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Bioremoval of Hexavalent Chromium from Aqueous Solutions by the Brown Seaweed *Dictyopteris polypodioides*

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ABSTRACT

In this study, the uptake of hexavalent chromium using biomass of the brown seaweed *Dictyopteris polypodioides* was studied to evaluate its biosorption capacity. Optimum conditions for Cr (VI) elimination were determined by studying the effect of initial solution pH, biomass dosage, contact time and initial Cr (VI) concentration. The elimination of hexavalent chromium was strictly pH dependent and maximum sorption was obtained at more acidic pH. The removal rate of Cr (VI) was relatively quick during the first 10 min of contact before reaching equilibrium in about 15 min. The isotherm data were found to be well fitted by linear Langmuir equation. Pseudo-second order model was found appropriate to explain the adsorption kinetics more effectively. The results of the present study suggest that *Dictyopteris polypodioides* biomass could be used as an effective and low-cost biosorbent for Cr (VI) removal from aqueous solution.

Key words: Phaeophycean seaweed, Dictyopteris polypodioides, Cr (VI), Biosorption

INTRODUCTION

Industrial world has contaminated soil sediments and aquatic resources with hazardous material. Metal water interaction is often resulting of industrial activities, such as mining, refining and electroplating (Azmat *et al.*, 2007; Basha *et al.*, 2008). Chromium is one of contaminants which exist in hexavalent and trivalent forms. It is one of the key pollutants in the wastewaters of industrial dyes and pigments, film and photography, galvanometry and electric, metal cleaning, plating and electroplating, leather and mining. The hexavalent form has been considered more hazardous to health due to its mutagenic and carcinogenic properties (Costa, 2003; Baral and Engelken, 2002). Therefore, removal of Cr (VI) from wastewater is essential before disposal. Conventional removal processes of dissolved chromium including ion-exchange, activated carbon adsorption, reverse osmosis and membrane filtration can be expensive or ineffective at low concentrations and may also lead to secondary environmental problems from waste disposal (Arslan and Pehlivan, 2007). Consequently, much research has been focused on identifying low-cost biological materials called biosorbents that can efficiently remove heavy metals from aqueous

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environments. The passive binding of metals by living or dead biomass is referred to as biosorption (Schiewer and Wong, 2000). Seaweeds or marine algae are extremely efficient biosorbents with the ability to bind various metals from aqueous effluents (Davis *et al.*, 2003; Tsui *et al.*, 2006). Numerous chemical groups may be responsible for metal biosorption by seaweeds e.g. carboxyl, sulphonate, hydroxyl and amino (Lacher and Smith, 2002) with their relative importance depending on many different factors, such as; the quantity of sites, their accessibility and the affinity between site and metal. The main metal binding mechanisms include; ion-exchange and complex formation. Among the various forms of algae, brown algal biomass has been found to show higher metal uptake capacities due to higher alginate and fucoidan contents (Davis *et al.*, 2003).

In the present study, the brown macroalgae *Dictyopteris polypodioides* was selected, as a biosorbent candidate for Cr (VI) removal in aqueous solution. The effect of different operational parameters on the elimination process of Cr (VI), such as; initial solution pH, biomass dosage, contact time and initial Cr (VI) concentration was studied to optimize the conditions leading to maximum removal efficiency.

MATERIALS AND METHODS

Biosorbent preparation: The brown seaweed *Dictyopteris polypodioides* was collected in the intertidal shoreline of El Jadida city (33°15'07.5" N 8°29'55.0" W) on the Atlantic coast of Morocco. The harvested biomass was washed several times with tap water followed by distilled water to remove extraneous debris and salts, afterwards dried in an oven at 60°C for 24 h and ground to obtain a powder.

