



Biosorption of Hexavalent Chromium from Aqueous Solutions by Chemically Modified Brown Algae of *Sargassum* sp. and Dried Activated Sludge

MEHDI FARZADKIA, MITRA GHOLAMI, MAJID KERMANI* and KAMYAR YAGHMAEIAN

Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

*Corresponding author: Fax: +98 21 88779487; Tel: +98 21 88779118; E-mail: majidkermani@yahoo.com

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The present study deals with the evaluation of biosorptive removal of Cr(VI) ions by pre-treated brown marine algae of *Sargassum* species and dried activated sludge treated with calcium chloride. Batch kinetics and isotherm experiments were performed in order to examine the effects of contact time, pH, initial metal concentration and biomass concentration, on the removal process. Biosorption of Cr(VI) was rapidly occurred onto biosorbents and most of the sorbed metal was bound within 1 h. The removal performance by the *Sargassum* sp. was found more than dried activated sludge. Results showed that the uptake of Cr(VI) increased with increasing pH for *Sargassum* sp. and decreased with increasing pH for dried activated sludge in initial pH from 2 to 6. The capacity of Cr(VI) biosorption at equilibrium increased with the increase of initial Cr(VI) concentration (10-100 mg L⁻¹) and decreased with the increase of biosorbents dose (0.5-5.5 g L⁻¹). The results showed that the equilibrium data for *Sargassum* sp. could be well by the Langmuir isotherm model, whereas the equilibrium data for dried activated sludge fitted the Freundlich isotherm model best within the concentration range studied. From the results obtained, the pseudo-second-order kinetic model best describes the biosorption of Cr(VI) ions.

Key Words: Biosorption, Brown algae, Activated sludge, Chromium(VI), Isotherms, Kinetics.

INTRODUCTION

The increase of industrial activities has accentuated environmental pollution problems causing the deterioration of several ecosystems with the accumulation of many pollutants, such as toxic metals¹. Hexavalent chromium is one of the major pollutants in the environment and is frequently present in wastewaters from industries such as electroplating, metal cleaning, leather industries, plating, photographic-film making, wood preservation, car manufacturing petroleum refining and agricultural activity. Cr(VI) containing effluents are also discharged from a wide range of industries, including dye, textile, tannery, petrochemical and many others²⁻⁵. These industries contain Cr(III) and Cr(VI) at concentration ranging from 10 to 100 mg L⁻¹. Cr(III) and Cr(VI) are two of the most stable states in aqueous phase. Hexavalent chromium is 500 times more toxic than the trivalent one. The toxicity to human beings is known as skin irritation, epigastric pain, nausea, vomiting, severe diarrhoea, haemorrhage and carcinogenicity. Therefore, Cr(VI) requires more concern⁷.

Conventional separation techniques for removing heavy metals from industrial effluents (e.g. chemical precipitation, chemical oxidation and reduction, ion exchange, reverse osmosis, membrane separation, electrochemical treatment and

evaporation) are often ineffective and costly when applied to dilute and very dilute effluents with heavy metal concentration of less than 100 mg L⁻¹ 6-11.

Biosorption is an alternative technology in which an increased amount of study is being focused¹²⁻¹⁴. Biosorption processes, defined as the sorption of heavy metal ions by biomass, are being employed as an alternative technique for the decontamination of industrial effluents and for the recovery of the retained metals¹⁴. The biological materials that have been investigated for heavy metal uptake include fungi, bacteria, yeast, micro-algae and macro-algae¹²⁻¹⁷.

Marine algae are biological resources, which are available in large quantities in many parts of the world¹⁸. Some seaweed collected from the ocean has indicated impressive biosorption of materials. Brown marine algae tend particularly to sequester heavy metals¹⁴. Numerous studies on metal biosorption by brown seaweeds such as *Sargassum* have been reported in the literatures^{8,9,12,19}. In brown algae *Sargassum* biomass, alginate in the cell wall is the main component responsible for the metal sorption. It is present in a gel form in the cell wall, which appears very porous and easily permeable to small ionic species. Ion exchange has been confirmed to be highly involved to a large degree in the metal sequestering by algal biomass¹⁴.

Activated sludge is an attractive biosorbent for heavy metals, dyes and organic compounds such as phenol because of its low cost and availability. Activated sludge from wastewater treatment systems contains both bacteria and protozoa. The cell wall of bacteria essentially consists of various organic compounds, such as carboxyl, acidic polysaccharides, lipids, amino acids and other components. However, activated sludge organisms in form of live or dead were also used for biosorption of heavy metal ions by different investigators using different types of reactors²⁰⁻²⁵.

