American Journal of Engineering Research (AJER)
e-ISSN: 2320-0847 p-ISSN : 2320-0936
Volume-6, Issue-6, pp-103-108
www.ajer.org
Research Paper Open Access

Study of Chromium Biosorption by Four Atlantic Algae: *Gelidium Sesquipedale, Gelidium Corneum, Corallina Officinalis, and Ulva Lactuca*

L. Trioui[1], F. Byoud[2], S. Channaoui[1], K. Belghmi[1], M. Azzi[2], M. Blaghen[1]
[1] *Laboratory of Microbiology, Pharmacology, Biotechnology and Environment, Faculty of Sciences Ain Chock, University Hassan II of Casablanca, Morocco.*
[2] *Laboratory of Interface, Materials and Environment, Team of Electrochemistry and Environmental Chemistry, Faculty of Science Ain Chock, University Hassan II of Casablanca, Morocco.*

Abstract: *Biosorption is a powerful process for the removal of heavy metal ions from aqueous solutions; the biomass of marine algae has been well known to have high biosorption capacities for a number of heavy metal ions. The aim of this review is to study the biosorption of chromium ions using a non- living biomass of four algae (Gelidium sesquipedale, Gelidium corneum, Corallina officinalis, and Ulva lactuca). The effect of pH, time contact and initial metal ion concentration on the biosorption were studied. The residual chromium in solution was determined using atomic absorption spectrophotometer. It was noted that the biosorption is pH-dependent and the optimum pH for the biosorption was pH 2. The biosorption is also time-dependent, the maximum biosorption was obtained after 2 h, the optimum initial chromium concentration for Gelidium sesquipedale and Gelidium corneum (red algae), was 50 mg/l, and for Corallina officinalis (brown algae) , and Ulva lactuca (green algae) was 30 mg/l. Sorption isotherms were described by Langmuir and Freundlich adsorption models.It was seen that the adsorption equilibrium data fitted very well to the Freundlich adsorption model. The results showed that the removal of chromium reached 94%, by Gelidium corneum, at biomass dosage 1g/l, pH 2, with an initial metal ion concentration of 50 mg/l and contact time 120 min. The red algae has given a better result, it's supposed due to their high porosity, so more available fixation sites, in comparison with the other three taxon. This study demonstrated that the red algae are more promising and efficient biomaterial for reducing the chromium pollution from effluent.*

Keywords: *Biosorption, Chromium, red algae, adsorption isotherm.*

I. INTRODUCTION

The industries activating in metal finishing, electroplating, leather tanning, stainless steel production, and textile, produce a large flows of contaminated water containing high concentrations of chromium [1]. At high concentrations, this metal is very toxic to animals and plants, It could be dispersed to human beings, through the food chain, chromium can cause serious health hazards [2]. Especially by genetic damage, because he is able to cross the cell and nuclear membranes [3]. It has also been noted that a long exposure to the chromium could cause skin allergies and cancer in human beings [4].

Recently, the commonly used methods applied to remove excessive chromium from aqueous solutions are: ion exchange, chemical precipitation, activated carbon adsorption, evaporation and membrane processes, all those methods are inappropriate for reaching levels of decontamination required by the regulations, and are in most of cases associated with the generation of secondary environmental problems by creating waste disposal [5]. The advantages of biosorption is the high removal performance, the low-cost, the possibility of regeneration for valorisation and it doesn't generate any sludge [6].

The use of non-living biomaterials for metal removal, has a big advantage because, they are not affected by toxic ions [7]. In addition, they require less care and maintenance (no addiction of nutriments), so cheaper [8]. A lot research about biosorption has proved that the non-living biomass can passively fix metal ions by a physicochemical mechanism [9], the mechanisms responsible for biosorption, is supposed to be a combination of ion exchange, complexation, coordination, adsorption, electrostatic interaction, chelation and micro precipitation [6], [10], [11], it's why different parameters such as pH, initial chromium concentration can impact the biosorption [12].