Preparation and analysis of metal solution: Stock solution of chromate was prepared by using, potassium dichromate $K_2Cr_2O_7$ in distilled water, thereafter serial dilutions of this solution were prepared to obtain concentrations (50-500 mg L⁻¹) of Cr (VI) solution. Two methods were employed to determine chromium concentration: The standard colorimetric method was employed to determine Cr (VI) concentration in solution (Clesceri *et al.*, 1998). This procedure measures hexavalent chromium by reaction with 1.5-diphenylcarbazide (DPC) in acid solution. A red-violet complex is formed and measured spectrophotometrically at 540 nm using a JENWAY 6300 spectrophotometer. For the initial pH effect on biosorption, the Atomic Absorption Spectroscopy (AAS) was used to quantify the total residual chromium under different pH from 1-9. The device employed is an UNICAM 929 model flame atomic absorption spectrophotometer. Both techniques have been employed to verify, if Cr (VI) ions were adsorbed onto the biomass or reduced to trivalent form (Cr (III)) and consequently not detected by the DPC method.

Batch biosorption studies: Biosorption experiments were conducted in batch mode to investigate the effects of various process parameters such as pH, biosorbent dose, contact time and initial metal concentration. In 250 mL conical flasks, 100 mL of chromium solution of known concentration were added to a given biosorbent dose and the mixture was then magnetically stirred. To study the effect of pH on the removal of hexavalent chromium, various solutions at 50 mg of Cr (VI) per liter with pH values ranging from 1-9 were prepared. Initial pH was adjusted using 1 M HCl and NaOH solutions depending on the desired pH value. The effect of pH on the biosorption process may also be explained in terms of pH of zero point charge (pH_{ZPC}), at which the net surface charge (internal and external) of the biosorbent surface is zero. This parameter was determined by fast alkalimetric titration according to Fiol and Villaescusa (2009) modified procedure.

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After equilibration time, samples were taken out and centrifuged at 4000 rpm for 20 min. Biosorption efficiency was determined as following:

Removal (%) =
$$\frac{C_0 - C_e}{C_0} \times 100$$
 (1)

where, $C_{\rm 0}$ and $C_{\rm e}$ are the initial and equilibrium concentrations of Cr (VI) (mg $L^{-1}).$

Kinetic experiments: Biosorption kinetic experiments were carried out in 250 mL flasks containing 100 mL of chromium solution and a known amount of powder from *Dictyopteris polypodioides*. The mixtures were magnetically stirred at room temperature for various time intervals (1-90 min). The samples were drawn at different time intervals, centrifuged and analyzed for residual chromium concentrations. The kinetic data were analyzed using pseudo-first order and pseudo-second order kinetic models.

Pseudo-first order kinetic model: Pseudo-first order kinetic model is based on the fact that the change in metal concentration with respect to time is proportional to the power one. The differential equation is described as follows:

$$\frac{\mathrm{d}\mathbf{Q}_{t}}{\mathrm{d}t} = \mathbf{K}_{1}(\mathbf{Q}_{e} - \mathbf{Q}_{t}) \tag{2}$$

where, Q_e and Q_t are the biosorption capacity (mg g⁻¹) at equilibrium and time t, respectively and K_1 is the rate constant (L min⁻¹) of pseudo first order kinetic model, determined by linear regression using plots log (Q_e - Q_t) versus t.

Equation 2 can be integrated and rearranged to give the Eq. 3:

$$\log(Q_{e} - Q_{t}) = \log Q_{e} - \frac{K_{1} \cdot t}{2.303}$$
(3)

Pseudo-second order kinetic model: Pseudo-second order kinetic model, as developed by Ho and McKay (1999), was employed to evaluate the kinetic parameters for the biosorption studies of Cr (VI). Pseudo second order model considers that the rate of occupation of biosorption sites is proportional to the square of the number of unoccupied sites.

$$\frac{\mathrm{d}\mathbf{Q}_{t}}{\mathrm{d}t} = \mathbf{K}_{2}(\mathbf{Q}_{e} - \mathbf{Q}_{t})^{2} \tag{4}$$

where, t is the time (min), Q_t is the uptake capacity at a given time t (mg g⁻¹), Q_e is the equilibrium constant of sorbate ion on surface of the biosorbent (mg g⁻¹) and K_2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg⁻¹ min⁻¹) determined by plotting t/ Q_t against t.