The main objective of this work was to investigate the ability of nonliving biomass of marine brown algae of *Sargassum* sp. and dried activated sludge as biosorbent for Cr(VI) ions from aqueous solutions. The influences of different parameters on Cr(VI) uptake, such as sorption time, pH, initial Cr(VI) concentration and biomass concentration was investigated. The Freundlich and Langmuir isotherm models were used to analyze the biosorption equilibrium. The pseudo-first-order and pseudo-second-order kinetic models were also used to correlate the data for both models.

EXPERIMENTAL

Preparation of biosorbents: Fresh samples of brown marine algae of *Sargassum* sp. were collected from coastal areas of the Persian Gulf, Iran. Activated sludge, a complex consortium of microorganisms mainly containing bacteria was taken from Shahrake Gharb Municipal Wastewater Treatment Plant, Tehran, Iran. The brown algae was washed with tap water to remove sand and other impurities and was sun-dried for 48 h. Dried biomass was ground in a laboratory blender and then washed with double-distilled water (DDW) and dried in an oven at 60 °C for 24 h. This material will be referred to as intact biomass¹. Activated sludge biomass was centrifuged at 2000 rpm for 5 min, washed twice with deionized water to remove easily suspended materials, dried at 60 °C until constant weight and then ground to a gritty consistency to yield granular biosorbent samples^{21,23}. The brown algae of *Sargassum* sp. and dried activated sludge (20 g) were treated with 0.1 M CaCl₂ solution (400 mL) for 15 min under slow stirring (Protonation). Both calcium treated biomasses were washed several times with deionized water to remove excess calcium from them and kept on a filter paper to reduce the water content. After that, biomasses were heated in an oven at 60 °C for 24 h and then sieved to obtain particle sizes under 250 μm and were further used as the biosorbent¹.

Hexavalent chromium [Cr(VI)] solution: Stock Cr(VI) solution (1000 mg L⁻¹) was prepared by dissolving 5.66 g of K₂Cr₂O₇ (Merck, Germany) in 1000 mL of deionized distilled water. Cr(VI) solution of different concentrations was prepared by adequate dilution of the stock solutions with double-distilled water²⁶. The range in initial concentrations of Cr(VI) prepared from stock solutions varied between 10-100 mg L⁻¹.

Determination of the Cr(VI) content in the solutions: The concentration of Cr(VI) in the solutions before and after the equilibrium was determined by flame atomic absorption spectrophotometry (FAAS), using a BRAIC WFX-130 atomic absorption spectrophotometer at the wavelength of 357.9 nm²⁶.

Kinetic experiments: Biosorption studies were conducted in a routine manner by the batch technique. Preliminary

experiments were performed to determine equilibrium time for biosorption of Cr(VI) by *Sargassum* biomass and dried activated sludge. For this purpose, 250 mg of each biomass (size of particles $d = 200-300 \mu$) was added to 250 mL metal solution with a known concentration (50 mg L⁻¹) and initial pH of 4 in 250 mL Erlenmeyer flasks. The flasks placed on a gyratory shaker with constant shaking at 150 rpm, at 23 ± 2 °C. The pH of solutions during the contact period (10-240 min) was adjusted at 4 ± 0.2 using small amount of 0.1 M H₂SO₄ or 0.1 M NaOH as required. All pH measurements were carried out with a pH meter model CG-710. Samples were periodically withdrawn from the shaker and the solutions were separated from the biomass by filtration through filter papers (Whatman No. 40 Ashless). After appropriate dilution, the concentration of Cr(VI) in the filtrate was determined by flame atomic absorption spectrophotometry. The effect of pH values (2-6), initial Cr(VI) concentration (10-100 mg L⁻¹) and biomass dose (0.5-5.5 g L⁻¹) on the biosorption of Cr(VI) by nonliving biomass of *Sargassum* and dried activated sludge was studied.

Equilibrium experiments: The equilibrium isotherms were determined at 23 ± 2 °C under optimized conditions, changing the Cr(VI) concentration into the range of 10-100 mg L⁻¹ and using an equilibrium time 1 h. Metal free and biosorbents free blanks were used as control. All biosorption experiments were carried out in duplicates and the average value were used for further calculations.

