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Adsorptive separation of Cr (III) and Cr (VI) from aqueous solution using fresh water microalgae and prior to determination using ICP-OES: Kinetic and equilibrium studies

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Abstract

The simple analytical procedure utilizes that, complete recovery and subsequent analysis of trace amount of chromium (III) and chromium (VI) in water and waste water samples by using some selected algae. Cr (III) and Cr (VI) during adsorption study was measured using inductively coupled plasma optical emission spectrometry (ICP-OES). Also investigated the separation conditions of analytes. The highest sorption percentage was at pH ~ zero using 1.0 M HCl. The adsorbed Cr (III) and Cr (VI) metal ions were quantitatively eluted by 10 mL of 1.0 mol L−1 NaOH. The endothermic nature of the chromium (VI) ions uptake with the help of thermodynamic parameter like ΔH was calculated and the results show that the positive value. The increased value of ΔG with low temperature which is favorable for adsorption process was spontaneous in nature.

Keywords: Cr (III) and Cr (VI), microalgae, ICP-OES, Thermodynamic.

Introduction

The water and wastewater in our environment is very often polluted by heavy metals due to various chronic disorders, damage nerves and anthropogenic sources in the form of mining operations, batteries, metal plating facilities, paper industries, tanneries, fertilizer industries and pesticides, etc. (Balintova et al. 2017). In recent years, heavy metal ions are discharged directly or indirectly into our environment created problems due to ability to form compounds which high in biological toxicity in our nature may increase the concentration levels either in water soluble or insoluble forms. The problems was obtained from every environmental sample to show that low level of concentrations of contaminants in water and wastewater and are in constant movement with the overlying water column; hence, the analysis of heavy metals in our environment permits the detection of contaminants of heavy metals are over the increased concentration levels in natural waters. (Xue et al. 1988).

A series of analytical techniques have been reported recently for the preconcentration and separation of chromium metal ion concentration in water, wastewater and other environmental samples by using efficient techniques and subsequent determination of organic and inorganic species in complex matrices such as HPLC, electro analytical methods and laser induced fluorescence. Recently great attention has been paid towards application of various types of algae modified or none modified with nanomaterials (1-100 nm) to recover the chromium metal ions in water and wastewater. Ag nanoparticles have been introduced for the removal and recovery of chromium metal ions in water, wastewater and environmental samples shows that better adsorption. Because of their selectivity, capacity, large surface area and anti-microbial property. Nowadays, the water and wastewater treatment cost is highly unfavorable for industrial activities. Many research papers reveals that, the recovery and removal of chromium metal ion in environmental samples by using sawdust, orange peel, almond husk, parthenium etc., which is favorable for cost effective and better removal. (Ngah and Hanafiah 2008). Several low cost adsorbents introduce in the field of biosorption and bioremediation technology for the removal and recovery of chromium metal ions by using suitable microorganism. Most of the industrial wastewaters and effluents treated by using suitable biosorbents for the removal and recovery of trace metal ions was studied and published recently (Andrade et al. 2010). The quality of water in lakes, rivers, ponds, and streams greatly influence water use. For well known, human metabolic activities Cr (III) was essential, where as Cr (VI) was highly toxic (Vajpayee et al. 1999). In natural water, very low level of chromium metal ion concentration was identified in the range of 0.1–0.5 g L^{-1} (Nriagu and Nieboer 1988; Ghaedi et al. 2006). The studies performed with Cr (VI) bioaccumulation by microorganisms have been reported (Singh et al. 2013). They have attributed the removal of chromium by the microorganisms. For the reduction of concentration of Cr (VI) to Cr (III), this is essential for safe environment, eco-friendly and avoid for toxic nature. (Namasivayam et al. 1996). Based on this literature, the recovery and removal of chromium metal ion concentration was present in water and wastewater samples finding out microorganism has to be a better over then the other conventional methods. (Cheung and Gu 2007).

The present method was investigated for this, to prepare a biosorbent then it is characterized. The quality removal of chromium metal ion concentration was identified by using green micro algae as an adsorbent and prior to determine ICP-OES. The effective parameters such as adsorption capacity, sample flow rate, retention and elution efficiency of the metal ions were studied by batch and column mode of operation respectively. The quantitative determination of adsorption study was carried out systematically and involving various parameters such as pH, agitation, influence of surfactant (anionic, cationic and neutral) and adsorption dose.

Materials and Methods

Preparation of biosorbent

Freshwater algal dried samples were brought from United Kingdom (Bacillariophyceae 4.2%, Chlorophyceae 0.3%, Cryptophyceae 2.3%, Cyanophyceae 6% and Dinophyceae 87.3 %). In this procedure 0.005 g of freeze-dried cells were weighed using an analytical balance. Dry biomass used as solid biosorbent for the extraction and recovery for Cr (VI) ion concentrations in water and wastewater samples at trace level.

Materials and Reagents

All the reagent chemicals and solvents are recommended for this study used for analytical grade quality and were used without purification for further usages. All the laboratory glassware was cleaned properly and it was kept with overnight in a 10 % (v/v) HNO_3 solution and then rinsed with de-ionized water throughout the experimental work. For the preparation of standard solution of Cr (III) and Cr (VI) metal ion concentrations were (1000 µg mL^{-1}) from $CrCl_3.6H_2O$ and K_2CrO_4 (BDH, USA). The adjustment of Cr (VI) solution (pH ~0) were used by HCl and HNO_3. The measured concentration of Cr (VI) ions were further stored in low density polyethylene pet bottles (LDPE), Nalgene, and it was kept in dark place for avoiding light.

Apparatus

Analyte ions were measured in Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES, Optima 4100 DC Shelton, CT, USA). The instrumental and operating conditions were presented in **Table 1**. pH meter (Thermo Fisher Scientific Orion model 720, USA) was used for all pH measurements. De-ionized water obtained from Mille-Q Waters Plus system (Milford, MA, USA). The Precision Scientific mechanical shaker obtained from (Chicago, CH, USA) and the shaking rate in the range from 10 – 250 rpm was used for this experimental study. UV/visible spectrophotometer from A Perkin-Elmer (model Lambda 25, USA) was used for measuring the absorbance of Cr (VI) at the recommended wavelength of 350 nm and 0.5 nm slit width before and after shaking under optimum conditions provided by the instrument. A variable shaking incubator (JSR) was also used for the retention of Cr (VI) by the biosorbent with shaking 10-120 rpm was used. Using glass columns (18 cm x 15 mm I.D) was for flow experimental study.

