Full Length Research Paper

Study of biosorptive potential in the peel of Citrus reticulata, Punica granatum, Daucus carota and Momordica charantia

Muhammad Aqeel Ashraf[1]*, Mohd. Jamil Maah[1], Ismail Yusoff[2], Karamat Mahmood[3] and Abdul Wajid[3]

[1]Department of Chemistry, University of Malaya, Kuala Lumpur 50603, Malaysia.
[2]Department of Geology, University of Malaya, Kuala Lumpur 50603, Malaysia.
[3]Department of Chemistry, The Islamia University of Bahawalpur 63100, Pakistan.

Different physiochemical parameters such as color, odour, taste, pH, Electrical conductivity, total dissolved solids, concentration of cations & anions were determined in the waste water samples that were collected in the vicinity of Kuala Lumpur city. Peel of Citrus reticulata (orange), Punica granatum (pomegranate), Daucus carota (carrot) and Momordica charantia (bitter gourd) were used to study biosorption potential of the dead biomass. Laboratory batch experiments indicated that C. reticulata, P. granatum, D. carota and M. charantia had an excellent ability to bind with these anions and cations. The role of cell structure, cell wall, micropores and macropores describe the potential of adsorbent. Batch laboratory time dependency, pH profile and concentration parameter were performed to determine the binding ability of biosorbents for cations and anions. Time dependency indicated that the first three samples showed maximum adsorption at 45 min and P. granatum at 60 min and at pH 12. More amount of biosorbent is used for that water sample, which contain maximum amount of cations and anions. These are recommended as good biosorbent due to their effectiveness.

Key words: Biosorption, physicochemical, heavy metals, plant materials.

INTRODUCTION

Heavy metals are among the most toxic contaminants present in the environment. Contamination of the aqueous environment by heavy metals is a worldwide environmental problem and as a result, their removal from waste water has attracted much attention from researchers in the past 20 years. Pollutant metals including Cu, Zn, Cd, Pb, Fe, Ni, Ag, Th, Ra and U released into the environment persist indefinitely, circulating and eventually accumulating throughout the food chain becoming serious threat to the environment and pose health problems. Heavy metals are traditionally removed by physical-chemical processes such as ion exchange, reverse osmosis, precipitation, solvent extraction, membrane technologies and electrochemical treatments. These techniques have significant disadvantages including incomplete metal removal, the need of expensive monitoring equipments and some physical methods not suitable to remove heavy metal concentration in the order of 1-100mg (Volesky and Holon, 1995).

Biosorption is a property of a living or dead biomasses to bind and concentrate heavy metals from dilute solutions. It is a form of adsorption process involving the removal of metal ions from liquid phase onto solid biomass material. Some biosorbents are competitive with existing non biomass based treatments (Brower et al., 1997). Previous studies on the mechanism of biosorption of metals have demonstrated that the process generally consist of two stages. The first stage has been described as a passive adsorption of ions and it is likely that a number of functional groups are involved in this process. This type of metal uptake is rapid and thought to be unrelated to the energy economy of cell. The second

---
*Corresponding author. E-mail: chemaqeel@gmail.com. Tel: +603-79674141. Fax: +603-79675149.

stage of uptake is slower and involves active transport mechanism (Chamberlian, 1992; Bender et al., 1987; Chang, 1994; Volesky, 1990).

Mechanism of biosorption is believed to occur in a variety of ways in which biosorbent accumulate the metal ion and this include, ion exchange, chelation, adsorption by physical forces, ion entrapment in inter and intracellular capillaries and spaces. The biosorption process involves a solid phase (sorbent, or biosorbent, biological material) and a liquid phase (solvent or normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of the sorbent for the sorbate species, the later is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of the solid- bound sorbate species and its portion remaining in the solution (Ahalya et al., 1999). An adsorption isotherm is used to characterize the equilibrium between the amount of adsorbate that accumulates on the adsorbent and the concentration of the dissolved adsorbate. The Langmuir adsorption isotherm and the Freundlich isotherm are two common isotherms used to describe equilibrium.

The aim of this study was to check biosorption potential of fruit peel of Citrus reticulata (orange), Punica granatum (pomegranate), Daucus carota (carrot) and Momordica charantia (Bitter gourd) towards treatment of waste water. Peels of C. reticulata, P. granatum, D. carota and M. charantia agricultural wastes were selected due to the fact that it is an agricultural by-product. The by-products resulting from processing represent a major disposal problem for industry and the environment. Therefore, the purpose of this study was to explore the feasibility of using different fruits peel for ion removal from aqueous solutions by conducting batch experiments as a function of solution pH, initial cadmium ions concentration and contact times.