Data evaluation: The Cr(VI) removal efficiency and amount of chromium ion biosorption onto the biosorbents were calculated by eqs. (1) and (2), respectively.

$$E = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

$$q = (C_i - C_f) \frac{v}{m} \quad (2)$$

where, E is the removal efficiency, C_i (mg L⁻¹) and C_f (mg L⁻¹) are the initial and final metal ion concentrations in the solution, respectively, q (mg g⁻¹) is the Cr(VI) biosorption capacity, v(L) is the solution volume and m (g) is the amount of biosorbent used.

RESULTS AND DISCUSSION

Effect of contact time: The biosorption data for the uptake of Cr(VI) *versus* contact time at 50 mg L⁻¹ initial Cr(VI) concentration with 1 g/L of each biosorbent were carried out in pH value of 4 ± 0.2 . In the biosorption of Cr(VI) by *Sargassum* biomass and dried activated sludge, most of the metal ions were sequestered from solution within the first 0.5 h and almost no increase in the level of bound metal occurred after 1 h. So, 1 h was used as the equilibrium time for two biosorbents. Fig. 1 shows the effect of contact time on the removal of Cr(VI) by *Sargassum* sp. and dried activated sludge. These results indicated that nonliving biomass of *Sargassum* sp. removed Cr(VI) most efficiently than dried activated sludge from aqueous solution. According to the results, the removal performance by the *Sargassum* sp. was found more than dried activated sludge, with maximum uptake values of 44.253 and 21.058 mg g⁻¹ dry weight biomass for *Sargassum* Sp. and dried activated sludge, respectively. Differences between algal

species in the magnitude of change in metal ion binding capacity may be due to the properties of the metal sorbate (e.g. ionic size, atomic weight, or reduction potential of the metal) and the algae (e.g. structure, functional groups and surface area, depending on the algal division, genera and species)¹⁴. Marine brown algae in particular are suited for binding metallic ions due to their polysaccharide material content (alginates, xylofocoglycuronans, xylofocoglucans and homofucans). These polysaccharides contain carboxyl and sulfate groups that have identified as the main metal-sequestering sites^{8,14,27}.

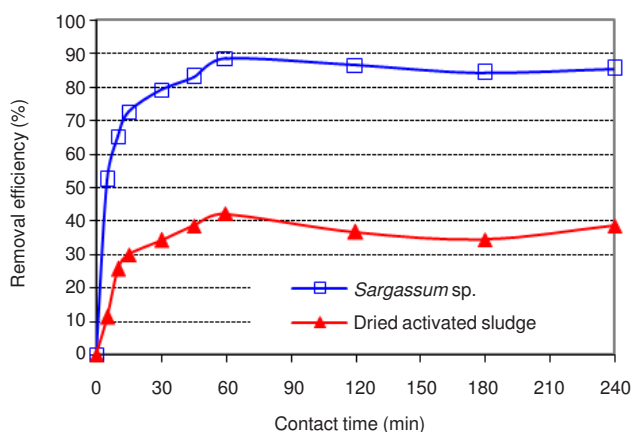


Fig. 1. Effect of contact time on the removal of Cr(VI) by *Sargassum* sp. and dried activated sludge

Effect of initial solution pH: The initial pH of the solution is a very important factor in heavy metal sorption uptake by biosorbent. Different metal ions may have different pH optima, possibly due to the different solution chemistry of the species. So, pH is an important parameter on biosorption of metal ions from aqueous solutions^{8,11,14,18,27}. *Sargassum* sp. presents a high content of ionizable groups (carboxyl groups from mannuronic acid and guluronic acid) on the cell wall polysaccharides, which makes it, at least in theory, very liable to the influence of the pH. So, the effect of initial pH on the equilibrium uptake of Cr(VI) ions was investigated between pH 2-6 since the precipitation of Cr(VI) may occur above pH 6. Fig. 2 represents the effect of initial pH on the removal of Cr(VI) by *Sargassum* sp. and dried activated sludge. Biomass dose, initial Cr(VI) concentration and equilibrium time were 1 g L⁻¹, 50 mg L⁻¹ and 1 h, respectively. *Sargassum* biomass was added separately in the pH range 2-6 and the results are depicted in Fig. 2. According to the results, the uptake of Cr(VI) showed a sharp increase with an increase in pH from 2 to 6 in the case of *Sargassum* sp. and a sharp decrease in the case of dried activated sludge (Fig. 2). In case of *Sargassum* sp., the uptake of free ionic Cr(VI) depend on pH, increasing with the increase in pH from 2 to 3 and then reaching a plateau in the pH range 3-4. Similar results were reported on literature^{8,11-13,18,19}. At the pH values lower than 3, Cr(VI) removal was strongly decreased, possibly as a results of the competition between hydrogen and Cr(VI) ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased (pH = 3.5-5), the ligands such as carboxylate groups

