Adsorption of Cr (VI) metal ion from aqueous solutions on low cost adsorbent

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ABSTRACT

An increase in population initiating rapid industrialization in the world was found to increase the effluents and domestic wastewater into the aquatic ecosystem. Heavy metals are major toxic elements found in industrial wastewaters; they make the water unsuitable for drinking. Conventional methods for the removal of heavy metals from waste waters are often cost prohibitive hence there is a need for cheap methods for effluent treatment. In this study, the potential to remove Cr (VI) from aqueous solutions through adsorption using the low cost adsorbent derived from spirogyra algae was investigated in batch experiments. The effect of pH, temperature, contact time, initial metal ion concentration and adsorbent dose on the adsorption of chromium (VI) by low cost adsorbent was investigated. The langmuir and freundlich isotherm were obtained, as well as pH dependence for chromium (VI) adsorption. The adsorption was found to be 92.5% from the initial Cr (VI) metal ion concentration of 200 mg/L with 1 g/100 ml adsorbent dose.

Keywords: *Adsorption, Batch studies, spirogyra algae, biosorption*

1. INTRODUCTION

Nowadays, water pollution is a serious issue as it affects the all living creatures, household, recreation, fishing, transportation and other commercial activities [1-2]. The growth of world population, industrialization and civilization, domestic and agricultural activities and other environmental and global changes are continuously affecting the quality of water. More than 700 organic and inorganic pollutants have been reported in water. Among these pollutants, heavy metal ions such as lead, chromium, mercury, selenium, zinc, arsenic, cadmium, gold, silver, copper, nickel, etc are most dangerous and toxic in nature. A conventional method for removing metals from industrial effluents includes chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion-exchange and adsorption. The cost of water purification by these technologies, except adsorption, ranges from 10 to 450 US$ per cubic meter of treated water. Oppositely, the cost of water treatment using activated carbon adsorption ranges 5 to 200 US$ per cubic meter of water. Besides, adsorption is supposed to be the best wastewater treatment method, due to its wide range of applications and ease of operation [3]. Many researchers have investigated the potential use of different plant material as adsorbent for heavy metals from water, such as coconut husk, palm fiber, water fern, peat moss, duck weed, wheat bran, *Rhizopus nigricans*, modified corn starch, modified onion skins, saw dust, water lettuce, *Alterneuthera triandra, Citrus aurantium*, *Musa paradiasca, Achras sapota* [4-14]. Chromium is one of the most abundant

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inorganic groundwater contaminant. It is used in various industries such as electroplating, glass, ceramics, fungicides, rubber, fertilizers, tanning, mining, metallurgical etc. [15-19]. The most common forms of chromium are trivalent chromium [Cr (III)] and hexavalent chromium [Cr (VI)]. Hexavalent chromium forms chromate (CrO_4^{-2}) or hydrogen chromate ($HCrO_4^{-}$) that is more toxic and more soluble. The exposure of Cr (VI) to human causes nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhage and respiratory problems. The maximum concentration limit for chromium (VI) for drinking water is 0.05 -0.1 mg/L as per Indian standard IS: 10500. Biosorption utilizes the ability of biological materials to accumulate heavy metals from wastewater by either metabolically mediated or physico-chemical pathways of uptake [20]. Application of biosorbents from various microbial sources, moss, aquatic plants and leaf-based adsorbents was reported by various investigators [21–22]. Spirogyra algae is capable of accumulating heavy metals like copper, chromium, zinc andfluoride [23], but still there is lots of scope available to use this abundantly available alga for the removal of other heavy metal ions from wastewaters. In the same sequence in this investigation, biosorption studies for the removal of Cr (VI) metal ion from low cost adsorbent prepared from spirogyra algae is carried out. In the present work, the Cr (VI) ions adsorption capacity of spirogyra derived low cost adsorbent was studied by a batch technique. The effect of pH, concentration of Cr (VI) ions, contact time, temperature and adsorbent dose on percentage of adsorption has been investigated.