The Eq. 4 could be integrated and rearranged to give the following expression:

$$\frac{t}{Q_{t}} = (\frac{1}{Q_{e}})t + \frac{1}{K_{2}Q_{e}^{2}}$$
(5)

Biosorption isotherms: Equilibrium experiments were carried out by taking known amount of *Dictyopteris polypodioides* in 250 mL flasks containing 100 mL of the chromium solution at different initial concentrations ranging from $50-500 \text{ mg L}^{-1}$. The mixture was magnetically stirred for the time required to reach the equilibrium. Isotherm data were analyzed using Langmuir and Freundlich adsorption equations. The parameters related to these models were then determined and correlation coefficients were calculated.

Langmuir model assumes a monolayer sorption of sorbate from the aqueous solution (Langmuir, 1918; Lawal *et al.*, 2010). The Langmuir equation is given below:

$$\frac{1}{Q_{e}} = \frac{1}{K_{L} Q_{max}} \cdot \frac{1}{C_{e}} + \frac{1}{Q_{max}}$$
(6)

where, Q_{max} is the maximum biosorption capacity describing a complete monolayer adsorption (mg g⁻¹), Qe is the amount adsorbed at equilibrium per specified amount of biosorbent (mg g⁻¹), Ce is the equilibrium concentration of metal ion in solution and K_L is the adsorption equilibrium constant. The values of Q_{max} and K_L were respectively calculated from intercept and slope of linear plot of 1/Qe versus 1/Ce.

The Freundlich equation was also employed to model equilibrium data of the biosorption process (Freundlich, 1907; Lawal *et al.*, 2010). This theorem considers multi-layers adsorption on the sorbent surface. The Freundlich model may be given by the equation below:

$$Q_{e} = K_{F} \cdot C_{e}^{\frac{1}{n}}$$
⁽⁷⁾

The Eq. 7 can be linearized as follows:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e$$
(8)

where, K_F is Freundlich empirical constant relative to sorption capacity, n is an empirical constant and rest of the terms have the usual significance. The values of the K_F and 1/n were calculated from the intercept and slope respectively from a linear plot of log Q_e versus log C_e .

RESULTS AND DISCUSSION

Effect of initial solution pH: The solution pH is one of the most parameters affecting the biosorption process (Donmez and Aksu, 2002), because it has a large influence on their solubility and adsorption capacity (Akkaya and Ozer, 2005). Solutions with different pH values ranging from 1-9 were used to examine the effect of initial solution pH on Cr (VI) sorption by *Dictyopteris polypodioides*. By comparing chromium measurements from standard colorimetric method, using 1.5-diphenylcarbazide (DPC) and Atomic Absorption Spectroscopy (AAS) method (Fig. 1), it can be concluded that analytical responses of both methods are similar under more acidic conditions (pH \leq 3). However, differences were noted at pH values greater than 3, this is probably due to the reduction of an amount of hexavalent chromium. Accordingly, the DPC method has been adopted for chromium analysis in the following experiments especially in very acidic medium.

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Fig. 1: Effect of pH on the removal of Cr (VI) from aqueous solution by Dictyopteris polypodioides