Table 1 ICP-OES operational conditions

Parameter	Unit and Operational details
Rf Power	1300W
Nebulizer Flow	0.8 L/min
Auxiliary Flow	0.2 L/min
Plasma Flow	15.0 L/min
Sample Pump Flow	1.5 ml/min
Plasma Viewing	Radial
Processing Mode	Area
Replicates	3
Nebulizer Type	Cross-flow (Gim Tip)
Spray Chamber	Scott (Ryton)
Injector	Scott (Ryton)

Batch experiments:

Effect of influence of pH on Cr (VI) adsorption

The effect of metal ion uptake was studied with aqueous solution of 250 mL sample volume containing 20 µg of Cr (VI). The analyte concentration ions were adjusted with HCl or NaOH for measuring pH. The solid biosorbent was shaken for 1 hour at 25 ± 1 ºC with aqueous solutions of Cr (VI) concentration at various pH. Once the equilibrium was reached, after that the concentration of Cr (VI) ions was retained on the biosolid adsorbent. The difference between the absorbance of solution at λ_{max} of 355 nm before (A_b) and after (A_a) was calculated from the used biosorbent. The percentage of sorption (% E) was finding out, the amount of adsorption of chromium (VI) metal ions were retained at equilibrium (q_e) by using per unit mass of solid biosorbent (µg) and the distribution coefficient (D) of Cr (VI) metal ions was onto the biosorbent can be calculated from the following equations:

$$\% E = \left(\frac{A_b - A_a}{A_b}\right) \times 100 \qquad (1)$$

$$q_e = (A_b - A_a) \times \frac{V}{W} \qquad (2)$$

$$D = \frac{\% E}{100 - \% E} \times \frac{V\,(mL)}{W\,(g)} \qquad (3)$$

where, V = chromium (VI) solution, volume in (mL), W - biosorbent grams in weight. The percentage (%) of measurements E and D were calculated by three independent averages and the precision was found to be ± 2%.

Influence of acidity on Cr (VI) uptake

To influence the study of various mineral acids concentrations (1.0, 2.0, 3.0 mol L^{-1}), with aqueous solution containing 100 mL of 20 µg of Cr (VI) and the sample volume was containing (0.005 ± 0.001g) of the solid biosorbent were placed in a series of conical flasks. The presence of various mineral acids was shaken for 1 hour at 25 ± 1 ºC. The Cr (VI) concentration of the metal ions was measured aqueous solution reached at equilibrium. The amount of Cr (VI) metal ions concentrations were retained on the biosorbent and then it was calculated from the above equation (1). The adsorption of Cr (VI) ions was then recovered and eluted with NaOH (1.0 mol L^{-1}) followed further analysis made by ICP-OES.

Column experiment

Preparation of biosorbent packed column

For column flow experimental study was performed with the help of using glass columns (18 cm x 15 mm I.D) with a glass wool over its stopcock was used for this study. Dry biosorbent powder was homogeneously packed and it was applying pressure in to the glass column about one-third of its original volume. The column was further usage preconditioned by the blank solution. During the measurements, tap (1) was connected to a suction pump, where as tap (2) was closed for avoiding air bubbles (EL-Shahawi et al. 2011a). For every 10 min of evacuation double distilled water was allowed to fill the column, which was gradually filled through tap (2) and while tap (1) was closed.

Chromatographic behavior of Cr (VI) onto biosorbent packed columns

The quantitative retention and elution of Cr (VI) onto biosorbent (0.005± 0.001 g) packed column containing Cr (VI) concentrations was varied from 0.001 - 20 µg mL^{-1} was investigated. The operated conditions set as follows: Distilled water (50 mL) and flow rate of solution 5 mL min^{-1}. The column was further usage washed with nitric acid (10 mL) at the flow rate of 3 mL min^{-1}. The concentration Cr (VI) metal ion solutions was calculated before and after percolation in the metal ion was measured by ICP–OES. After absorption, the retained Cr (VI) metal ions on the biosorbents were quantitatively using 10 mL of NaOH.

Retention and recovery of Cr (III)

To estimate the concentration of chromium (III) retention and recovery of the present study, an aqueous solution containing ≤ 10 µg mL^{-1} Cr (III) in conical flask followed by adding 5 mL of (30 % w/v) hydrogen peroxide. The solution is adjusted with pH~9 using NaOH. After that, the concentration of chromium (III) reaction mixture was boiled and allowed to cool for few minutes. To set pH~zero adjusted to using HCl. The test solution was percolated and passed through biosorbent packed column with 5 mL min^{-1} . The adsorbed Cr (VI) ions were recovered and eluted with 10 mL of NaOH. The analyte contents were measured by the recommended procedure.

Binary mixtures of chromium (III & VI) analysis

To find out the concentration of binary mixtures such as Cr (VI) and Cr (III) ions in the present study was investigated. The mixture of solutions containing 100 mL of Cr (VI) and Cr (III) aliquot and the total concentration was ≤ 20 µg mL^{-1}. Further, the oxidation of Cr (III) to Cr (VI) by using hydrogen peroxide (0.5 mL, 30 %v/v) was used. From the procedure, to find out the net signal intensity of Cr (VI) (I_1) of the first aliquot was measured, while the net signal intensity of chromium (III & VI) the second aliquot (I_2) was measured. Therefore, binary mixture was calculated from the difference of (I_2-I_1) the net signal intensity of Cr (III).

Results and Discussion

Retention of chromium onto biosorbent adsorption

To find out the Cr (III) & (VI) compounds are consider as one of the inorganic chromium present in water and waste water samples were studied. The high soluble of inorganic compounds of Cr (VI) was soluble at neutral pH (**Becker** 1983**).** While, Cr (III) derivates are water insoluble at neutral pH and vital role for human health and metabolism activities (**Lloyd and Lovley 2001)**. These species are ecologically important (**Viggi** et al. 2010). Thus, in recent years chemical speciation and properties of Cr (VI) as compared with Cr (III) was attracted with interest in view of the toxic nature. Thus, a detailed study was carried out to use selected algae as biosorbent solid phase consider for the removal and chemical speciation of total chromium was more important determination.

Absorption spectra

The absorption electronic spectrum of Cr (VI) ion in HCl (2M) is shown in **Fig. 1.** The spectrum showed two well defined maxima at 280 and 355 nm. Therefore, in all further subsequent work, all the Cr (VI) absorbance measurements was before and after carried out at 355 nm.