2. EXPERIMENTAL SECTION

2.1. Preparation of the Biomass. The pond scum or *Spirogyra* algae were collected from the big pond of Bhopal, India. The collected biomass first crushed into smaller particle by hand and then washed with distilled.

2.2. Preparation of metal solution. The Cr (VI) stock solution was prepared by dissolving analytical grade 3.734 gm of K_2CrO_4 (Merck) in 1000 ml volumetric flask and made up to the mark with deionised water. All the required working solutions were prepared by diluting the stock solutions. The pH of each solution was measured by a digital pH meter and adjusted by the addition of 0.1 mol/L HNO_3 or 0.1 mol/L NaOH solutions.

2.3. Batch Experiment. The adsorption experiments were carried out in a batch process and effect of different parameters such as effect of contact time, metal ion concentration; adsorbent dose, pH and temperature were studied. The known weight of biosorbent material was added to 100 mL of the Cr (VI) metal ion solution with an initial concentration of 50 mg/L to 300 mg/L. The contents were shaken thoroughly using a mechanical shaker rotating with a speed of 120 rpm. The solution was then filtered at preset time intervals and the residual metal ion concentration was measured by UV-Visible spectrophotometer.

3. RESULTS SECTION

Batch experiments were carried out to investigate the effects of pH, contact time, initial Cr (VI) concentrations, adsorbent dose and temperature on adsorption of the metal ions from its solutions.

3.1. The effect of contact time on Cr (VI) adsorption. The effect of contact time on the adsorption of Cr (VI) from its solution is shown in Figure-1. It is observed that the adsorption increases with the contact time to a particular level then in becomes slow because of non availability of active sites on the adsorbent. The maximum adsorption 70% of Cr (VI) was obtained at 100 min.

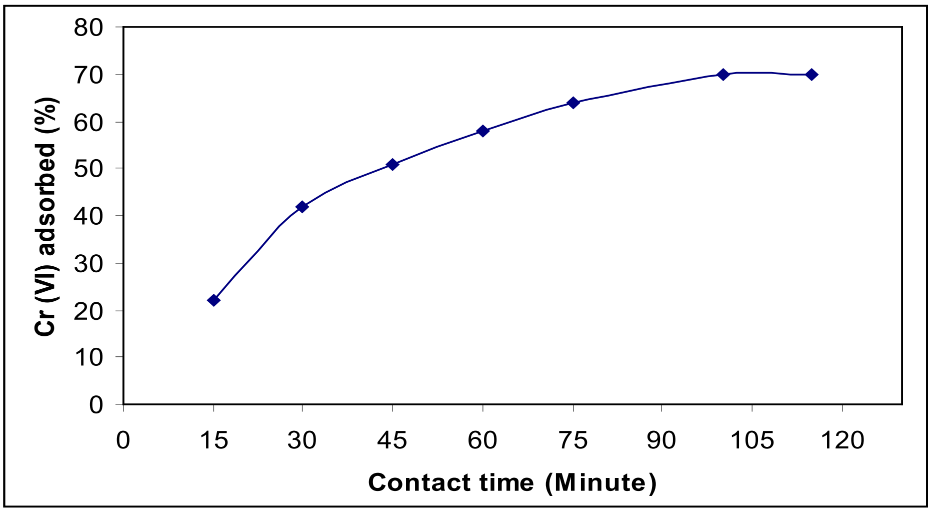

Figure 1: Effect of contact time on the adsorption of Cr (VI). (Metal ion concentration = 200 mg/L, Adsorbent dose = 1g /100 ml and Temperature = 30°C)

3.2. Effects of Cr (VI) metal ion concentration. Cr (VI) adsorption is significantly influenced by the concentration of Cr (VI) in aqueous solutions. Figure-2 shows the effect of initial concentration on percentage removal of Cr (VI) and adsorption capacity of the adsorbent. To see the effect of Cr (VI) concentration, 1.0 g of the biomass was taken and mixed with 100 ml of Cr (VI) solution of varying concentrations (50, 100, 150, 200, 250, and 300 mg/L) in different Erlenmeyer flasks.