MATERIALS AND METHODS

Sample collection and analysis of physico-chemical parameters

Five water samples were collected from the vicinity of Kuala Lumpur city and labeled as samples 1 to 5. Physio-chemical parameters such as color, order, taste, pH, electrical conductivity, total dissolved solids, concentration of cations and anions were measured in situ by AquaSensors DataStick™ multiparameter probe, while anions (CO_3^{--}, HCO_3^{-}, Cl^{-}) (APHA,1998), cations (Na^{+}, Ca^{++} + Mg^{++}) (APHA,1998), heavy metals like Mn, Ni, Cr, Pb, Cu, Co, Fe, Zn were measured in the laboratory using atomic absorption spectrophotometer (AAS; Perkin Elmer Mode 2380). AAS was calibrated for each element using standard solution of known concentration before sample injection (APHA, 1992).

Adsorbent preparation

C. reticulata, P. granatum, D. carota and M. charantia peel wastes were obtained from Chow Kit fruit market, Kuala Lumpur. These were washed with 0.1 M HCl, followed by rinsing with deionized water and dried in an oven at 60°C for 24 h. The dried biomaterials were ground using domestic mixer and stored in airtight plastic bottles for further use as biosorbent without any chemical or physical treatment.

Time-dependence studies for ion binding

The time-dependence batch experiments were performed using a procedure reported previously (Gourdon et al., 1990a). The time intervals chosen for the time dependence studies were 15, 30, 45, 60 and 90 min. Speed of orbital shaker was kept 200 rpm. This procedure was repeated for each different cations and anions with all four biosorbents.

pH profile for ion binding studies

The effect of pH was investigated by maintaining the pH of the sample using buffers of 4, 6, 8, 10 and pH 12 (Gourdon et al., 1990a). Optimum time for first three biosorbents was 45 min. and for last sample 60 min. Speed of orbital shaker was kept 200 rpm. Percentage removals of metals were calculated at each pH and pH was optimized.

Effect of biosorbent concentration

The adsorption of cations and anions at concentrations of .5, 1, 1.5, 2.0, 2.5 g of biosorbents were calculated (Gourdon et al., 1990a.). Time and pH was already optimized and speed of orbital shaker is 200 rpm. Maximum Percentage efficiency of adsorbents was calculated.

Data evaluation

Sorption models were:

(1) The Langmuir model, $C/Y = C (1/Ym) + 1 / (KYm)$

Where, Ym is the maximum amount of metal adsorbed (mg g^{-1}), the slope = 1/Ym, K is the equilibrium constant related to the affinity of binding site, C is the residual metal concentration (mg) and Y is the adsorption at residual metal concentration (mg g^{-1}). The essential characteristics of the Langmuir isotherm can be expressed in terms of equilibrium parameter R, which is defined by the following equation: $R = 1 / [1 + (K C_0)]$ (Nassar et al., 1995), where C_0 is the equilibrium concentration.

Values of R type of isotherm are; R > 1 Unfavourable; R =1 Linear; 0 < R < 1 Favourable; R = 0 Irreversible.

(2) The Freundlich model, $\log (x/m) = \log K + 1/n (\log C)$.

Where x is the amount of adsorbate, m is the amount of adsorbing material, C is the equilibrium concentration of adsorbate in the solution, K and n are Freundlich constant and are the indicators of the adsorption capacity and adsorption intensity, respectively.

Separation factor

The shape of the isotherm can be used to predict whether adsorption system is favorable or unfavorable in a batch adsorption system. Accordingly, the essential feature of Langmuir isotherm

was expressed in term of dimensionless constant called the separation factor. It is defined by the following relationship.

$$Sf = 1/(1 + bC_i)$$

Where SF is a dimensionless equilibrium parameter or separation factor, b, the constant from Langmuir equation and C_i is the initial metal ion concentration. The parameter, SF, indicates the shape of the isotherm and nature of the sorption process. If SF > 1 then unfavorable isotherm; SF = 1 then linear isotherm; SF = 0 then irreversible Isotherm; 0 < SF < 1 then favorable isotherm (Horsefall and Spiff, 2005).

Surface coverage (θ)

To account for adsorption behavior of the metal ions on the biomass the Langmuir type, equation related to surface coverage was used. The equation is expressed as follow.

$$bC_i = \theta(1-\theta) \quad \text{and} \quad \theta = bC_i/(1+bC_i)$$

Where b is the adsorption coefficient, Ci the initial concentration and θ the surface coverage.