in *Sargassum* sp. would be exposed, increasing the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing the biosorption onto the cell surface. Nasser *et al.*²⁸ reported the removal of chromium using *A. oryzae*, where maximum removal was observed at pH 5. In the case of dried activated sludge, the effect of initial pH on the equilibrium uptake shows that the uptake of Cr(VI) decreased with increasing initial pH from 2 to 6. Aksu *et al.*²⁵ reported that removal of Cr(VI) using dried activated sludge, decreased with increasing pH. The biosorption of Cr(VI) on dried activated sludge is mainly due to ionic attraction. Solution pH affected the zeta potentials or surface charges of dried activated sludge and also the solubility of the chromium ions. At pH values higher than 6, biosorption studies could not be performed due to the precipitation of Cr(VI) ions. As seen from the results, in pH values higher than 6, insoluble Cr(VI) start precipitating from the solution. So, these pH values making true sorption studies impossible and we chose pH = 4 for further experiments.

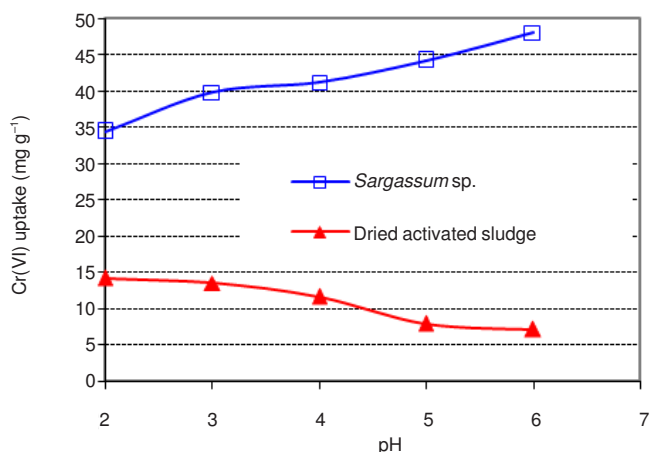


Fig. 2. Effect of pH on the removal of Cr(VI) by *Sargassum* sp. and dried activated sludge

Effect of initial Cr(VI) concentration: The capacities of Cr(VI) biosorption at equilibrium time by biomass obtained from experimental data at different initial concentrations are presented in Fig. 3. Biomass dose, equilibrium time and pH were 1 g/L, 1 h and 4, respectively. As seen from results, at the optimal conditions, metal ion uptake increased with initial Cr(VI) ion concentration upto 100 mg L⁻¹. Increasing the initial Cr(VI) concentration would increase the mass transfer driving force and therefore the rate at Cr(VI) molecules pass from the bulk solution to the biomass surface. This would results in higher Cr(VI) biosorption capacity¹⁵. In agreement with our study, Wang *et al.*²¹ have shown that the equilibrium adsorption capacities increased with the increasing of initial metal ion concentration. On a relative basis, however, the percentage biosorption of Cr(VI) decreases as its initial concentration increase. The equilibrium uptake and biosorption yield were highest for the *Sargassum* sp., which was expected.

Effect of biosorbent dose: Fig. 4 shows the uptake of Cr(VI) (as mg g⁻¹) as a function of adsorbent dose (as g L⁻¹) by *Sargassum* sp. and dried activated sludge. The initial Cr(VI) concentration, equilibrium time and pH were 50 mg L⁻¹, 1 h

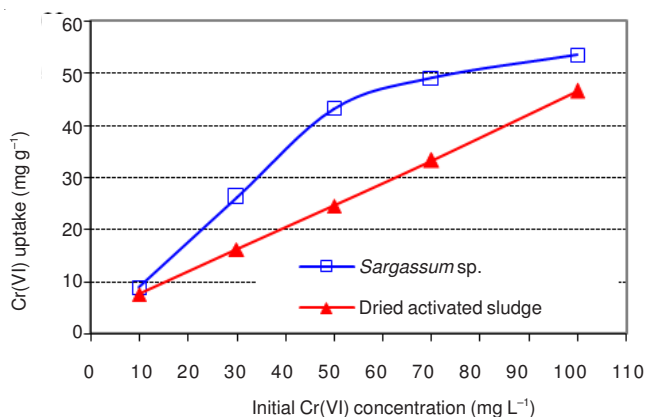


Fig. 3. Effect of initial Cr(VI) concentration on the capacity of its biosorption by *Sargassum* sp. and dried activated sludge