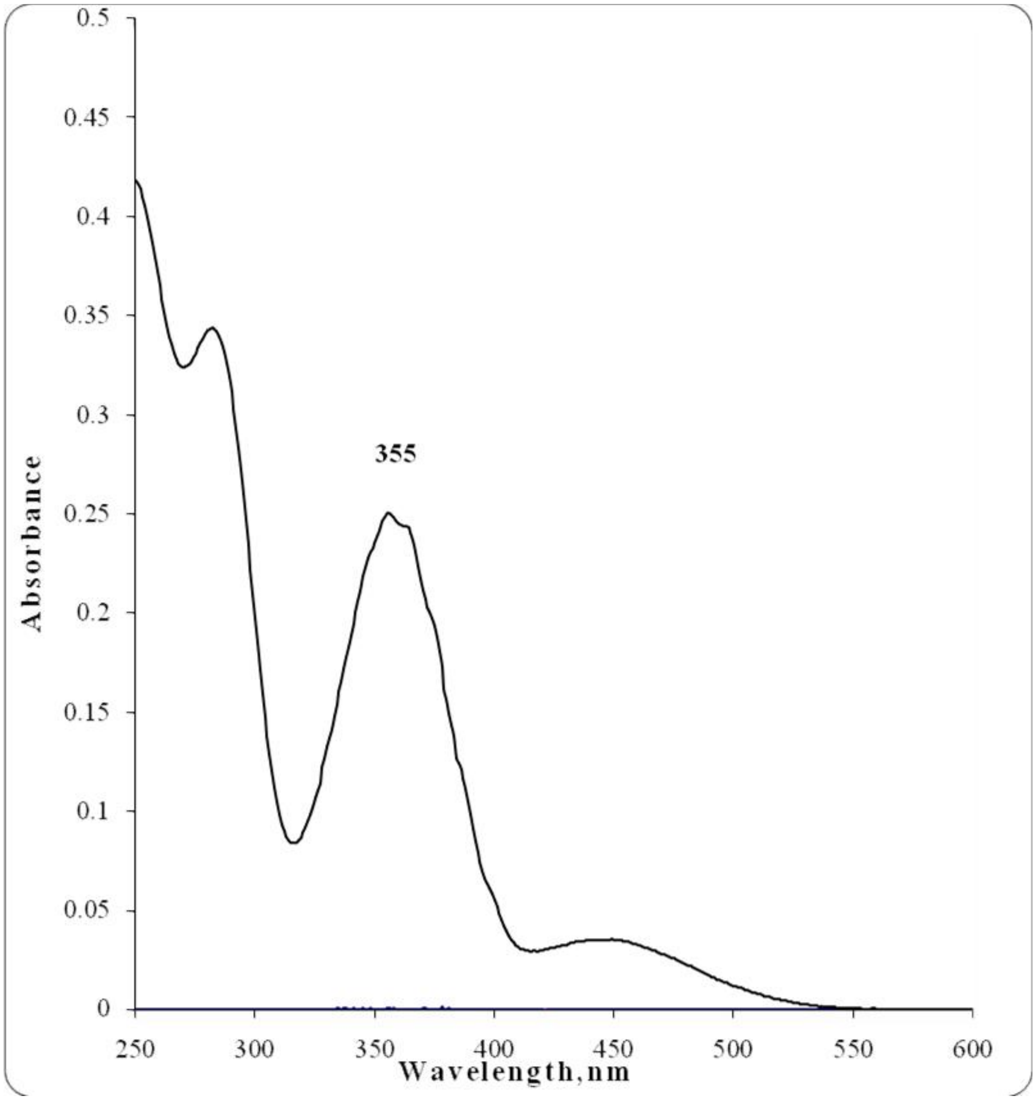

Fig. 1. Absorption electronic spectrum of chromium (VI) species ion in aqueous HCl (1.0 mol L^{-1}).

Effect of acidity of the aqueous solution by pH

To the effect of subsequent determination of traces and ultra traces amount of Cr (VI) in water samples, the development of suitable pre concentration and separation procedures was more important. Preliminary investigation has shown that, the amount of uptake of Cr (VI) by the tested biosorbent, due to the depends of aqueous media at different pH (2.2-11.7). Critical absorbance efficacy of the algae was analyzed after 1 h shaking under room temperature to act as solid phase biosorbent. The results were presented in **Fig. 2.** From the results obtained and clearly indicate that, the adsorption % of E and D of Cr (VI) ions was tested onto the solid biosorbent decreased with increasing pH value of the aqueous solution was maximum adsorption uptake was measured at pH~zero. In some species (marine algae cellulose) can be lacking with a smaller and more variable proportion than in higher plants. While other green algae have 70% of the dry weight contains cellulosic wall. Algal cellulose is rarely a pure ß-1, 4 glucan; more frequently it contains 51 sugars other than glucose, commonly xylose. Skeletal polysaccharides cellulose in the algal cell walls replacing by xylans (Baldan et al. 2001) and mannans (mainly ß-1, 4 linked). The cell walls perform a structural function, the physico-chemical properties cellulose matrix was reported (Ksheminska et al. 2005).

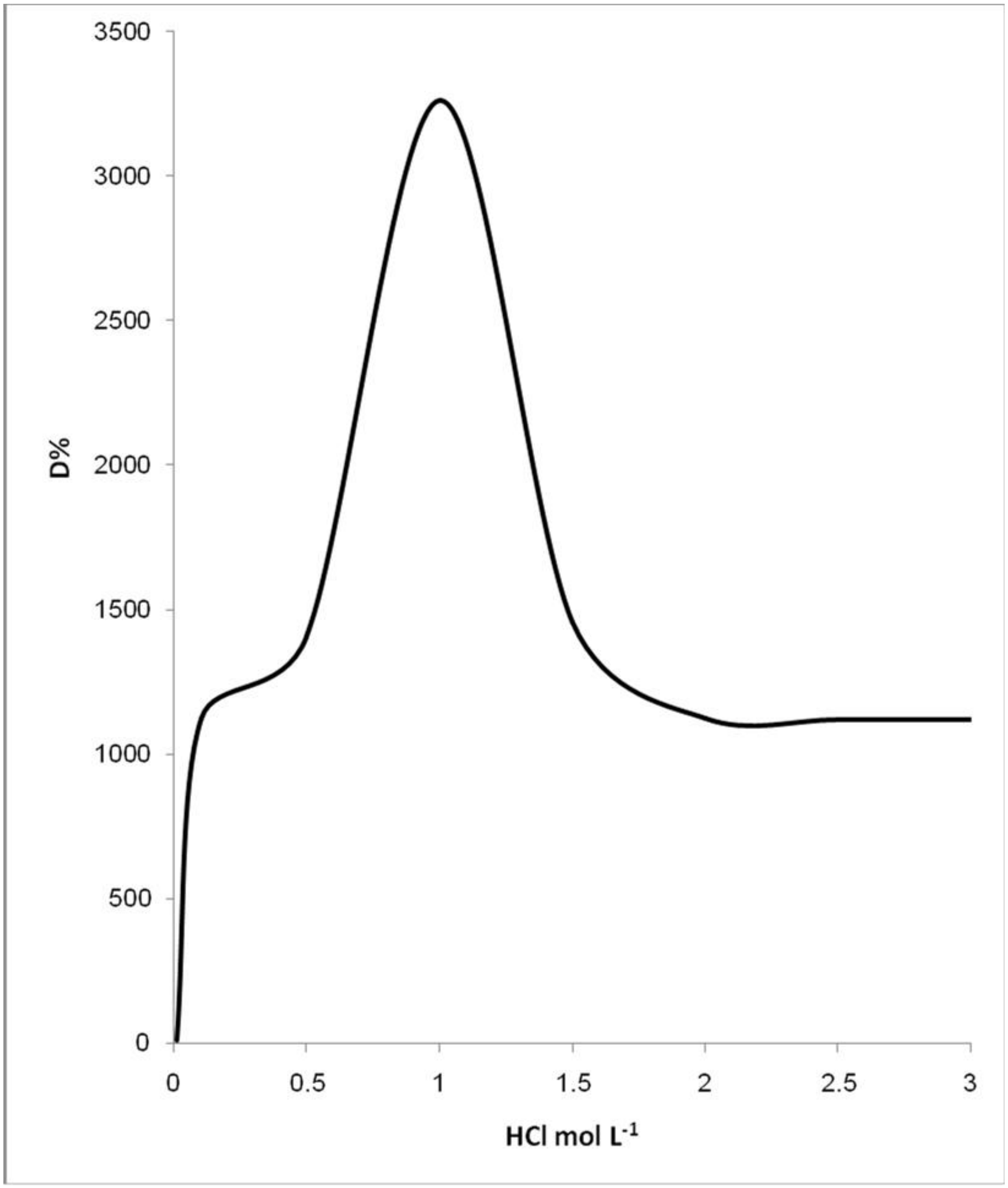

Fig. 2. Plot of HCl concentration (M) versus distribution ratio (D) on the sorption of chromium (VI) from the aqueous solution onto the biosorbent.