On the other hand, the sorption percentage of metal was found to be favored by acidic pH and maximum sorption of Cr (VI) by *Dictyopteris polypodioides* (98.78%) was observed at pH 1. By increasing the solution pH, removal efficiency of Cr (VI) decreased. This may be due to the decrease in electrostatic force of attraction between the biosorbent and chromium ions. At low pH values (1-4) where chromium removal efficiencies exceed 50%, the dominant species of hexavalent chromium ions in solution are $HCrO_4^{-}$, $Cr_2O_7^{-2}$, $Cr_3O_{10}^{-2}$ and $Cr_4O_{13}^{-2}$ (Bai and Abraham, 2001). These chromate ion species could be sorbed on the protonated active sites of the biosorbent like carboxylate of polysaccharides (alginates and fucan) of the cell walls of the seaweeds. As the pH increased (4-9), the dominant species of hexavalent chromium ions in solution is CrO_4^{2} however, the overall surface charge on the cells became negative and biosorption decreased (Donmez and Aksu, 2002). Without a doubt, pH has a great importance in cation sorption, because it influences chemical speciation of the metal in solution but also on the ionization of chemically active sites on the sorbent. Thus, the net charge of sorbent surface might play a crucial role in sorption processes and the characterization of protonation/desprotonation behavior of sorbent materials in aqueous media could be useful to explain sorption mechanism. In this context, the zero point charge (pH_{ZPC}), which is a useful parameter to evaluate the effect of pH on the biosorption process, has been determined. At this pH, the charge of the positive surface sites is equal to that of the negative ones. The knowledge of pH_{ZPC} allows to hypothesize on the ionization of functional groups and their interaction with metal species in solution; at solution pHs higher than pH_{ZPC}, sorbent surface is negatively charged and could interact with metal positive species while at pHs lower than pH_{ZPC}, solid surface is positively charged and could interact with negative species (Fiol and Villaescusa. 2009). The net titration curve for Dictyopteris polypodioides biomaterial were plotted to obtain pH of zero point charge. The value of pH_{ZPC} of the studied biomass found to be 4.00. Below this pH, the surface charge of the adsorbent is positive and above pH 4, Dictyopteris polypodioides biomass would have a net negative charge. The results of the present study are in agreement with previously published literature where biosorption of Cr (VI) has been investigated under acidic pHs by Sargassum muticum (Lopez-Garcia et al., 2012), Nizamuddina zanardinii, Stoechospermum marginatum, Cystoseira indica, Dictyota cervicornis, Padina australis and Sargassum glaucescens

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Fig. 2: Effect of biomass dose on the biosorption of Cr (VI) from a queous solution at 50 mg $\rm L^{-1}$ for a contact of 4 h

(Koutahzadeh *et al.*, 2013). From this result, pH 1 was defined as pH of study for following experiments. This is generally in agreement with the normal pH of the wastewaters containing chromium, which are generally very acidic (Barnhart, 1997).

Effect of biomass dose: The minimum dose of *Dictyopteris polypodioides* biomass necessary to achieve maximum chromium elimination was studied by increasing the biomass concentration from 0.1-4 g. The effect of sorbent dose on the removal of Cr (VI) was shown in Fig. 2. As it can be seen, the sorption of metal ions increases with increasing biomass dosage. The removal of chromium reaches its maximum (~100%) using biomass dose higher than or equal 3 g per 100 mL of hexavalent chromium solution at 50 mg L⁻¹. It remained then almost constant after this mass which is considered to be the optimum. The biosorption ability of algae has been attributed mainly to the cell wall, alginates and some sulfated polysaccharides, such as; fucoidan, which are important components of the cell walls of brown algae (Sheng *et al.*, 2004). The higher percentage removal at high biosorbent dosage may be attributed to the presence of tall number of active sites at higher biomass concentration (Deng *et al.*, 2009). Several researchers have reported that the increase in the percentage removal with increase in the adsorbents dosage is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent (Gupta and Rastogi, 2009; Yu *et al.*, 2003).

Effect of contact time: Biosorption of heavy metals ions by algae occurs in two steps. The first takes place rapidly through the adsorption on the surface of cell walls. The second is lengthy and relies on cell metabolism "absorption" or "intracellular uptake" (Basha *et al.*, 2008; Fourest and Volesky, 1995; Schiewer and Wong, 2000). As can be seen in Fig. 3, Cr(VI) removal was fast during the first 10 min of contact time and thereafter, the sorption process reached equilibrium in about 15 min of contact time.