and 5, respectively. Adsorbent doses were varied from 0.5 to 5.5 g L⁻¹. According to the results, it is evident that for the quantitative removal of different values of Cr(VI) in 250 mL, a high dosage of *Sargassum* sp. and dried activated sludge is required. The data clearly shows that the *Sargassum* sp. is more effective than dried activated sludge for removal of Cr(VI). The results also clearly indicate that the removal efficiency increases up to the optimum dosage beyond which the removal efficiency is negligible. Fig. 4 showed that with increasing concentration of biosorbent dose, rate of biosorption (as mg g⁻¹) was decreased. However, with increasing biosorbent dose, removal percentage of Cr(VI) was increased. Increases in biosorbent dose resulted in increased binding sites on the biosorbent when initial Cr(VI) ion concentration was constant at 50 mg L⁻¹. Therefore, lower fractions of biosorbent surfaces were occupied by Cr(VI) ions as the biosorbent dose increased which yielded lower solid phase Cr(VI) concentrations (q_e). Pamukoglu and Kargi²⁹ have shown that biosorbed Cu(II) ions decreased with increasing powdered waste sludge concentration.

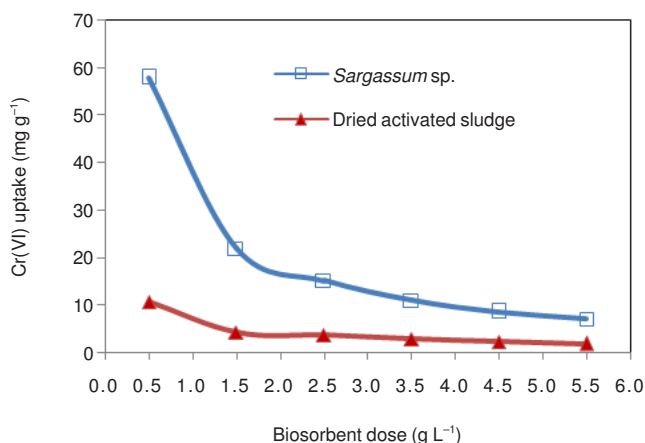


Fig. 4. Effect of adsorbent dose on the uptake of Cr(VI) by *Sargassum* sp. and dried activated sludge

Biosorption isotherms: Two different biosorption isotherms, the Langmuir and the Freundlich isotherms, were used to correlate the equilibrium data. The Langmuir isotherm has been successfully applied to many pollutant adsorption processes and has been the most widely used adsorption isotherm for the adsorption of a solute from a liquid solution.

A basic assumption of the Langmuir theory is that adsorption takes place on a homogeneous surface by monolayer sorption.

The well-known Langmuir expression [Eq. (3)] is given as follows³⁰:

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \quad (3)$$

Which may be written in linearized form as follows:

$$\frac{1}{q_{eq}} = \frac{1}{q_{max}} + \frac{1}{b q_{max}} \frac{1}{C_{eq}} \quad (4)$$

where, q_{eq} (mg g⁻¹) is the equilibrium metal biosorption capacity of the biosorbent, C_{eq} (mg L⁻¹) is the equilibrium metal ion concentration in the solution, q_{max} (mg g⁻¹) is the maximum biosorption capacity of the biosorbent and b (L mg⁻¹) is a constant related to the affinity of the binding sites.

The Freundlich isotherm proposes a multilayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The Freundlich isotherm has the following form [Eq. (5)]³¹:

$$q_{eq} = k_f C_{eq}^{\frac{1}{n}} \quad (5)$$

Which may be written in linearized form as follows:

$$\log(q_{eq}) = \log(k_f) + \frac{1}{n} \log(C_{eq}) \quad (6)$$

where, q_{eq} (mg g⁻¹) is the equilibrium metal biosorption capacity of the biosorbent, k_f (mg g⁻¹) and n (g L⁻¹) are Freundlich constant related to biosorption, respectively and C_{eq} (mg L⁻¹) is the equilibrium metal ion concentration in the solution.