The ability of binding sites towards the Cr (VI) ions was enhanced by biosorbent through the formation of complex. The protonation and deprotonation of the chromium metal ions present in the available active sites (amino acids, hydroxyl and carboxyl groups). On the other hand, at low acidity (1.0 mol L^{-1}), Cr (VI) species exist only at anionic species depending on the solution of pH, Cr (VI) concentration and ionic strength. The most studied chemical equations involving Cr (VI) species in solution can be summarized in the following equilibrium:

$$H_2CrO_4 \rightleftharpoons HCrO_4^{-} + H^{+} \qquad k_1 = 0.18 \qquad \textbf{(4)}$$

$$HCrO_4^{-} \rightleftharpoons CrO_4^{2-} + H^{+} k_2 = 3.2\times10^{-7} \qquad \textbf{(5)}$$

From the (Equation 3.2), the quantity of $HCrO_4^{-}$ions also increases. At low pH, the equilibrium concentration was shifted to the left. The produced hydrogen chromate ($HCrO_4^{-}$) species at HCl ≥ 2 mol L^{-1} are converted into chlorochromate anion (CrO_3Cl^{-}) based on the following equation:

$$HCrO_4^{-} + Cl^{-} + H^{+} \rightleftharpoons [CrO_3Cl^{-}] + H_2O \qquad \textbf{(6)}$$

The dominant form of Cr (VI) is CrO_3Cl^- in HCl medium. This is because, the strong affinity to interact with the protonated oxygen and / or nitrogen functional groups available on the bio- sorbent. At acid concentration >3 M, the uptake decreased which is most likely attributed to the possible degradation of the algae in such media (**Gadd** 2009)**.** The uptake of Cr (VI) onto the biosorbent decreases with increasing pH solution and shows that the highest adsorption percentage was at pH ~ zero using 1.0 M HCl. The decrease in the Cr (VI) uptake by the biosorbent at higher pH is most likely due to the adsorption decrease due to the protonation and deprotonation of percentage active sites present in the algae. In further subsequent work, the solution pH was kept at pH close to zero using 1.0 mol L^{-1} of HCl act as a suitable extraction media.

Influence of shaking time on Cr (VI) uptake

In solid phase extraction, the influence of shaking time is the important parameter was to be analyzed. The Cr (VI) was uptake from the aqueous media containing HCl (1.0 M) by the biosorbent. The shaking time was varied from 0, 50, 100, 150, 200 min. After shaking the solutions for 200 min at 25ºC. The amount of Cr (VI) in aqueous solution was measured by spectrophotometer at 355 nm and the amount retained on the algae was estimated as detailed in methodology section. The maximum adsorption of Cr (VI) ions equilibrium was reached within 80-90 min was fast shaking time. The values of half-life time ($t_{1/2}$) of Cr (VI) adsorption was calculated from the plot of -log C_e/C_O *vs* time was found 5.1 min. From the results demonstrated that, the shaking time was 80-90 min adopted in the subsequent experimental work was suggesting that, the possible use of the biosorbent in the extraction of Cr (VI) from the aqueous solution media.

Effect of temperature

To study the effect of temperature was varying from 25-75˚C was investigated. The sorption of Cr (VI) by the biosorbent was critically investigated at the operational conditions of Cr (VI) were retained by the solid biosorbent. The retention of Cr (VI) by the solid biosorbent increasing on increasing temperature as demonstrated. The fact of increasing temperature may increases the diffusion of the bulky anion (CrO_3Cl^-) to be transferred from the bulky hydrochloric solution at the optimum acidity to the sorbent in its protonated form.

Influence of media polarity on Cr (VI) uptake

To influence the medium polarity on the Cr (VI) ions uptake by the algae was critically studied using various concentrations (0 - 20 % v/v) of ethyl alcohol. The extraction of media was employing the batch mode of separation. The obtainable results are demonstrated. From the results clearly indicate that, the sorption increases as the ethanol content increases up (10% v/v). At concentration of ethanol higher than 10% ethanol the uptake of chromium decreased suddenly. The change of the environmental conditions in and around Cr (VI) species and the binding sites of the microbial algae varied at 10% v/v ethanol became more hydrophilic and diminishing. The uptake of chromium concentration was enhanced by 10% ethanol and minimized by higher ethanol. Further subsequent work was used by 10% (v/v) ethanol content.

Influence of cation size and ionic strength on Cr (VI) uptake

To study and influence the various metal cations using chloride salts such as (Li^+, Na^+, K^+, and Rb^+) and ionic strength at various concentrations individually varied from 1.0 – 10 % w/v. The uptake of Cr (VI) on to the biosorbent from HCl media was critically investigated. The values are summarized in **Table 2.** From the values in Table 2, increase in the Cr (VI) sorption was observed due to the presence of chloride salts respectively. The distribution ratio of the Cr (VI) uptake at various salts concentrations from 1.0 up to 5% w/v followed the sequence.

$$Rb^+ > Na^+ > K^+ > Li^+ \qquad \textbf{(7)}$$

Due to the presence of repulsive forces between adjacent adsorbed Cr (VI) ions was partially nullified. No significant effect on the extraction efficiency of Cr (VI) with increasing concentration of Na^+ and Rb^+ was observed. On the other hand, the sorption percentage of Cr (VI) decreased on increasing the concentrations higher than 5% (w/v). The oxygen sites of the biosorbent were not a predominating factor in the extraction of Cr (VI), because of the ion-dipole interaction of K^+. The results of the present study were in agreement with earlier studies performed by EL-Shahawi et al. (2011b). The adsorption of Cr (VI) ions affected by adding ions. This is may be reduced, due to the number of water molecules available at active sites and become diluted. Further, Cr (VI) as appear at chlorochromate anion of the general formula [CrO_3Cl].

Table 2 Influence of cation size and concentration (1-10 % w/v) on (Li^+, Na^+, K^+ and Rb^+) on the distribution ratio (D) of chromium (VI) uptake onto the algae.