Statistical analysis

Results were tested by one-way analysis of variance (ANOVA). ANOVA effects and treatments differences were considered significant at $p < 0.05$.

RESULTS AND DISCUSSION

Time-dependent biosorption

Agitation time is one of the most important parameter for measuring percentage efficiency. Generally it is reported that the uptake of metal ions can be divided into two stages: rapid and slow stage. In the rapid stage the metal ions are adsorbed onto the surface of biosorbents and in the slow stage the metal ions are transported inside the cell membrane (Ting et al., 1989). In this study, rapid biosorption was observed at the start and then reached at the equilibrium (Swift and Forciniti, 1997). The experimental results obtained with all biosorbents revealed that percentage efficiency increased with the increase in time till the equilibrium was achieved. Maximum % efficiency is observed in that sample that contain less amount of metal ions but comparatively large amount of ions are removed from that sample that contain large amount of ions. (Senthikumar et al., 2005)

Optimum time for C. reticulata, Daucus carota and M charantia was 45 min, while for P. granatum was 60 min. Moreover, C. reticulata showed maximum of 90 and 93% efficiency for Ca^{2+} and Mg^{2+}, D. carota showed maximum of 76.67 and 84.62% efficiency for Ca^{2+} and Mg^{2+}, M. charantia showed maximum of 80% efficiency for both Ca^{2+} and Mg^{2+}, while P. granatum showed maximum of 68 and 74.03% efficiency for Ca^{2+} and Mg^{2+}.

pH profile studies

The pH was also reported to be the most important factor for all ions uptake, and the removal capacity was shown to increase with Ph, but the upper limit of working pH was limited by hydroxide precipitation (Geddie and Sutherland, 1993). Results showed that as pH increases % efficiency also increased and this was due to the fact that increase in pH decreased the hydrogen ions concentration. At acidic pH, hydrogen ion concentration was high which competed with the metal cations for biosorption. The increase of pH resulted in an increased negative charge on the surface of the cell which favored electrochemical attraction and adsorption of metal (Gourdon et al., 1990a.). Hence, % removal was lowest at low pH, became higher with increasing pH and then decreased as observed for different water samples.

Physio-chemical parameters such as color, order, taste, pH, electrical conductivity, total dissolved solids, concentration of cations and anions were measured for all collected water samples. Results of the water quality are shown in Figure 1a. While in all biosorbents % efficiency increased with increasing pH for cations, reverse results were however obtained for anions. Figure 1b showed that optimum pH was almost 10 for all biosorbents, although slight increase in efficiency was observed at pH 12 in some samples. C. reticulata showed maximum 89 and 93% efficiency for Ca^{2+} and Mg^{2+}, D. carota showed maximum 76.67 and 86% efficiency for Ca^{2+} and Mg^{2+}, M. charantia showed a maximum of 82 and 83.2% efficiency for Ca^{2+} and Mg^{2+}, while P. granatum showed a maximum of 77 and 80% efficiency for Ca^{2+} and Mg^{2+}.

Effect of concentration

Concentration is one of the most important parameter for studying the % efficiency. With an increase in biosorbent concentration, % efficiency also increased till an optimal dose because of the availability of large amount of binding sites. Over optimal amount of biosorbent in suspension would cause the aggregated particles to re-disperse in the suspension and would also disturb particle settling (Chan and Chiang, 1995). The initial cations concentration also influenced the metal uptake (Volesky, 1990). With an increase in metal ion concentration % efficiency is decreased.

Adsorption isotherm

The adsorption isotherm models were used to characterize the interaction of cations with four different kinds of biomass as shown in Table 1, the values of K_f and n were higher than that of K. The higher the values of K_f and n the lower the value of K, while the higher the
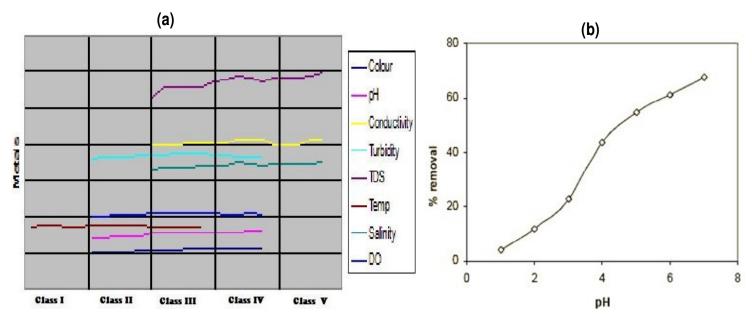
(a)

(b)

Figure 1. (a) Characterisation of waste water used for analysis. (b) Removal efficiency of biosorbent against pH.