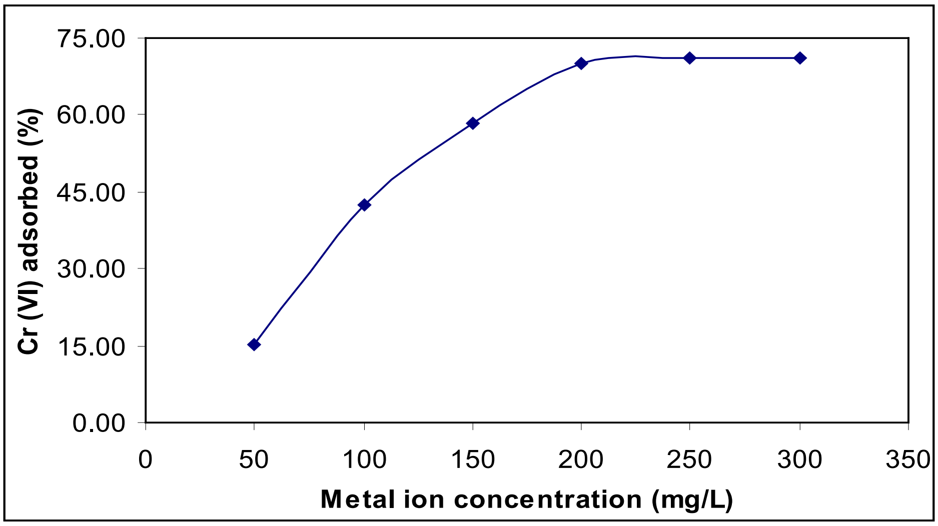

Figure 2: Effect of metal ion concentration. (Contact time = 100 min, Adsorbent dose = 1 g /100 ml and Temperature = 30°C)

The mixture was continuously agitated in a temperature controlled water bath with agitation rate of 120 rpm. The adsorbed amount was determined from the difference in the initial and residual concentrations of Cr (VI) in the liquid phase. The adsorption of Cr (VI) ions by the adsorbent initially increased rapidly with increasing Cr (VI) concentration and become constant when Cr (VI) concentration reached 250 mg/L. It may be due to the interaction between the metal ions and the active sites of the adsorbent. At higher concentrations more Cr (VI) ions are left un-adsorbed in solution due to the total saturation of binding sites of the adsorbent.

3.3. Effect of adsorbent dosage. The removal of chromium (VI) by low cost adsorbent at different adsorbent doses (0.2-2.0 g in 100 mL) was studied. All process parameters like, contact time, agitation speed, and pH was fixed. Figure-3 shows that, the adsorption capacity of Cr (VI) increased rapidly with increase in the dose of spirogyra water weed. The adsorption rate of adsorbent to remove Cr (VI) ion increase with increase in biomass dose from 0.2 to 1.7 g/L of solution and after then it becomes stationary.