II. MATERIAL AND METHODS

1) Experimental methods:

2.1 Biomass preparation:

The algae were collected from Moroccan Atlantic coast at Casablanca region (Tamaris), during summer, it was rinsed thoroughly with distilled water to remove salts and impurities, like sand, samples were oven dried at 60◦C for 24h, then they were grounded and sieved to a particle size of 0,25–0,5mm. The biomass was protonated by acid contact (0.3 N H_2SO_4) for 3 h (this allowed stabilizing the biomass to become efficient for removing and to drop out fixed metals), then the biomass was rinsed many times with distilled water. The pre-treated biomass was then dried overnight at 60 °C. The prepared biomass was stored in airtight dark bottles until required.

2.2 Reagents and equipment:

A standard solution of chromium (1000mg/L) was prepared using potassium dichromate ($K_2Cr_2O_7$), by dissolving the required amounts of the compound in distilled water. The metal concentrations in solution were determined using flame atomic absorption spectrophotometer (AAS) type Shimadzu 7000 AA with deuterium background corrector. All measurements were carried out in an air/acetylene flame.

2.3 The optimum pH determination:

For the determination of the optimum pH, 100ml of chromium at 50mg/l, for Gelidium sesquipedale and Gelidium corneum, and at 30mg/l, for Corallina officinalis, and Ulva lactuca, was added to 100mg of algal biomass, in 250ml capacity conical flasks, solutions were adjusted to pH 1, 2, 3, 4, 5, 6,7 and pH 8, using 0.1 M NaOH or 0.1 M HNO_3. Flasks were shaken for 2 h at 200 rpm and room temperature (25 ± 1◦ C).

The adsorbate was decanted and separated from the adsorbent using Whatman grade 41 filter paper.

The samples were analysed via (AAS) the percentage of biosorption was calculated according to the following equation:

$$Q = \frac{(C_0 - C_e) \times 100}{C_0} \qquad (1)$$

Where C_0 is the initial ion concentration (mg/l), C_e is the equilibrium or final ion concentration (mg/l), and Q is the percentage of metal biosorption.

2.4 Determination of equilibrium time:

The equilibrium time for chromium biosorption was investigated by adding 1g/l, algal biomass (100mg) to 100ml of heavy metal solution at 50mg/l, for Gelidium sesquipedale and Gelidium corneum, and at 30mg/l, for Corallina officinalis, and Ulva lactuca. The solution was adjusted to pH 2, Flasks were shaken at 200 rpm and room temperature (25 ± 1 ◦C), the supernatant was analysed for residual metal at different time intervals, using flame atomic absorption spectrophotometer.

2.5 The effect of initial chromium concentration on chromium biosorption:

The effect of the initial concentration of chromium on its biosorption was carried out using a concentration range of 10 to 90 mg/l. 100mg of algal biomass was added to 100ml of chromium at pH 2 in a 250ml capacity conical Erlenmeyer. Flasks were shaken for 2 h at 200 rpm and room temperature (25 ± 1◦ C).

The adsorbate was decanted and separated from the adsorbent using Whatman No. 41 filter paper.

2.6 Batch equilibrium and kinetic studies procedure:

The result obtained by the study of the optimum initial concentration was analysed using Langmuir [13] and Freundlich [14] isotherms, the first one suppose that the number of adsorption sites on the surface of the biomass is fixed and that each site may adsorb a single particle, ignoring interactions between adsorbed particles, the second one suppose that the sorption happens on heterogeneous surface suggesting that the adsorption sites are not equivalent and/or independent.

The langmuir isotherm can be defined according to the following equation [13]:

$$Q_e = \frac{Q_{\max} K_c C_e}{1 + K_c C_e} \qquad (2)$$

The linear Equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} K_c} + \frac{C_e}{Q_{\max}} \qquad (3)$$

Where, Q_e (mg/l) is the equilibrium chromium concentration on the algae, C_e (mg/L) is the equilibrium chromium concentration in the solution, Qmax (mg/g) is the maximum biosorption capacity corresponding to the site saturation [15], and K_c is the Langmuir biosorption constant (L/mg) relating the free energy of biosorption.