The adsorption kinetic data were modeled using, the pseudo-first-order and pseudo-secondorder kinetic equations (Fig. 4 and 5). The calculated values of respective parameters of first and

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Fig. 3: Effect of contact time on the biosorption of Cr (VI) (pH = 1, initial concentration of Cr (VI) = 50 mg L^{-1} , volume = 100 mL, biosorbent mass = 3 g)



Fig. 4: Pseudo-first order kinetic model

second order kinetic models are summarized in Table 1. The shape of the lines indicates that the first-order Lagergren equation did not fit well to the adsorption process ($R^2 = 0.88$). Mostly, the first order kinetic model is not fitted well for whole data range of contact time and can be applied for preliminary stage of biosorption mechanism (Akar *et al.*, 2009). As it can be seen, significant difference was observed between calculated and experimental uptake values. However, the results obtained show a better fit with the pseudo-second order model, the value of regression coefficient is close to unity ($R^2 = 1$). The calculated Qe values agree very well with the experimental data. These results indicate that the adsorption system studied belongs to the second-order kinetic model.

Effect of Cr (VI) initial concentration: The initial concentration provides an important driving force to overcome all mass transfer resistance of metal ion between the aqueous and solid phases.



Fig. 5: Pseudo-second order kinetic model

Table 1: Kinetic parameters for the biosorption of hexavalent chromium onto Dictyopteris polypodioides

Parameters	Pseudo-first order	Pseudo-second order
$K (g mg^{-1} min^{-1})$	-0.85	1.28
$Q_e experimental (mg g^{-1})$	1.43	1.43
Q_e calculated (mg g ⁻¹)	0.42	1.44
\mathbb{R}^2	0.88	1.00

K: Rate constant, Q.: Biosorption capacity at an equilibrium, R²: Regression co-efficient

The biosorption of Cr (VI) was carried out at different initial Cr (VI) concentrations ranging from 50 to 500 mg L^{-1} .

The results regarding the effects of initial concentration of chromium solution on the biosorption capacity of brown algae are given in Fig. 6. The chromium uptake capacity decreases from 96.3-37.6%, this is due to the saturation of the sites responsible for the retention. Since cells offer a finite number of surface binding sites, uptake showed saturation at higher metal ion concentration (Bermudez *et al.*, 2012). Similar behavior was found by Koutahzadeh *et al.* (2013) when studying the effect of hexavalent chromium concentration (ranging from 10-40 mg L⁻¹) on its adsorption on a defined biomass of algae (2 g L⁻¹) at pH = 1 and for a contact time of 3 h. By using a small amount of biomass and increasing the chromium concentration, the contact between chromium ions and biomass is more favored. According to Yu *et al.* (2003), in case of low concentrations of hexavalent chromium, the ratio of the initial number of moles of metal ions to the available surface area is larger and subsequently the fractional biosorption becomes independent of initial concentrations. However, at higher concentrations the available sites of biosorption becomes independent of metal ions, which depends upon the initial concentration, decreases.

Biosorption isotherms: Adsorption isotherms are essential for the description of how a metal ion concentration will interact with a sorbent surface and are useful to optimize the experimental conditions for obtaining maximum metal uptake (Emmanuel *et al.*, 2007). Freundlich and Langmuir adsorption isotherms were both used to model the equilibrium adsorption data obtained for adsorption of hexavalent chromium on *Dictyopteris polypodioides*. These isotherms are characterized by some constants values which express the surface properties and affinity of the sorbent and can also be used to compare biosorption capacities of different biomass. The Langmuir

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Fig. 6: Effect of initial Cr (VI) concentration on its biosorption onto *Dictyopteris polypodioides* (pH = 1, volume = 100 mL, biosorbent mass = 3 g, contact time 2 h)

Table 2: Isotherm constants related to	the removal of Cr(VI) by the br	rown macroalgae Dictyopteris polypodioides

Langmuir		Freundlich		
Parameters	Values	Parameters	Values	
$Q_{max} (mg g^{-1})$	21.78	KF	6.96	
$K_L (L mg^{-1})$	00.16	n	4.73	
\mathbb{R}^2	00.98	R^2	0.67	

 \overline{Q}_{max} : Maximum value of Q_e , Q_e : Biosorption capacity at an equilibrium, K_L : Adsorption equilibrium constant, K_F : Freundlich empirical constant, n: Empirical constant, R^2 : Regression co-efficient