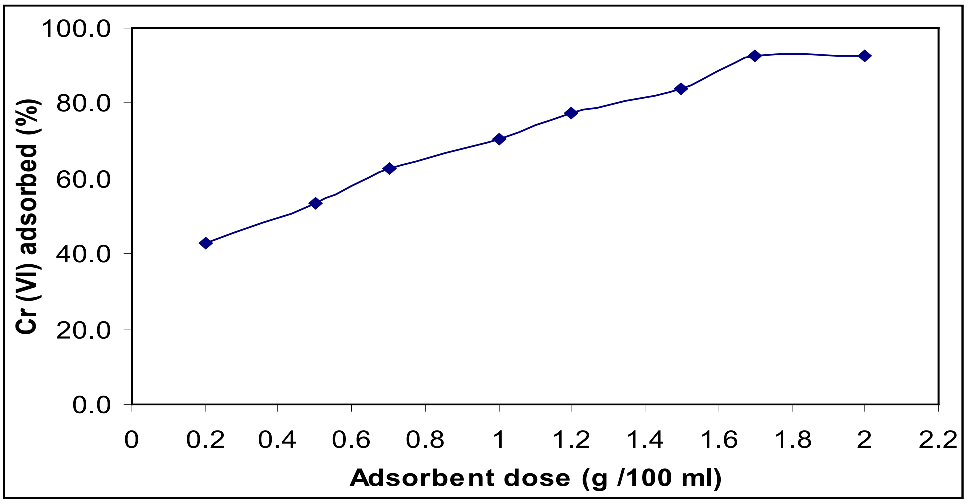

Figure 3: Effect of Adsorbent dose on adsorption of Cr (VI). (Metal ion concentration = 200 mg/L, Contact time = 100 min and Temperature = 30°C)

3.4. Effects of pH on metal ion adsorption. The pH of the solution is an important parameter in the adsorption process because it affects the solubility of the metal ions concentration of the counter ions on the functional groups of the adsorbent. From Figure-4, it is shown that, there is a sharp decrease of adsorption from pH 1 to pH 4 after that the adsorption is becomes slow. At low pH, there are a large number of H^+ ions which makes solution acidic and favors the adsorption by neutralizing the negatively charged adsorbent surface. As pH increases, the concentration of H^+ ions decreases and OH^- ions increases which causes hindrance in the sorption of negatively charges Cr (VI) ions like $Cr_2O_7^{-2}$, CrO_4^{-2} and $HCrO_4^-$.

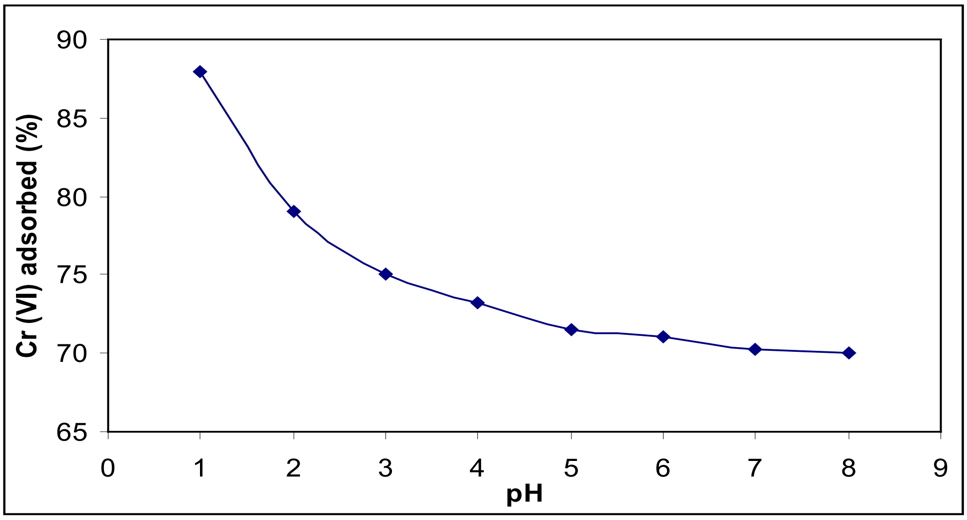

Figure 4: Effect of pH on adsorption of Cr (VI). (Metal ion concentration = 200 mg/L, Contact time = 100 min, Adsorbent dose = 1 g/100 ml and Temperature = 30°C)”

3.5. Effect of temperature on Cr (VI) adsorption. The adsorption of Cr (VI) from aqueous solutions at different temperatures (i.e. 30, 40 and 50°C) was studied. Figure-5 shows that, the adsorption capacity increases on increasing the temperature. The maximum adsorption capacity of 73.1% was obtained at 50ºC. It is observed that, the oxidizing power of Cr (VI) increases when solution temperature was increased resulting the reduction of Cr (VI) into Cr (III) and bounding strongly on the organic material.