Table 1. Comparison of Langmuir and Freundlich isotherm for *Citrus reticulata, Daucus carota, Momordica charantia* and *Punica granatum*.

Peel	Langmuir isotherm parameters			Experimental value	Freundlich isotherm parameters			
	q-max	b	R2	q-max	q-max	K	1/n	R2
Citrus reticulata	71.42	0.0637	0.905	27.46	28.43	5.0629	0.7169	0.9395
Daucus carota	37.73	0.0388	0.9926	23.39	22.9	1.7187	0.761	0.996
Momordica charantia	20.36	0.0651	0.9203	18.83	20.95	1.6765	0.631	0.9301
Punica granatum	28.82	0.0373	0.9951	20.328	20.31	1.624	0.6541	0.9846

affinity of biomass (Jalali et al., 2002). The results also showed that the values of K, K_f and n for cations were higher than those for anions. From these observations, we can say that all four tested biomass could have a high adsorption capacity and high binding affinity for cations. The values of the Freundlich exponent, n, were greater than one, indicating that cations are favorably adsorbed by all four tested biomass. The correlation coefficient (R^2) for biosorbent showed the most suitable model for describing these sorption processes. The biosorption of cations with all four tested biomass were more consistent with Freundlich isotherm, where the high correlation coefficient. Results for Freundlich and Langmuir isotherms are given in Figures 2 to 5.

Separation factor and surface coverage

The maximum absorption capacity was observed in peel of P. granatum, suggesting that it is a potential biosorbent for removal of lead as well as the other three tested metals. The shape of the Langmuir isotherm can be used to predict whether a biosorption system is favorable or unfavorable in a batch adsorption process. Accordingly, the essential features of the Langmuir isotherm was expressed in terms of a dimensionless constant called the equilibrium parameter, separation factor, SF, which is defined by the following relationship;

$$SF = 1 / (1 + bCi)$$

Where SF is the dimensionless equilibrium parameter or separation factor, b is the constant from Langmuir equation and C_i the initial metal ion concentration of 100 mgL^{-1}. The parameter, SF, indicates the shape of the isotherm and nature of the sorption process. SF value between 0 and 1 represents favorable isotherm. The SF values for C. reticulata, P. granatum, D. carota and M. charantia biomass was calculated from aforementioned equation and plotted against initial metal ion concentration (Hanif et al., 2007).

The trend presented by SF in Fig.2A is also providing information that the Musa sapientum biomass is more effective and excellent adsorbent for metal at lower metal concentrations. SF values for C. reticulata, P. granatum, D. carota and M. charantia are between 0 and 1, which
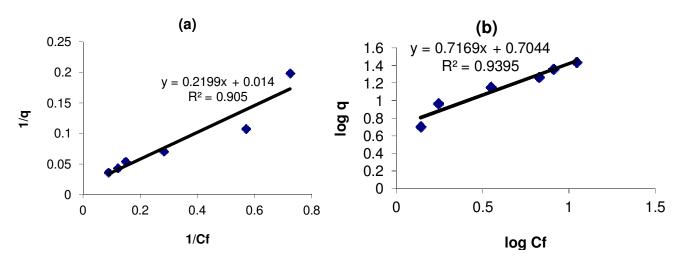
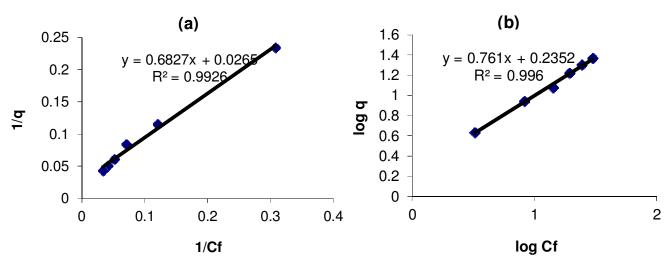**Figure 2.** Langmuir (a) and Freundlich (b) isotherms for *Citrus reticulata.*