The linearized Freundlich and Langmuir adsorption isotherms of each biosorbent for Cr(VI) are shown in Figs. 5 and 6. The initial Cr(VI) concentration, equilibrium time and pH were 50 mg L⁻¹, 1 h and 4, respectively. The results showed that the equilibrium data for *Sargassum* sp. could be well by the Langmuir isotherm model, whereas the equilibrium data for dried activated sludge fitted the Freundlich isotherm model best within the concentration range studied. But, in general, R^2 values, which are a measure of goodness-of-fit, show that both the Langmuir and Freundlich isotherm models could adequately describe the biosorption data. According to Langmuir and Freundlich models, the maximum biosorption capacity (q_{max}) was given 53.506 and 46.557 mg g⁻¹ dry weight

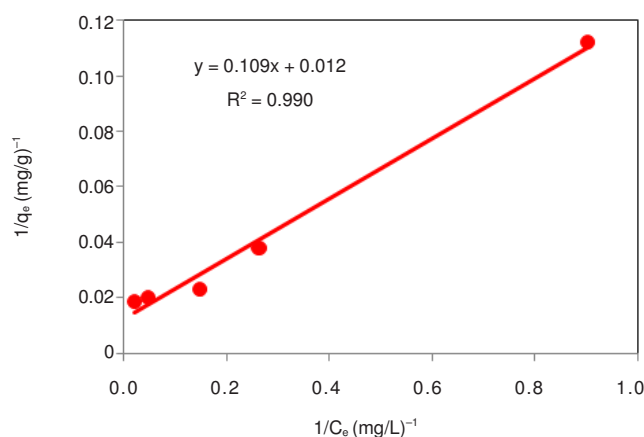


Fig. 5. Langmuir biosorption isotherm for Cr(VI) with non-living biomass of *Sargassum* sp.

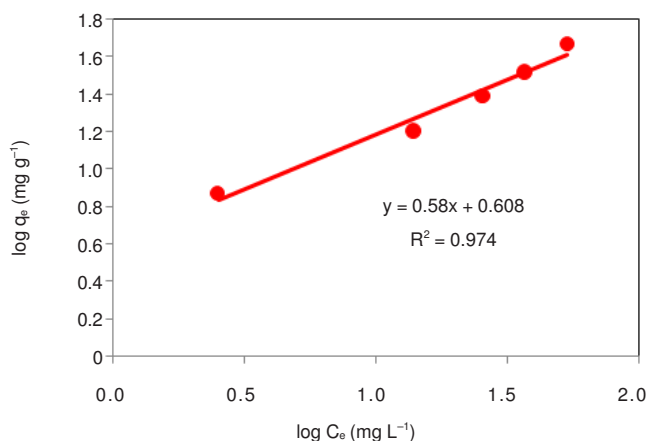


Fig. 6. Freundlich biosorption isotherm of Cr(VI) with *dried activated sludge*

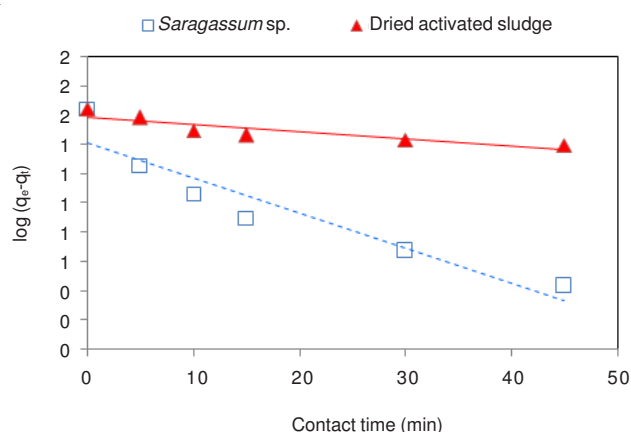


Fig. 7. Pseudo-first-order kinetic model for biosorption of Cr(VI) by *Sargassum* sp. and dried activated sludge

biomass for *Sargassum* Sp. and dried activated sludge, respectively. The q_{max} ($mg\ g^{-1}$) of both biosorbent in this study was compared with those in some other reported studies (Table-1). Differences in the biosorption capacity data are most likely due to different properties of each adsorbent, such as structure, functional groups and surface area.