Ion	**D**		
	1%	5%	10%
Li^+	400	750	660
Na^+	1100	1140	1090
K^+	1000	1090	900
Rb^+	1143	1660	1500

Influence of surfactant (anionic, cationic and neutral) on Cr (VI) uptake

The influence of surfactant (anionic, cationic and neutral) at various percentages (1.0 – 10 % v/v) on Cr (VI) uptake by the biosorbent was examined. Results are clearly indicated that, there is no significant change on the Cr (VI) uptake was noticed on using cationic surfactant, while in the adsorption of Cr (VI) also increases with increasing SDS or Triton-X100 surfactant was up to 5% v/v. This behavior is suggested that, there is a progressive change in the micro environment due to the physical properties of the of the produced complex ion always associate with $[CrO_3Cl^-]$ and protonated form of the biosorbent. The percentage adsorption of competition between the surfactant and the anionic complex of Cr (VI) towards the protonated from of the biosorbent may also predominate in the viscosity enhances the dissociation and / or the formation of aggregate complex species with low diffusion constants to be observed (El-Shahawi et al. 2005).

Effect of sample volume

The recoveries of the analytes from sample solutions in different volumes were evaluated. The sample volume can be varied from 25 to125 mL. The aqueous solution containing (20, 40, 60 μ g ml^{-1}) Cr (VI) by using biosorbent was investigated. The results are indicated that, the extraction of Cr (VI) from the aqueous solution adsorption was gradually decreases with increasing the sample volume. The uptake of Cr (VI) decreased up to 55% uptake on raising the sample volume from 25 to 125 mL.

Effect of biosorbent dose

The influence of the biosorbent dose on the extraction of Cr (VI) was investigated. The sorption of Cr (VI) onto the biosorbent increased on increasing the biosorbent dose. The sorption of the Cr (VI) increased on raising the biosorbent dose up to more or less 0.005g of the biosorbent. Further experimental work, 0.005g of biosorbent was used.

Kinetic behavior of Cr (VI) sorption onto algae

The kinetic behavior of sorption of Cr (VI) ions onto the biosorbents was found to be become fast and the Cr (VI) ions equilibrium was attained a constant value within short period of time in batch experimental study. The values of the half-life time ($t_{1/2}$ = 5.1 min). Thus, the rate-controlling step for adsorption gel diffusion is not only for sorbent and it was considered as exchange resin (El-Shahawi et al. 2005). Therefore, the kinetic behavior of adsorption of Cr (VI) ions depends on film diffusion and intra particle diffusion. From the adsorbed Cr (VI) ions onto the solid algae adsorbent was subjected to Weber–Morris model (El-Shahawi et al. 2011a).

$$q_t = R_d\,(t)^{1/2} \qquad \textbf{(8)}$$

where, Rd is the intraparticle transport in $mgg^{-1}\ min^{-1/2}$ and q_t is the Cr (VI) concentration of ions (mg g^{-1}) at time t. The results are clearly show that, the plots of q_t versus time were found to be linear (R^2=0.975- 0.980) in the initial stage for chromium(VI) retention onto the sorbent up to 30 min and deviate on increasing the shaking time. The rate of diffusion was high and slowed down with passage time which revealed the rate of the retention step is film diffusion at the early stage of extraction. The data also indicated that for up to 30 min the relationship holds well and deviates on increasing the shaking time. The values of R_d were then computed from the two distinct slopes of the Weber-Morris plots for the solid phase extractor towards Cr (VI) species. The initial stage up to 30 min of agitation time the adsorption was decreased at higher shaking time and the value R_d was 0.85 mol.$g^{-1}min^{-1/2}$ and the value of R_d at higher time was found0.0776 mol $g^{-1}min^{-1/2}$. Sahan et al.(2010) reported due to existence of different pore size was the reason behind the changes in adsorbent slope.

From the discussion, the straight lines do not pass through the origin to confirm for particle diffusion. The rate controlling step depends on the values of R_d . The kinetics of retention of Cr (VI) from aqueous HCl solution using algae as solid phase extractor was also subjected to Lagergren model for pseudo – first order according to the following equation:

$$\log (q_e - q_t) = \log q_e - \frac{K_{Lager}}{2.303} t \qquad \textbf{(9)}$$

where, q_e is the amount of Cr (VI) sorbed at equilibrium per unit mass of sorbent (µ moles g^{-1}), K_{Lager} is the first order overall rate constant for the retention process per min and t is the time in min. From the two different concentrations of chromium (VI) at 20 and 40 µg mL^{-1} were found to be linear with correlation coefficients (R^2) in the range 0.95-0.99. The results were plotted of log (q_e – q_t) vs time. The results were presented in **Fig. 3.** The k_{lager} values calculated from the slopes were found to be 2.07 and 2.49 s^{-1} towards 20 and 40 µg mL^{-1}Cr (VI) ions respectively. The value of k_{lager} increases with increasing adsorbate concentration was confirm that, the formation of monolayer of Cr (VI) ion species onto the surface of the active site was used as adsorbent as well as the adsorption isotherm was followed by first order kinetics.

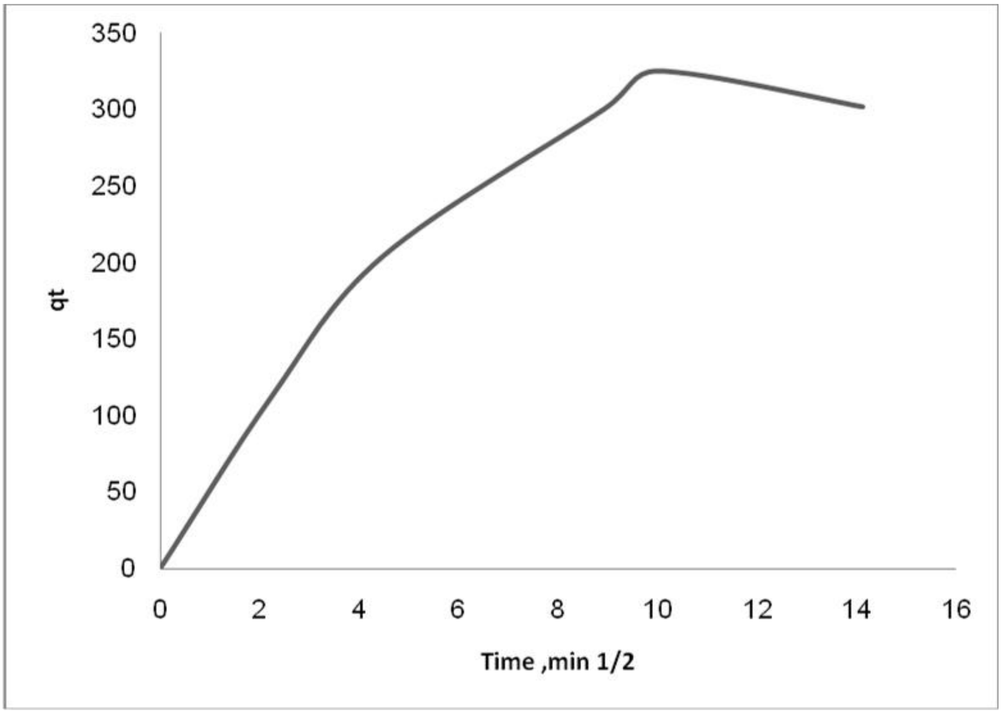

Fig.3 Weber-Morris plots of the sorbed chromium concentration from the aqueous HCl solution *vs.* square root of shaking time onto biosorbent at 25±1 ˚C.