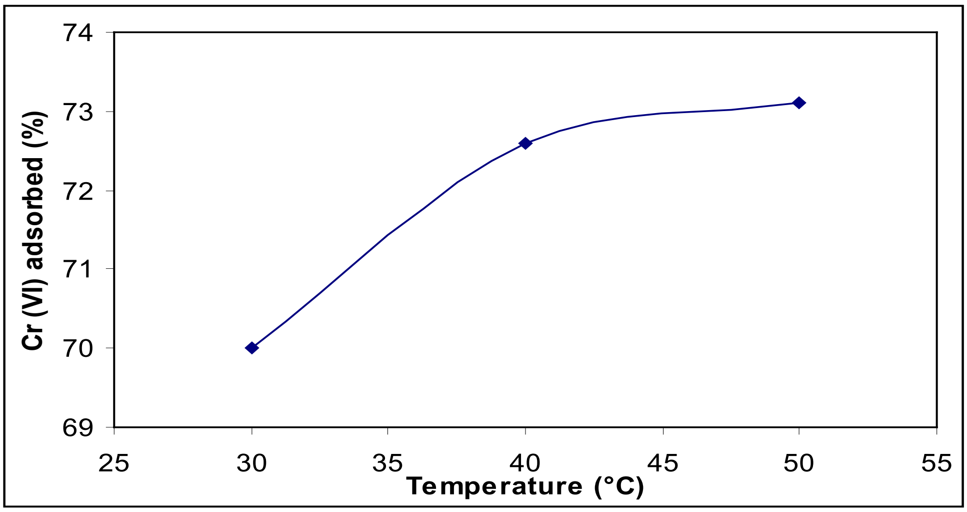

Figure 5: Effect of temperature on the adsorption of Cr (VI). (Metal ion concentration = 200 mg/L, Contact time = 100 min and Adsorbent dose = 1 g /100 ml)"

3.6. Adsorption equilibrium studies. The experimental data are analyzed by the Langmuir and Freundlich equilibrium adsorption isotherm. The Langmuir isotherm was represented by the following equation:

$$Ce/Qe = 1/Qmb + Ce/Qm$$

Where, Ce = Equilibrium concentration (mg/L), Qe = Amount adsorbed at equilibrium (mg/g) Qm = Langmuir constants related to adsorption efficiency, b = Langmuir constants related to energy of adsorption.

The linear plots of Ce/Qe versus Ce suggest the applicability of the Langmuir isotherms (Figure-6). The values of Qm and b were determined from slope and intercepts of the plots and are presented in Table-1. The results of adsorption efficiency Qm and adsorption energy b of the adsorbent conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface. To confirm the favorability of the adsorption process, the separation factor (RL) was calculated and presented in Table-2. The values were found between 0 and 1 confirms the ongoing adsorption process is much more favorable [24].

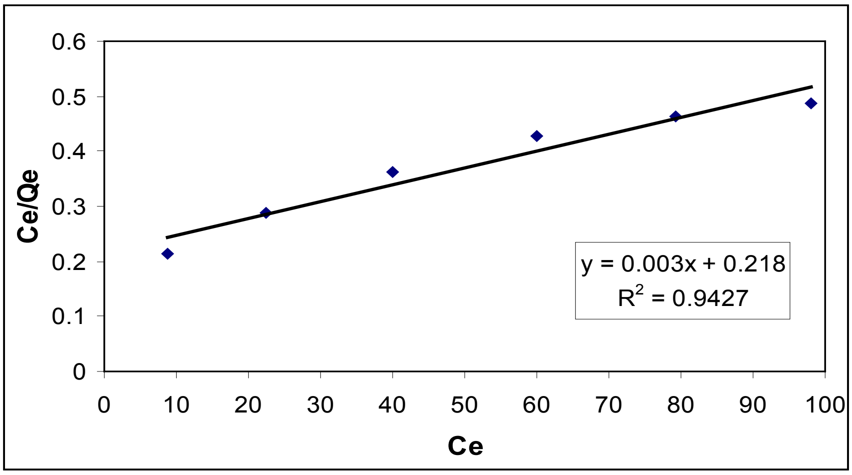

Figure 6: Langmuir adsorption isotherm for the adsorption of Cr (VI) metal ion

The Freundlich isotherm was represented by:

$$\log Qe = \log K_f + 1/n \log Ce$$

Where, Qe = Amount of Cr (VI) adsorbed (mg/g) Ce = Equilibrium concentration of dye in solution (mg/L)