TABLE-1
MAXIMUM BIOSORPTION CAPACITY FOR DIFFERENT BIOSORBENTS

Heavy metal	Biosorbent type	q_{max} ($mg\ g^{-1}$)	pH	Temp. ($^{\circ}C$)	Ref.
Cr(VI)	Grape waste	99.31	4	30	[32]
Cr(VI)	Bagasse	102.43	3	25	[33]
Cr(VI)	<i>Oedogonium hatei</i> (raw)	31.00	2	25	[34]
Cr(VI)	<i>Spirogyra</i> sp.	14.70	2	25	[34]
Cr(VI)	<i>Bacillus coagulans</i>	39.90	-	25	[35]
Cr(VI)	<i>Zoogloa ramigera</i>	2.00	-	25	[35]
Cr(VI)	<i>Pseudomonas</i> sp.	95.00	-	25	[35]
Cr(VI)	<i>Sargassum</i> sp.	53.506	4	25	This study
Cr(VI)	Dried activated sludge	46.557	4	25	This study

Kinetic model studies: To examine the controlling mechanism of biosorption process such as mass transfer and chemical reaction, the Lagergren's pseudo-first-order and the pseudo-second-order kinetic models were used to test the experimental data of Cr(VI) biosorption by both *Sargassum* sp. and dried activated sludge. The linear form of the pseudo-first-order equation by Lagergren³⁶ is given as Eq. (7):

$$\log(q_{eq} - q_t) = -\frac{k_{1.ad}}{2.303}t + \log q_{eq} \quad (7)$$

where, q_{eq} and q_t ($mg\ g^{-1}$) are the biosorption capacity at equilibrium and at time t , respectively and $k_{1.ad}$ (min^{-1}) is the rate constant of pseudo-first-order sorption. Experimental data were plotted in form of $\log(q_{eq} - q_t)$ against time to evaluate the suitability of the pseudo-first-order model line (Fig. 7). The values of $k_{1.ad}$ and the calculated $q_{eq,cal}$ were obtained from slope and intercept of straight line (Fig. 7). These values along with the corresponding correlation coefficient (R^2) for both biosorbent were shown in Table-2. The value determined from the model is not in good agreement with the experimental value of $q_{eq,exp}$ (44.253 and $21.058\ mg\ g^{-1}$ for *Sargassum* Sp. and dried waste activated sludge, respectively). Therefore the

TABLE-2
LAGERGREN'S PSEUDO-FIRST-ORDER KINETIC MODEL PARAMETERS FOR Cr(VI) IONS REMOVAL BY *Sargassum* sp. AND DRIED ACTIVATED SLUDGE

Parameters	Unit	Type of biosorbent	Pseudo-first-order model
$K_{1.ad}$	min^{-1}	<i>Sargassum</i> sp.	0.023
		dried activated sludge	0.005
$q_{eq,cal}$	$mg\ g^{-1}$	<i>Sargassum</i> sp.	26.002
		dried activated sludge	39.084
$q_{eq,exp}$	$mg\ g^{-1}$	<i>Sargassum</i> sp.	44.253
		dried activated sludge	21.058
R^2	-	<i>Sargassum</i> sp.	0.891
		dried activated sludge	0.804

pseudo-first-order model is not suitable to biosorption of Cr(VI) onto the *Sargassum* sp. and dried activated sludge. The pseudo second-order model is more suitable for the description of the kinetic behaviour of adsorption in which chemical sorption is the rate-controlling step. This equation is in the following form³⁶:

$$\frac{t}{q_t} = \frac{1}{k_{2.ad}q_{eq}^2} + \frac{1}{q_{eq}}t \quad (8)$$

where, q_{eq} and q_t ($mg\ g^{-1}$) are the biosorption capacity at equilibrium and at time t , respectively and $k_{2.ad}$ [$g\ (mg\ min)^{-1}$] is the rate constant of pseudo-second-order sorption. Experimental data were plotted in form of t/q_t versus time to show the suitability of the pseudo-second-order kinetic model (Fig. 8). The values of $k_{2.ad}$ and the calculated $q_{eq,cal}$ were obtained from slope and intercept of straight line (Fig. 8). These values along with the corresponding correlation coefficient (R^2) for both biosorbent were shown in Table-3. The correlation coefficient (R^2) for the pseudo-second-order equation is high and the calculated $q_{eq,cal}$ value agrees with the experimental $q_{eq,exp}$ (44.253 and $21.058\ mg\ g^{-1}$ for *Sargassum* Sp. and dried waste activated sludge, respectively). This strongly suggests that the biosorption of Cr(VI) onto the *Sargassum* Sp. and dried waste activated sludge can be represented more appropriately by the pseudo-second-order. The very fast sorption kinetics observed with *Sargassum* biomass represents an advantageous aspect when effluent treatment systems are designed (Fig 8). In agreement with our results, Wang *et al.*²¹ were reported that pseudo-second-order kinetic model represented the data better than the pseudo-