Sorption isotherms of chromium (VI) onto adsorbents

The equilibrium concentrations of Cr (VI) was identified from the aqueous solution containing HCl in the range of 4.1×10^{-6} – 2.58×10^{-4} mol L^{-1} and the retention profile of biosorbents was determined. The amount of adsorption of Cr (VI) ions was retained onto the biosorbent and their equilibrium concentrations in the bulk aqueous solution are shown in **Fig. 4.** At low or moderate analyte concentration, the amount of Cr (VI) retained on the biosorbent varied linearly with the amount remained in the bulk solution. The equilibrium was followed by first-order, because of the direction of Cr (VI) ions rich aqueous phase. The adsorption capacity of Cr (VI) ions towards the biosorbent was at 19 – 19.5 ±0.7 mg g^{-1}. For diluted solutions, The D values decreased. The D values decreased on raising the Cr (VI) concentration rapidly within 15 - 20 min of shaking time and the sorbent membranes became saturated with the retained species respectively. The results are presented in **Fig. 5.** The results revealed the adsorption of Cr (VI) from the aqueous solution was by solute diffusion through an hypothetical film layer. Biosorbent adsorption potential of Cr(VI) was evaluated by wide range of equilibrium concentration to best fit with Freundlich and Langmuir models linear regression. The Freundlich model is expressed in the following form:

$$\log C_{ads} = \log A + \frac{1}{n}\log C_e \qquad \textbf{(10)}$$

where, A and $\frac{1}{n}$ are Freundlich parameters related to the maximum sorption capacity of solute (mol g^{-1}) and C_{ads} is the sorbed chromium(VI) concentration onto the per unit mass of sorbents of the biosorbent (mol g^{-1}) at equilibrium. Plots of log C_{ads} *vs*. log C_e for the Cr (VI) retention onto the biosorbent was linear (R^2=0.96) recorded perfect fit for the experimental data. The slope and intercept values found to be 15.5 ± 0.2 mmol.g^{-1} and 0.54 ± 0.01 for the sorbent. The value 1/n <1 indicating that, the adsorption of favorable for Cr (VI) ions were onto the tested solid sorbent. Reduction in sorption capacity was recorded at lower equilibrium concentration and also the isotherm prediction does not confirm adsorbate to saturate the solid surface of the absorbent.

The Langmuir sorption isotherm revealed the below linear form:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \qquad \textbf{(11)}$$

where, C_e is the equilibrium concentration (mmol L^{-1}) of chromium(VI) in solution . The constant Q is the Langmuir parameter related to the maximum adsorption capacity of solute per unit mass of adsorbent required for monolayer coverage of the surface. b is an equilibrium constant related to the binding energy of solute sorption which is independent of temperature. Plots of C_e / C_{ads} *vs*. C_e over the entire range of concentration of Cr (VI) ions was presented. The plots were found linear (R^2 = 0.991) confirming that the adsorption characteristics of the analyte concentration onto the sorbent obey the Langmuir sorption model. The sorption parameters Q and b found to be 0.103 ± 0.02 mmol.g^{-1} and 50.83 ± 1.2 $mmol^{-1}$ for the sorbent towards Cr (VI) retention. The chromium adsorption was uptake on the surface adsorption due to the added component (El-Shahawi et al. 2005). The retention of chromium on biosorbent, the proposed model can be expressed as follows:

$$C_r = C_{abs} + C_{ads} = DC_{aq} + \frac{SK_L C_{aq}}{1 + K_L C_{aq}} \qquad \textbf{(12)}$$

Where- C_r and C_{aq} - equilibrium concentrations of chromium(VI) ions onto the biosorbent. The parameters C_{abs} and C_{ads} are the equilibrium concentration of Cr (VI) ions onto the used solid sorbent like absorbed and adsorbed species respectively, S and K_L are the saturation value.

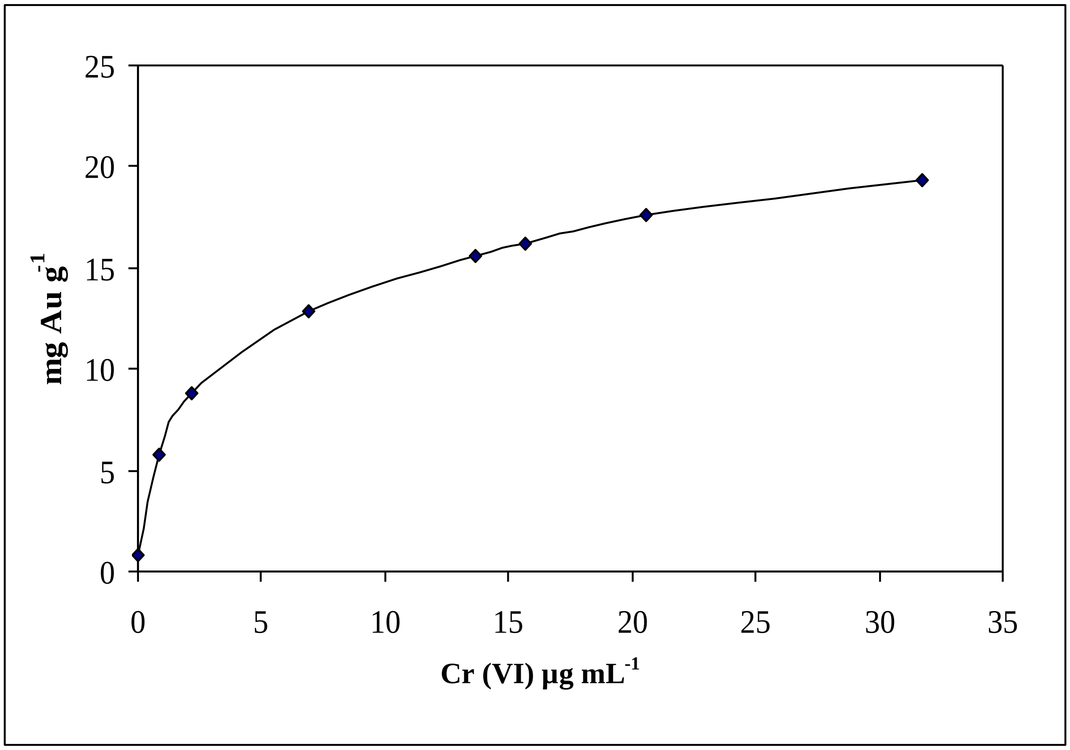

Fig. 4. Sorption isotherms of chromium (VI) uptake from the aqueous HCl solution onto the biosorbent at 25±0.1ºC