Sorbents	$Q \max (mg g^{-1})$	Optimum pH	Sorbent/solution ratio (g L ⁻¹)	References
Treated sawdust of sal tree	9.55	3.5	0.1	Baral <i>et al.</i> (2006)
Gracilaria salicornia	45.95	4	1	Khorramabadi and Soltani (2008)
Sargassum muticum	196.1	2	2	González Bermúdez et al. (2012)
Sargassum sp.	33.25	4	1	Khorramabadi and Soltani (2008)
Spirogyra condensata	14.82	5	10	Onyancha et al. (2008)
Sawdust exchanger	16.86	2-4	0.4	Kumar <i>et al.</i> (2009)
Riverbed sand	6.34	2.5	20	Sharma <i>et al.</i> (2007)
Fireclay	0.23	2	20	Bajpai (2001)
Sugar cane bagasse	13.23	2.0	4	Sharma <i>et al.</i> (1994)
Coconut shell charcoal	10.88	2.5	1.5	Babel <i>et al.</i> (2000)
Coconut coir	6.30	2.0	125	Gonzalez et al. (2008)
Hydrous stannic oxide	3.48	2.0	4	Goswami <i>et al.</i> (2005)
Dictyopteris polypodioides	21.78	1	10	This study

Table 3: Maximum amount of Cr(VI) adsorbed at equilibrium per gram of Dictyopteris polypodioides and other biosorbents

Q_{max}: Maximum value of Q_e, Q_e: Biosorption capacity at an equilibrium

and Freundlich constants determined from the slopes and intercepts of the respective plot (Fig. 7 and 8) are given in Table 2. As it can be seen, in the concentration range studied, regression correlation coefficient obtained by the use of Langmuir model is higher ($R^2 = 0.98$) than that stemming from to Freundlich model ($R^2 = 0.67$). The applicability of Langmuir model to the hexavalent chromium-algae system implies that the biosorption onto the adsorbent surface is homogeneous in nature (Donmez and Aksu, 2002). The Q_{max} value is the maximum value of Q_e , which is important to identify the biosorbent material having the highest uptake capacity and useful in scale-up considerations (Bermudez *et al.*, 2012). The magnitude of the Q_{max} was found of values (21.78 mg g⁻¹) for *Dictyopteris polypodioides*, this results suggest that this species exhibit

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Fig. 7: Langmuir adsorption isotherm for Cr (VI) biosorption by *Dictyopteris polypodioides* at optimum operating conditions



Fig. 8: Freundlich adsorption isotherm for Cr (VI) biosorption by *Dictyopteris polypodioides* at optimum operating conditions

very important uptake capacity compared to other types of materials (Table 3), such as sugar cane bagasse having a Q_{max} of 13.23 mg g⁻¹ (Sharma and Forster, 1994), Treates sawdust of sal tree with a Q_{max} of 9.55 mg g⁻¹ (Baral *et al.*, 2006), etc. Although a direct comparison of biomass with other reported biosorbents is difficult due to the varying experimental conditions related to each study.

CONCLUSION

The obtained results revealed that the brown seaweed *Dictyopteris polypodioides* is a promising biosorbent for the removal of hexavalent chromium Cr (VI) from aqueous solution. The biosorption of Cr (VI) by the aforementioned biomass was highly pH dependent, favoring higher metal uptake at low pH. The removal efficiency was enhanced with increasing biomass dosage and decreased with the increasing initial concentration of metal ion in the solution. Sorption process reached

equilibrium in about 15 min and it follows the pseudo-second order rate kinetic. The results indicated that the Langmuir model provided the best correlation of the experimental data, the maximum uptake is about 21.78 mg Cr (VI) g^{-1} of algae. So, this brown seaweed exhibits very important uptake capacity compared to other types of biomass.

This study revealed that *Dictyopteris polypodioides* has much potential as a sorbent for the removal of Cr (VI) from polluted waters and constitute a promising, efficient, cheap and biodegradable biomaterial for lowering the heavy metal pollution in aquatic environment.