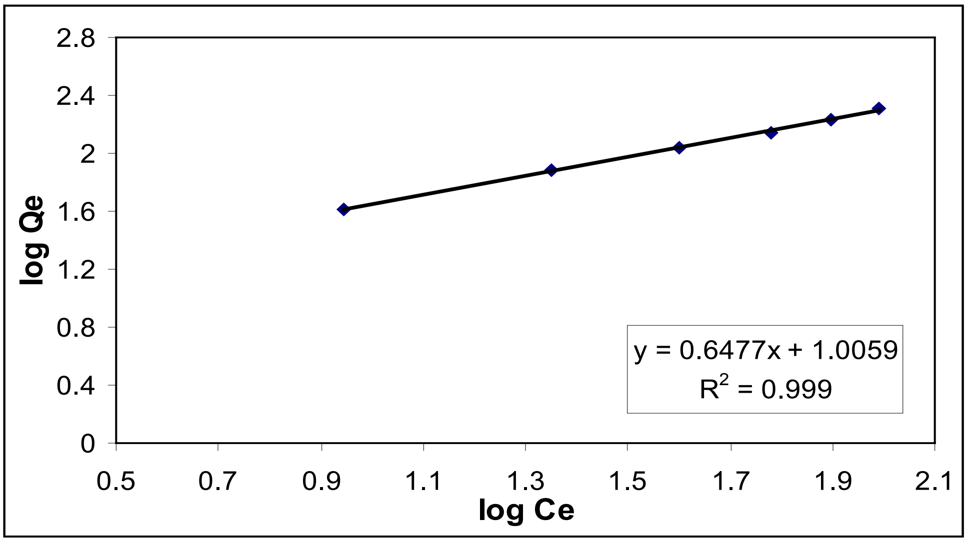

Figure 7: Freundlich adsorption isotherm for the adsorption of Cr (VI) metal ion

K_f and n are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of log Qe versus log Ce shows that the adsorption of Cr (VI) metal ion obeys the Freundlich adsorption isotherm (Figure-7). The values of K_f and n given in the Table 5 show that the increase in negative charges on the adsorbent surface that makes electrostatic forces between the adsorbent surface and Cr (VI) metal ion.

Table 1: Equilibrium parameters for the adsorption of Cr (VI) metal ion

C_0 (mg/l)	**C_e (mg/l)**	**Q_e (mg/l)**	**Cr (VI) removed (%)**
50	8.80	41.20	82.40
100	22.40	77.60	77.60
150	39.90	110.10	73.40
200	60.00	140	70.00
250	79.25	170.75	68.30
300	98.10	201.90	67.30

Table 2: Langmuir and Freundlich isotherm results

Adsorbent	**Langmuir Isotherm**				**Freundlich Isotherm**		
Spirogyra algae Biomass	Qm	b	Correlation Coefficient (r^2)	Separation Factor (RL)	Kf	n	Correlation Coefficient (r^2)
	333.3	0.014	0.9427	0.26	10	1.54	0.999

4. CONCLUSIONS

This study identified *Spirogyra* algae as a suitable low cost biosorbent for chromium (VI) removal in batch experiments. The adsorption process was depended on pH of the solution, adsorbent mass, initial Cr (VI) concentration, contact time and adsorbent mass. The optimum pH and optimum temperature was 1 and 50°C respectively for biosorption of chromium (VI). The experimental data are well correlated with Langmuir and Freundlich adsorption isotherms. The separation factor (RL) shows that the *Spirogyra* biomass is efficient and can be used for the adsorption of Cr (VI) metal ion from aqueous solution.

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6. ACKNOWLEDGMENT

The authors would like to thank the Center for Microbiology & Biotechnology, Bhopal, India for providing research facilities and encouragement.