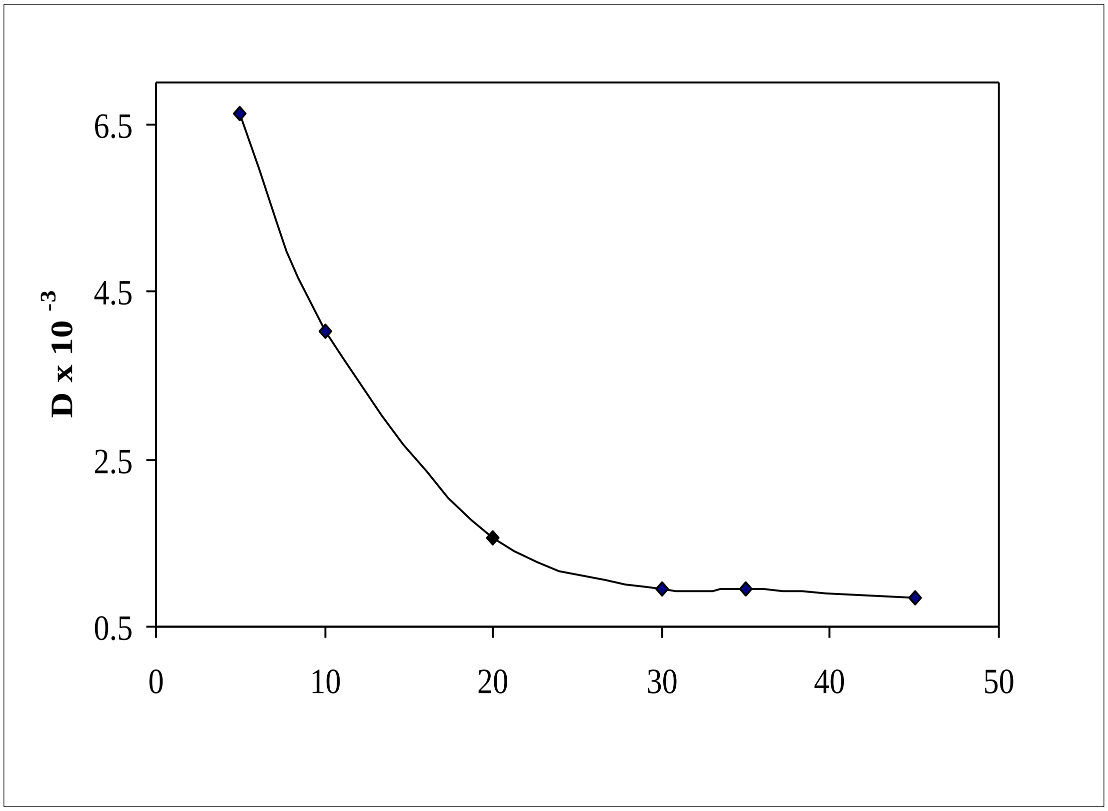

Fig.5 Plots of the distribution ratio (D) of chromium (VI) sorption from aqueous HCl solution of onto biosorbent as a function of the initial chromium (VI) concentration at 25±0.1°C.

Thermodynamic characteristics of Cr (VI) retention using algae

The influence of temperature on the $[CrO_3Cl^-]$ sorption onto the algae was investigated in the temperatures in the of range of 20 – 70 ◦C. The thermodynamic parameters (ΔH, ΔS, and ΔG) were assessed using the equations:

$$\Delta G = \Delta H - T\Delta S \qquad (13)$$

$$K_C = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (14)$$

$$\Delta G = -RT \ln K_C \qquad (15)$$

where, ΔH, ΔS, ΔG, and T are the enthalpy, entropy, Gibbs free energy changes and temperature measured in Kelvin, respectively and R is the gas constant (≈ 8.3 J K-1 mol-1). K_C is the equilibrium constant depending on the adsorption process was fractional. The retention of value of Cr (VI) ion Kc at equilibrium from the aqueous media onto the algae was calculated followed by the equation:

$$K_C = \frac{F_e}{1-F_e} \qquad (16)$$

The plot of ln Kc *vs.* 1000/T for the Cr (VI) retention onto the tested biosorbent was found linear over the tested temperatures range (298 - 343 K). The retention process of Cr (VI) species onto the used sorbents is an endothermic process due to the value of Kc increased on increasing temperature. The values of ΔH, ΔS and ΔG calculated from the slope and intercept of the linear plot of ln KC versus 1000/T were found to be equal at $6.7039 \pm 1.1 Jmol^{-1}K^{-1}$, $20.484 \pm 2.3 Jmol^{-1}K^{-1}$ and -6.098 ± 0.57 K $Jmol^{-1}K^{-1}$, respectively. The positive value of ΔH confirms the endothermic nature of the Cr (VI) uptake at moderate temperature.

Chromatographic behavior of Cr (VI) onto the algae packed columns

To study the chromatographic behavior of Cr (VI) onto the algae packed columns was investigated. In this experiment, an aqueous solution containing Cr (VI) was (5 µg/mL) of 100 mL and HCl (2 mol L^{-1}). The column was packed with percolated through the algae and the flow rate was 5 mL/min. Cr(VI) free aqueous solution (100 mL) was used as distinct blank passed through the algal columns under similar experimental conditions. Spectrophotometric determination of Cr (VI) at λ 350 nm of the effluent solution of algae column against effluent of the reagent blank indicated complete sorption of Cr (VI). The adsorbed concentration of Cr (VI) on the algae was then recovered with 1.0 mol L^{-1} of NaOH. The adsorption percentage (≥ 85 %) was satisfactory for the recovery of the tested Cr (VI) ions.

Chromatographic separation of Cr (VI) sorption

The kinetic and thermodynamic characteristics have clearly indicated that the possible usage of the biosorbent flow at column mode respectively. Preliminary investigation on the use of dry algae of biosorbent packed with columns for the collection of Cr (VI) ions from aqueous media. Thus, aqueous solutions containing various concentrations (0.01-10 µg ml^{-1}) of chromium(VI) ions in hydrochloric acid (2 mol/L^{-1}) were percolated through the biosorbent packed columns at flow rate of 5-10 mL min^{-1} . The analyte concentration was measured by ICP-OES. From the determination of Cr (VI) ions in the effluent samples was packed with columns against a reagent blank. The column adsorption was indicated complete (98 ± 3.1%) retention of Cr (VI) species. A series of various reagents was tested e.g. HNO_3, EDTA, NaOH, NH_4OH. Tested for Cr (VI) from the biosorbent packed column. Among them, NaOH (1.0 mol L^{-1}) was found the best and more suitable for complete recovery of Cr (VI) ions. The influence of concentrations of sodium hydroxide as a proper eluting agent from complete elution of Cr (VI) species from the biosorbent packed column was investigated. The results revealed that, the recovery percentage was good (98% ± 2.9) of Cr (VI) using NaOH (1.0 mol L^{-1}). Thus, in the subsequent work sodium hydroxide (1.0 mol L^{-1}) was used as a suitable eluting agent of Cr (VI) from the sorbent packed column at 5 ml min^{-1} flow rate was determined by ICP-OES.