The Freundlich equation is:

$$Q_e = K C_e^{\frac{1}{n}} \qquad (4)$$

The linearized form of Freundlich adsorption isotherm is:

$$\ln(Q_e) = \ln K + \frac{1}{n} \ln(C_e) \qquad (5)$$

Where C_e is the equilibrium concentration (mg/l), Q_e is the amount adsorbed (mg/g) and K and n are constants expressing all parameters affecting the adsorption process, such as adsorption capacity and intensity respectively. The chromium ions adsorbed by each gram of biomass at equilibrium (Q_e) was calculated according to the mass balance on the ions expressed in this equation:

$$Q_e = \frac{(C_0 - C_f) \times M}{V} \qquad (6)$$

Where V (l) is the sample volume, C_0 (mg/l) is the initial ion concentration, C_f (mg/l) is the final ion concentration, M is the biomass dry weight (g).

III. RESULTS AND DISCUSSIONS

1) Effect of pH:

The effect of pH on chromium adsorption was investigated by varying the pH from 1 to 8. As shown in Fig.1, the removal efficiency of chromium decreases with the increase of pH from 2 to 8 and the maximum of biosorption by biomasses was observed at pH 2, in which the maximum of removal was obtained with Gelidium corneum. The order of adsorption capacity is as the following order: Gelidium corneum, Gelidium sesquipedale, Corallina officinalis, and Ulva lactuca. This result obtained confirm the earlier report that the biosorption is pH-dependent [16]. The cell walls of algae are composed of polysaccharides, proteins and lipids; it offers a host of functional groups capable of fixing heavy metals. These functional groups, such as amino, carboxylic, and phosphate groups, have different affinity as well as specificity for metal binding [17], the pH control the adsorption, by affecting the surface charge of the functional groups in the surface of the adsorbents (algae) and even the forms of chromiumions in solution [18]. The chromium is presented generally as anionic form: $HCrO^{4-}$, $Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$ or $Cr_4O_{13}^{2-}$in solutions, the surface of the adsorbents is surrounded by H^+ at low pH values, which enhance the attraction between thechromium ions and the active sites of the adsorbent [19]. When we increase gradually the pH, it enhances the electronegativity of surface of the adsorbents, the solution is concentrated by hydroxyl radials (OH^-) that may compete with the anionic species of Chromium, which results in the decrease of the removal efficiency. Thus, the biosorption involved during this study is mainly due to an electrostatic attraction between the functional groups in the surface of the algae and anionic form of chromium.

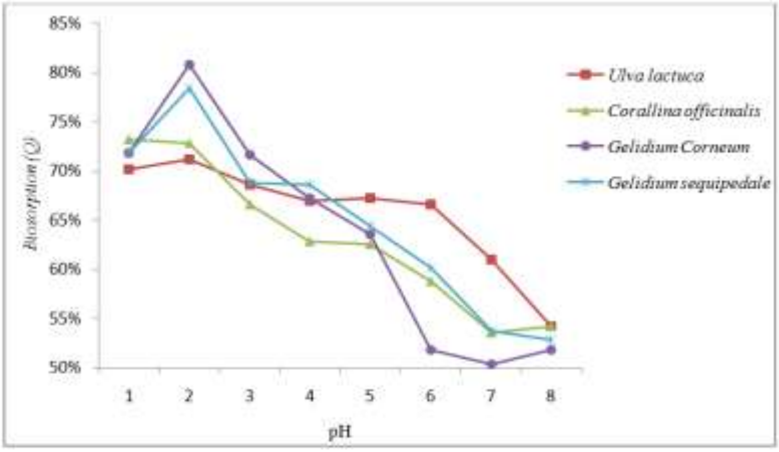

Figure 1: Effect of pH on the rate of the biosorption of chromium by the four algae.