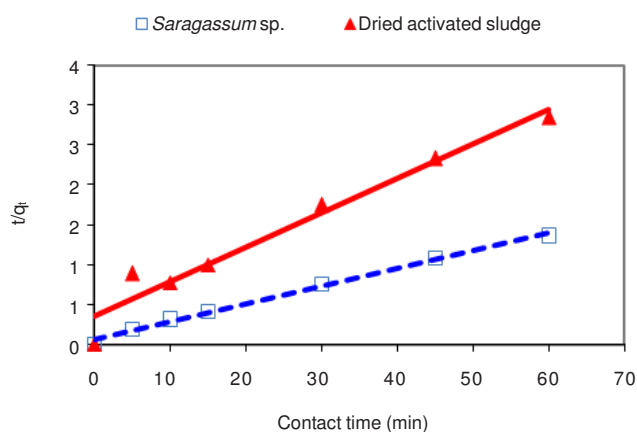


Fig. 8. Pseudo-second-order kinetic model for biosorption of Cr(VI) by *Sargassum* sp. and dried activated sludge

Parameters	Unit	Type of Biosorbent	Pseudo-second-order model
$K_{2,ad}$	$g (mg \text{ min})^{-1}$	<i>Sargassum</i> sp. dried activated sludge	0.0076 0.005
$q_{eq,cal}$	$mg \text{ g}^{-1}$	<i>Sargassum</i> sp. dried activated sludge	45.455 23.256
$q_{eq,exp}$	$mg \text{ g}^{-1}$	<i>Sargassum</i> sp. dried activated sludge	44.253 21.058
R^2	-	<i>Sargassum</i> sp. dried activated sludge	0.994 0.957

first-order model for biosorption of dye by anaerobic sludge. Also in the other studies were shown that pseudo-second-order kinetic model correlated the data better than the pseudo-first-order model for biosorption of different metal ions^{12,20,37,38}.

Conclusion

Biosorption of Cr(VI) ions from aqueous solution onto *Sargassum* sp. and dried activated sludge was investigated as functions of important operating variables, such as contact time, pH, concentration of adsorbate (Cr^{6+} ions) and also concentrations of both biosorbent dose. The obtained results showed that *Sargassum* biomass have a high biosorption capacity to remove Cr(VI) ions. On the other hand, the removal performance by the *Sargassum* sp. was found more than dried activated sludge. A comparison of sorption capacity of *Sargassum* sp. with those obtained in the literature for the sorption of Cr(VI) also showed that *Sargassum* biomass is more effective for this purpose. The effect of initial pH on the equilibrium uptake showed that the uptake of Cr(VI) increased with increasing pH for *Sargassum* sp. and decreased with increasing pH for dried activated sludge in initial pH from 2 to 6. *Sargassum* sp. presents a high content of ionizable groups (carboxyl groups from mannuronic acid and guluronic acid) on the cell wall polysaccharides, which makes it, at least in theory, very liable to the influence of the pH. The biosorption of Cr(VI) on dried activated sludge was mainly due to ionic attraction. Solution pH affected the zeta potentials or surface charges of dried activated sludge and also the solubility of the chromium ions. At pH values higher than 6, biosorption studies

could not be performed due to the precipitation of Cr(VI) ions. Therefore, the optimal pH yielding maximum extent of biosorption without any Cr(VI) ion precipitation was pH 4, which resulted in minimum zeta potential. Initial chromium (VI) ion concentration also affected the extent of biosorption at constant dried activated sludge concentration. The capacity of Cr(VI) biosorption at equilibrium increased with the increase of initial Cr(VI) and decreased with the increase of biosorbents dose. Because, increasing the initial Cr(VI) concentration would increase the mass transfer driving force and therefore the rate at Cr(VI) molecules pass from the bulk solution to the biomass surface. This would results in higher Cr(VI) biosorption capacity. The Freundlich and Langmuir adsorption models were used for the mathematical description of the biosorption equilibrium of both biosorbent. The results showed that the equilibrium data for *Sargassum* sp. could be well by the Langmuir isotherm model, whereas the equilibrium data for dried activated sludge fitted the Freundlich isotherm model best within the concentration range studied. Also, pseudo-first-order and Pseudo-second-order kinetic models were used to correlate the data for both models. Pseudo-second-order kinetic model represented the data better than the Pseudo-first-order model for biosorption of Cr(VI) ions onto biosorbents. Finally, it may be concluded that *Sargassum* sp. and dried activated sludge may be used as a low-cost, natural and abundant sources for the removal of heavy metals as an alternative to more costly materials such as activated carbon.

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