Quantitative extraction and recovery of Cr (III)

In order to estimate the retention and recovery of the present study, an aqueous solution containing ≤ 10 µg mL^{-1} Cr (III) to Cr (VI) by boiling the test solution with hydrogen peroxide (5 mL, 30%v/v) for 10 min. The solution pH was adjusted to pH~9 with NaOH. The reaction mixture was boiled and allowed to cool for few minutes. The pH of the solution was adjusted to pH~zero with HCl. The test solution was then percolated through the biosorbent packed column and the flow rate was maintained at 5 mL min^{-1}. The adsorption of Cr (VI) ions were recovered with 10 mL of 1.0 mol L^{-1}NaOH at the flow rate was 5 mL min^{-1}. The analyte content was measured by the recommended procedure.

Interference Study

To study the effect of potential interference on the chromium(VI) ions. The 100 ml of solution containing 10 µg ml^{-1} chromium(VI) ions added with various salt ions such as Fe^{3+}, Al^{3+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, and Cd^{2+} and the recommended procedure was investigated. The recovery of chromium ions is considered free from interference. But the tolerance limit was less than ± 4 %. The quantitative recovery of Cr (VI) ions was achieved with successfully in the presence of the investigated diver's ions show that good extraction efficiency (95± 5%) was respectively. At high concentration there is no significant effect was observed. Aluminum and iron ions decreased the recovery of Cr (VI) sorption by 20-50%. Addition of NaF (100 µg ml^{-1}) to the test aqueous solution eliminated the interference of these two ions. Thus the procedure was applicable for the determination of Cr (III) and Cr (VI) in water and wastewater samples.

Analytical applications

Retention and recovery of Cr (VI) ions in tap and seawater samples by sorbent packed Column

To study the retention and recovery of total chromium water samples collected from Red Sea (northern coastal area of Jeddah City, Saudi Arabia) were used. The samples were filtered through cellulose membrane filter paper with 0.45 µm pore size. The samples were after collection digested with HNO_3-H_2O_2 and further boiled for 15 min and low concentrations (0.05-10 µg ml^{-1}) of the spiked Cr (VI) ions onto tap and / or industrial water samples under the optimum conditions, after the samples was stored in pre-cleaned polyethylene pet bottles. The Cr (III) retention required with hydrochloric acid. The sample solutions were centrifuged for 15 min and passed through biosorbent packed column at 5 ml min^{-1} flow rate. The retained species were then recovered quantitatively with sodium hydroxide (10 mL, 1.0 mol L^{-1}) as indicated from the ICP-OES measurement. The results are summarized in **Table 3.**

Table 3 Result of the analysis of chromium (IV) in tap and Red sea water by the developed biosorbent packed column*

Concentration, µg mL^{-1}	Recovery %
0.05	102 ± 2 (105 ± 3.1)
0.5	97±1.5(102 ± 4.1)
5.0	96 ± 1(105 ± 2.7)
10	97± 1 (102 ± 4.7)

* Data of analysis of chromium in sea water are given in parentheses.

Analysis of Cr (VI) ions in wastewater samples

The present proposed method for chromium is applied to Industrial and treated wastewater samples were collected from municipal discharge station samples, Jeddah city. The water samples were filtered through a 0.45 µm cellulose membrane filter paper respectively. The samples were after collection digested with HNO_3-H_2O_2 and further boiled for 15 min and low concentrations (0.05-10 µg ml^{-1}) of the spiked Cr (VI) ions onto tap and / or industrial water samples under the optimum conditions, after the samples was stored in pre-cleaned polyethylene pet bottles. The solutions were boiled for 5 min and spiked with various amount of (0.05-0.5 µg) of Cr (VI) in the presence of hydrochloric acid (1.0 mol L^{-1}) was also added. The sample solutions were centrifuged for 10 min and percolated through biosorbent packed column at flow rate of 5 mL min^{-1}. The adsorbed chromium species were then recovered (95±3.1 %) from the column with NaOH (10, 1.0 M). The recovered solution was measured by using ICP-OES. The results for the determination of Cr (VI) ions in wastewater sample values are summarized in **Table 4** using the standard addition method.

Table 4 Result for the retention of chromium (VI) in tap water (A) and wastewater (B) by the developed biosorbent packed column*

Chromium(VI) µg ml^{-1}	Recovery, %*	
	A	B
0.05	102 ± 2	100 ± 2
0.5	99±1.5	99±1.5
5	98 ± 1	98 ± 1
10	97.5 ± 1	97 ± 1

* Average of five measurements ± relative standard deviation.

Retention of Cr (III) & (VI) in tap water

To find out the retention of Cr (III) and Cr (VI) ions in tap water samples were investigated respectively. The tap water sample approximately 0.5 L of spiked with ≤ 20 µg mL^{-1} Cr (III) and Cr (VI) concentration was percolated through the biosorbent. The flow rate of the column was adjusted with 5 mL min^{-1} at the optimum conditions of Cr (VI) uptake was maintained. The retention of Cr (VI) ions are quantitatively took place, while the Cr (III) was identified without adsorption. The recovered Cr (VI) species retained on the biosorbent packed column was quantitatively (93-102 %) by percolating with 10 mL of NaOH (1.0 mol L^{-1}) at 2 mL min^{-1} flow rate. Another aliquot sample Cr (III) was oxidized to Cr (VI) with H_2O_2 in alkaline solution for the conversion. Good recovery of total chromium (96-100%) was obtained for the analyzed samples.

Conclusion

The use of dry algae as biosorbent in batch and flow modes showed good results towards Cr (III) and (VI) retention and recovery after oxidation of the former to the hexavalence by hydrogen peroxide in alkaline solution. The kinetics of the retention step was subjected to kinetic models to get the overall rate constants and reaction order. The data were also subjected to many sorption models to assign the retention mechanism of Cr (VI) from the bulk solution. The present method was simple to operate and over the conventional methods. The biosorbent packed column can be reused for many times, and the recovery percentages of chromium ions are still over 95%. The developed method could be extended for chemical speciation and continuous monitoring of different chromium forms in industry. Algal culture offers a simple approach for wastewater treatments, due to potential tertiary biotreatment coupled with valuable biomass production. Thus, algae exhibited very high Cr (VI) biosorption capacities in packed column compared to most of the biosorbents. Application of the algae as biosorbent revealed with high biosorption efficiency with cheap cost derives an ultimate adsorption technology to remove heavy metals in wastewater.

Nomenclature

A_b (mg/L) initial metal ion concentration
A_a (mg/L) final metal ion concentration
(% E) the sorption percentage
Ce (mg/L) concentration at the equilibrium state
Qe (mg/g) adsorption capacity at equilibrium
Q (mg g−1) Langmuir constants b (dm3 mg−1) Langmuir constants
R2 (dimensionless) correlation coefficient
R (8.314J/molK) universal gas constant
ΔH enthalpy
ΔS entropy
ΔG (kcal/mol) Gibbs free energy change
Kc equilibrium constant
Kf (L/g) Freundlich constant 1/n (dimensionless) Freundlich parameter related to intensity of adsorption
T (K) absolute temperature
t (min) contact time

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