2) Effect of contact time:

The effect of the contact time is shown in Fig 2, the mechanism of chromium adsorption was observed by varying the contact time from 10 min to 24h, Experimental data were measured over the period of 24h to make sure that full equilibrium was attained, in the beginning of the experiments, the removal efficiency increases progressively with increase in contact time, and the equilibrium was attained after 60 min, the low removal efficiency in the initial stage of adsorption, of Corallina officinalis, and Gelidium sesquipedale, can be explained with the fact of the particles aggregation after addiction to the chromium solution, but it increases gradually after dissolution of aggregates, after 120 min, the removal efficiencies of Gelidium corneum, Gelidium sesquipedale, Corallina officinalis, and Ulva lactuca, for chromium are about 94%, 80%, 76%, and 70%, respectively. The equilibrium time of biosorption is found after 120 min, even after 24h from the equilibrium time we have the same rate, witch, revealing that adsorption sites are saturated [17]. As reported the biosorption is biphasic [17]. The initial phase is fast, this can be explained by surface adsorption on the biomass. The second phase is slow (after 60 min) its due to complexation of the metal ions into the inner of the surface of the biomass.

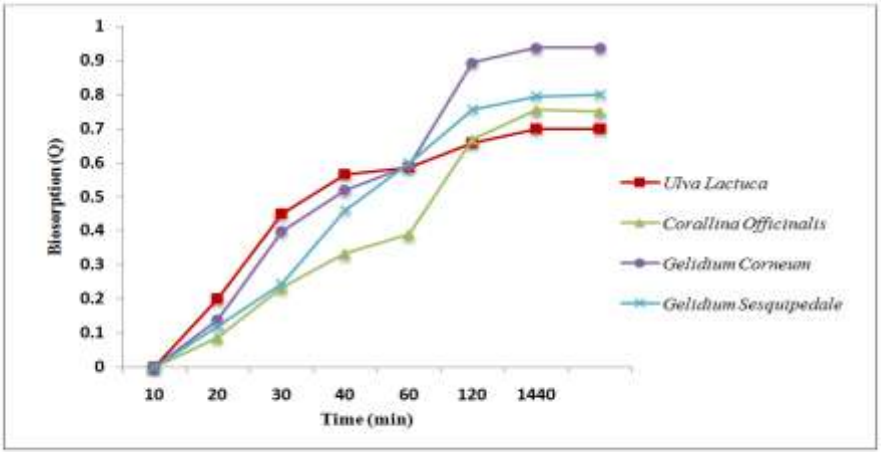

Figure 2: Effect of Time contact on chromium biosorption by the four algae.

3) The effect of the metal initial concentration:

The effect of initial chromium concentration on the biosorption capacity shows that the maximum of it, was adsorbed at the initial concentration of 50 mg/l within the first 120 min, for Gelidium sesquipedale and Gelidium corneum, and the maximum of biosorption was 30 mg/l for Ulva lactuca, and Corallina officinalis.
The gradual increase in the efficiency of the biomass adsorption over 50mg/l, for Gelidium sesquipedale and Gelidium corneum, and over 30 mg/l for Ulva lactuca, and Corallina officinalis, shows, nearness to saturation of the available binding sites on the algae [20]. It can be explained by the fact that Gelidium sesquipedale and Gelidium corneum, have more available sites than Ulva lactuca, and Corallina officinalis.