REFERENCES

- Akar, T., B. Anilan, A. Gorgulu and S.T. Akar, 2009. Assessment of cationic dye biosorption characteristics of untreated and non-conventional biomass: *Pyracantha coccinea* berries. J. Hazard. Mater., 168: 1302-1309.
- Akkaya, G. and A. Ozer, 2005. Biosorption of Acid Red 274 (AR 274) on *Dicranella varia*: Determination of equilibrium and kinetic model parameters. Process Biochem., 40: 3559-3568.
- Arslan, G. and E. Pehlivan, 2007. Batch removal of chromium(VI) from aqueous solution by Turkish brown coals. Bioresour. Technol., 98: 2836-2845.
- Azmat, R., Uzma and F. Uddin, 2007. Biosorption of toxic metals from solid sewage sludge by marine green algae. Asian J. Plant Sci., 6: 42-45.
- Babel, S. and T.A. Kurniawan, 2004. Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. Chemosphere, 54: 951-967.
- Bai, R.S. and T.E. Abraham, 2001. Biosorption of Cr (VI) from aqueous solution by *Rhizopus nigricans*. Bioresour. Technol., 79: 73-81.
- Bajpai, S.K., 2001. Removal of hexavalent chromium by adsorption onto fireclay and impregnated fireclay. Sep. Sci. Technol., 36: 399-415.
- Bajpai, S.K. and V.K. Rohit, 2009. Removal of hexavalent chromium from aqueous solutions by sorption into a novel sawdust anion exchanger (SAE) sorbent. J. Environ. Prot. Sci., 3: 23-33.
- Baral, A. and R.D. Engelken, 2002. Chromium-based regulations and greening in metal finishing industries in the USA. Environ. Sci. Policy, 5: 121-133.
- Baral, S.S., S.N. Dasa and P. Rath, 2006. Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust. Biochem. Eng. J., 31: 216-222.
- Barnhart, J., 1997. Occurrences, uses and properties of chromium. Regul. Toxicol. Pharmacol., 26: S3-S7.
- Basha, S., Z.V.P. Murthy and B. Jha, 2008. Biosorption of hexavalent chromium by chemically modified seaweed, *Cystoseira indica*. Chem. Eng. J., 137: 480-488.
- Bermudez, Y.G., I.L.R. Rico, E. Guibal, M.C. de Hoces and M.A. Martin-Lara, 2012. Biosorption of hexavalent chromium from aqueous solution by *Sargassum muticum* brown alga. Application of statistical design for process optimization. Chem. Eng. J., 183: 68-76.
- Clesceri, L.A., E. Greenberg and A.D. Eaton, 1998. Standard Methods for the Examination of Water and Wastewater. 20th Edn., APHA, AWWA and WEF, Washington, DC., Pages: 366.
- Costa, M., 2003. Potential hazards of hexavalent chromate in our drinking water. Toxicol. Applied Pharmacol., 188: 1-5.
- Davis, T.A., B. Volesky and A. Mucci, 2003. A review of the biochemistry of heavy metal biosorption by brown algae. Water Res., 37: 4311-4330.
- Deng, L., Y. Zhang, J. Qin, X. Wang and X. Zhu, 2009. Biosorption of Cr (VI) from aqueous solutions by nonliving green algae *Cladophora albida*. Miner. Eng., 22: 372-377.