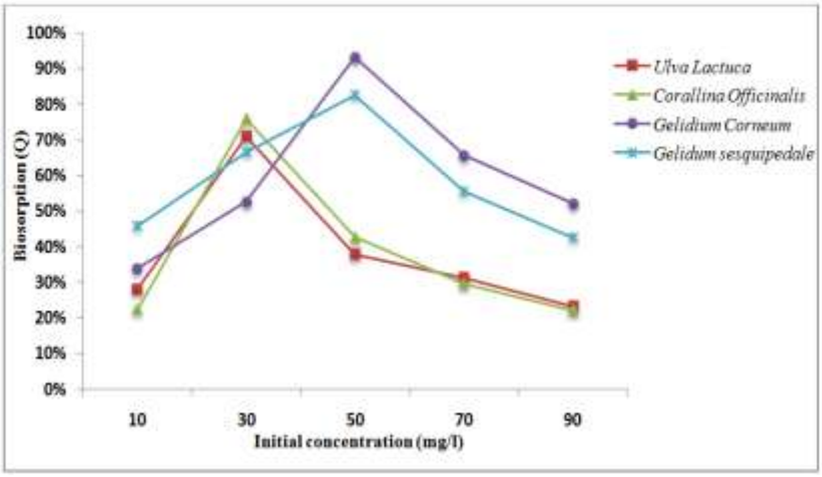

Figure 3: Effect of chromium initial concentration on its biosorption by the four algae.

4) Batch biosorption studies:

The Figures 4 and 5, respectively, show the Langmuir and the Freundlich model. The correlation coefficients (R^2) in the Langmuir model is very low for the four algae, the high coefficient of determination in the second model, ranged from 0.831 to 0.950, show that the Freundlich equation gives a good fit to the adsorption isotherm for the adsorption of chromium by the four algae.

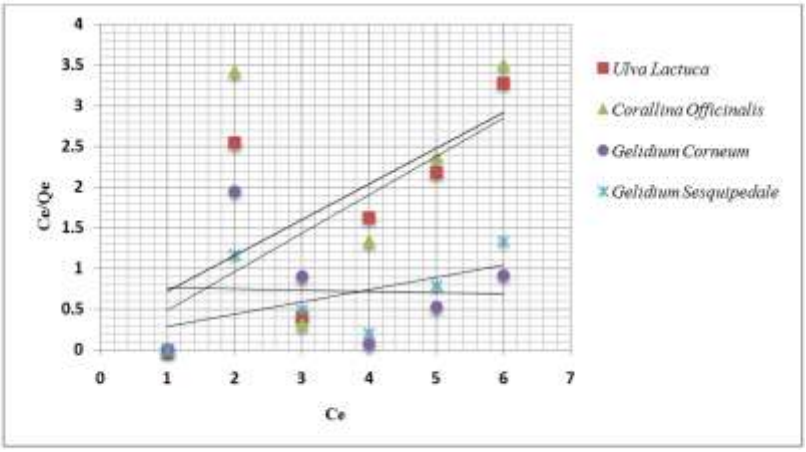

Figure 4: The linear Langmuir isotherm plots of C_e/Q_e vs C_e for biosorption of chromium onto different algal biomasses (biomass dosage 1g/L, contact time 120 min, pH=2, T= 25°C).

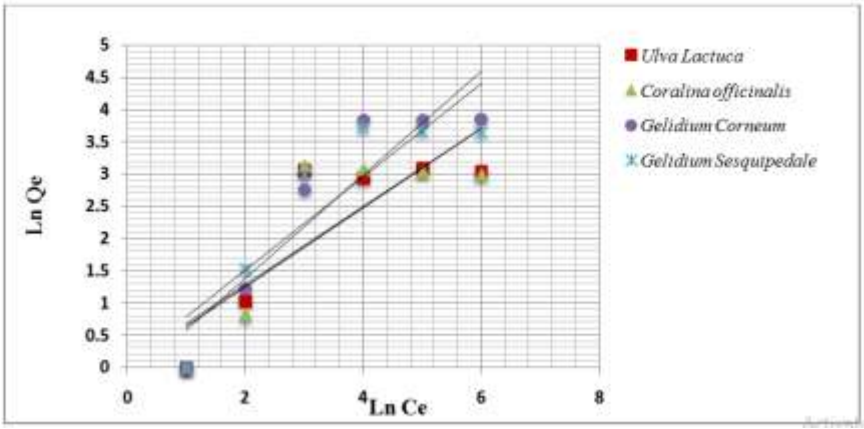

Figure 5: The logarithmic Freundlich isotherm plots of Ln Q_e vs LnC_e for biosorption of chromium onto different algal biomasses (biomass dosage 1g/L, contact time 120 min, pH= 2, T=25 °C).

The isothermal biosorption parameters for these isotherms are shown in Table1, according to results presented, the experimental data for the four types of samples are well fitted by the Freundlich isotherm (R^2 = 0.95; 0.94; 0.86; 0.83). This indicates that the adsorption of Chromium by four algae happens on heterogeneous surface.

Table 1: Freundlich and Langmuir isothermal biosorption parameters.

	Langmuir parameters			Freundlich parameters		
Algae	R^2	Q_{max}	K_c	R^2	1/n	K
Ulva lactuca	0.487	2.114	22.63	0.869	1.886	1.134
Corallina officinalis	0.438	2.28	1.53	0.831	1.915	1.076
Gelidium corneum	0.001	-67.56	0.019	0.95	2.398	0.955
Gelidium sesquipedale	0.283	6.614	1.071	0.94	2.227	1.165

The 1/n values for the four algae are higher than 1, this result show that the choice of ranges of concentration was too low. The adsorption can be more favourable in higher concentration, because at low concentrations, such compounds are in competition with water for adsorption sites [21]. The biosorption capacities of the tested red algal biomasses for heavy metals are higher than the other algal biomasses Therefore, it can be noteworthy that Gelidium corneum and Gelidium sesquipedale, have a high potential for the removal of metal ions from aqueous solution, even in high concentration of chromium.

IV. CONCLUSION

This study focused on the biosorption of chromium by four algae, it has been noticed that the operating parameters such as pH of solution, contact time and initial concentration of chromium, affected the biosorption efficiency, therefore, the chromium reduction is more performant under strongly acidic conditions (pH<2.5), the maximum of adsorption was attained after 120 min, and the maximum of chromium was adsorbed at the initial concentration 50 mg/l for Gelidium sesquipedale and Gelidium corneum, and the maximum of biosorption was obtained at the initial concentration 30 mg/l for Ulva lactuca, and Corallina officinalis, which mean that the first two algae have more available sites than the others.

The red algal biomass (Gelidium sesquipedale, Gelidium corneum) gives a higher efficiency of chromium uptake (94% and 80%), because they have more available sites in comparison with Corallina officinalis, and Ulva lactuca (70% and 74%), which is confirmed by their behaviour in the sorption isotherms.

The presence of a larger number of sites in red algae, can be explained by the fact that these algae are more rich in agar agar, which is completely solubilized during the acid attack, while leaving place for an important porosity and irregularity, allowing more adsorption sites.

According to these results, the red algal biomass (Gelidium sesquipedale, Gelidium corneum) can be more effective for the removal of chromium from effluents, due to its high biosorption capacity.

Those materials can be more advantageous for a bioremediation process, being natural, renewable and cheap solution. This work can be used as a draft for invention of an efficient process to remove chromium from contaminated aqueous solutions.

REFERENCES

[1]. M. Abdel-Jawad, S. Al-Shammari, and J. Al-Sulaimi, Non-conventional treatment of treated municipal wastewater for reverse osmosis,ElsevierDesalination, vol. 142, pp. 11–18, 2002.

[2]. M. Costa, Potential hazards of hexavalent chromate in our drinking water,Toxicol. Appl. Pharmacol., vol. 188, no. 1, pp. 1–5, 2003.

[3]. H. Niu and B. Volesky, Characteristics of anionic metal species biosorption with waste crab shells,Hydrometallurgy, vol. 71, pp. 209–215, 2003.

[4]. F. Abu Al-Rub, M. Kandah, and N. Aldabaibeh, Nickel Removal from Aqueous Solutions Using Sheep,Eng. Life Sci, vol. 2, no. 4, pp. 111–116, 2002.

[5]. N. Ahalya, R. D. Kanamadi, and T. V. Ramachandra, Biosorption of chromium (VI) from aqueous solutions by the husk of Bengal gram (Cicer arientinum),Electron. J. Biotechnol., vol. 8, no. 3, pp. 258–264, 2005.