- Donmez, G. and Z. Aksu, 2002. Removal of chromium(VI) from saline wastewaters by *Dunaliella* species. Process Biochem., 38: 751-762.
- Emmanuel, K.A., K.A. Ramaraju and K.S. Rao, 2007. Removal of Mn (II) from aqueous solutions using bombax malabaricum fruit shell substrate. J. Chem., 4: 419-427.
- Fiol, N. and I. Villaescusa, 2009. Determination of sorbent point zero charge: Usefulness in sorption studies. Environ. Chem. Lett., 7: 79-84.
- Fourest, E. and B. Volesky, 1995. Contribution of sulfonate groups and alginate to heavy metal biosorption by the dry biomass of *Sargassum fluitans*. Environ. Sci. Technol., 30: 277-282.
- Freundlich, H., 1907. Ueber die Adsorption in Loesungen. Z. Phys. Chem., 57: 385-470.
- Gonzalez, M.H., G.C.L. Araujo, C.B. Pelizaro, E.A. Menezes, S.G. Lemos, G.B. de Sousa and A.R.A. Nogueira, 2008. Coconut coir as biosorbent for Cr(VI) removal from laboratory wastewater. J. Hazard. Mater., 159: 252-256.
- Goswami, S. and U.C. Ghosh, 2006. Studies on adsorption behaviour of Cr(VI) onto synthetic hydrous stannic oxide. Water SA, 31: 597-602.
- Gupta, V.K. and A. Rastogi, 2009. Biosorption of hexavalent chromium by raw and acid-treated green alga *Oedogonium hatei* from aqueous solutions. J. Hazard. Mater., 163: 396-402.
- Ho, Y.S. and G. McKay, 1999. Pseudo-second order model for sorption processes. Proces. Biochem., 34: 451-465.
- Khorramabadi, G.S. and R.D.C. Soltani, 2008. Evaluation of the marine algae *Gracilaria salicornia* and *Sargassum* sp. for the biosorption of Cr (VI) from aqueous solutions. J. Applied Sci., 8: 2163-2167.
- Koutahzadeh, N., E. Daneshvar, M. Kousha, M.S. Sohrabi and A. Bhatnagar, 2013. Biosorption of hexavalent chromium from aqueous solution by six brown macroalgae. Desalination Water Treatment, 51: 6021-6030.
- Lacher, C. and R.W. Smith, 2002. Sorption of Hg(II) by *Potamogeton natans* dead biomass. Miner. Eng., 15: 187-191.
- Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc., 40: 1361-1403.
- Lawal, O.S., A.R. Sanni, I.A. Ajayi and O.O. Rabiu, 2010. Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead (II) ions onto the seed husk of *Calophyllum inophyllum*. J. Hazard. Mater., 177: 829-835.
- Lopez-Garcia, M., P. Lodeiro, R. Herrero and M.E.S. de Vicente, 2012. Cr (VI) removal from synthetic and real wastewaters: The use of the invasive biomass *Sargassum muticum* in batch and column experiments. J. Ind. Eng. Chem., 18: 1370-1376.
- Onyancha, D., W. Mavura, J.C. Ngila, P. Ongoma and J. Chacha, 2008. Studies of chromium removal from tannery wastewaters by algae biosorbents, *Spirogyra condensata* and *Rhizoclonium hieroglyphicum*. J. Hazard. Mater., 158: 605-614.
- Schiewer, S. and M.H. Wong, 2000. Ionic strength effects in biosorption of metals by marine algae. Chemosphere, 41: 271-282.
- Sharma, D.C. and C.F. Forster, 1994. A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents. Bioresour. Technol., 47: 257-264.
- Sharma, Y.C. and C.H. Weng, 2007. Removal of chromium(VI) from water and wastewater by using riverbed sand: Kinetic and equilibrium studies. J. Hazard. Mater., 142: 449-454.

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- Sheng, P.X., Y.P. Ting, J.P. Chen and L. Hong, 2004. Sorption of lead, copper, cadmium, zinc and nickel by marine algal biomass: Characterization of biosorptive capacity and investigation of mechanisms. J. Colloid Interface Sci., 275: 131-141.
- Tsui, M.T.K., K.C. Cheung, N.F.Y. Tam and M.H. Wong, 2006. A comparative study on metal sorption by brown seaweed. Chemosphere, 65: 51-57.
- Yu, L.J., S.S. Shukla, K.L. Dorris, A. Shukla and J.L. Margrave, 2003. Adsorption of chromium from aqueous solutions by maple sawdust. J. Hazard. Mater., 100: 53-63.