[6]. J. Wang and C. Chen, Biosorption of heavy metals by Saccharomyces cerevisiae : A review,Biotechnol. Adv., vol. 24, pp. 427–451, 2006.

[7]. A. S. Moffat, Plants Proving Their Worth in Toxic Metal Cleanup ENVIRONMENTAL BIOLOGY, vol. 269, pp. 302–303, 1995.

[8]. A. Hansda, V. Kumar, and Anshumali, A comparative review towards potential of microbial cells for heavy metal removal with emphasis on biosorption and bioaccumulation,World J Microbiol Biotechnol, vol. 170, no. 32, pp. 1–14, 2016.

[9]. B. Volesky and Z. R. Holan, Biosorption of Heavy Metals,Biotechnol. Prog, vol. 11, pp. 235–250, 1995.

[10]. F. Veglio and F. Beolchini, Removal of metals by biosorption : a review, vol. 44, pp. 301–316, 1997.

[11]. K. Vijayaraghavan and Y. Yun, “Bacterial biosorbents and biosorption,” Biotechnol. Adv., vol. 26, pp. 266–291, 2008.

[12]. A. R. Netzahuatl-Munoz, M. D. C. Cristiani-Urbina, and E. Cristiani-Urbina, Chromium biosorption from Cr(VI) aqueous solutions by Cupressus lusitanica bark: Kinetics, equilibrium and thermodynamic studies,PLoS One, vol. 10, no. 9, 2015.

[13]. I. Langmuir, THE ADSORPTION OF GASES ON GLASS,GLASS, MICA AND PLATINUM., in THE ADSORPTION OF GASES ON PLANE SURFACES OF GLASS, MICA AND PLATINUM., vol. 345, 1918, pp. 1361–1403.

[14]. V. J. Freundlich, Ueber die adsorption in loesungen, in CHEMISCHE REVUE, vol. 12, 1907, pp. 385–47.

[15]. K. H. Chong and B. Volesky, Description of Two-Metal Biosorption Equilibria by Langmuir-Type Models, Biotechnol. Bioeng., vol. 47, pp. 451–460, 1995.

[16]. P. Pavasant, R. Apiratikul, V. Sungkhum, P. Suthiparinyanont, S. Wattanachira, and T. F. Marhaba, Biosorption of Cu2+,Cd2+,Pb2+, and Zn2+ using dried marine green macroalga Caulerpa lentillifera, vol. 97, pp. 2321–2329, 2006.

[17]. Y. Liu, X. Chang, Y. Guoa, and M. Shuangming, Biosorption and preconcentration of lead and cadmium on waste Chinese herb Pang Da Hai, J. Hazard. Mater., vol. 135, pp. 389–394, 2006.

[18]. P. K. D. Chathuranga, N. Priyantha, S. S. Iqbal, and M. C. M. Iqbal, Biosorption of Cr (III) and Cr (VI) species from aqueous solution by Cabomba caroliniana : kinetic and equilibrium study,Env. Earth Sci, 2012.

[19]. D. Mohan, S. Rajput, V. K. Singh, P. H. Steele, and C. U. Pittman Jr., Modeling and evaluation of chromium remediation from water using low cost bio-char , a green adsorbent,J. Hazard. Mater., vol. 188, no. 1–3, pp. 319–333, 2011.

[20]. N. A. A. Babarinde, J. O. Babalola, and S. O. Sanni, Isotherm and thermodynamic studies of the biosorption of Cd(II) from solution by maize leaf,Int. J. Phys. Sci., vol. 2, no. 8, pp. 207–211, 2007.

[21]. L. zhi Huang, G. ming Zeng, D. lian Huang, L. feng Li, C. yan Du, and L. Zhang, Biosorption of cadmium(II) from aqueous solution onto Hydrilla verticillata,Environ. Earth Sci., vol. 60, no. 8, pp. 1683–1691, 2010.