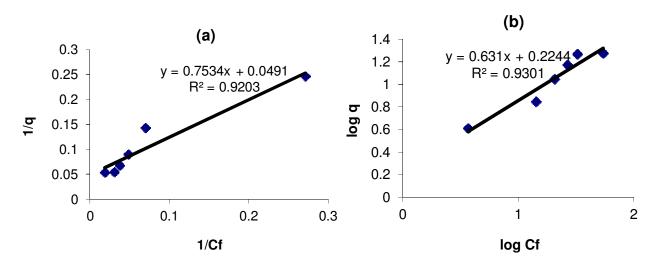**Figure 3.** Langmuir (a) and Freundlich (b) isotherms for *Daucus carota.*

Figure 4. Langmuir (a) and Freundlich (b) isotherms for *Momordica charantia.*
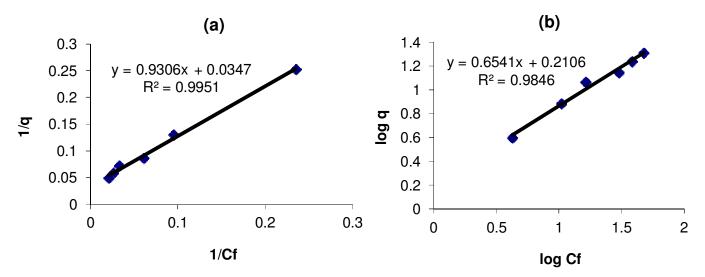
(a)

$$y = 0.9306x + 0.0347$$
$$R^2 = 0.9951$$

(b)

$$y = 0.6541x + 0.2106$$
$$R^2 = 0.9846$$

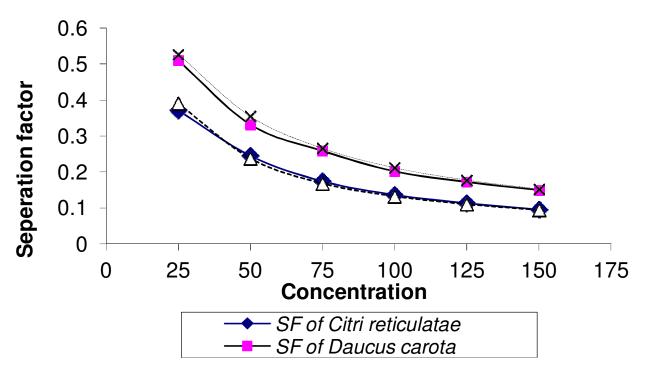**Figure 5.** Langmuir (a) and Freundlich (b) isotherm for *Punica granatum.*

Figure 6. A plot of separation factor against concentration for *Citrus reticulata, Daucus carota, Momordica charantia and Punica granatum.*

represents favorable isotherms for all the tested metal ions. The SF values for C. reticulata, P. granatum, D. carota and M. charantia biomass was calculated from aforementioned equation and plotted against initial metal ion concentration. Figure 6 showed that the sorption of metals on C. reticulata, P. granatum, D. carota and M. charantia biomass increased as the initial metal ion concentration increased, thus indicating that adsorption is even favorable for the higher initial metal ion concentrations (Figure 6). The sorption process was therefore favorable for metal removal at all concentrations investigated.

To account for absorption behavior of the metal ions on the biomass the Langmuir type equation related to surface coverage is used. The equation is expressed as follow;

$$bC_i = \theta / (1 - \theta) \text{ and } \theta = bC_i / (1 + bC_i)$$
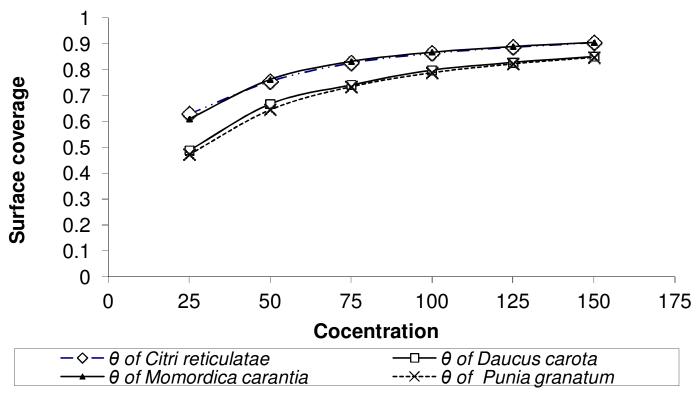
Figure 7. A plot of surface coverage (θ) against concentration for *Citrus reticulata, Daucus carota, Momordica charantia and Punica granatum*.

Where b is the absorption coefficient, Ci the initial concentration and θ the surface coverage. The fraction of biomass surface covered by metal ion was studied by plotting the surface coverage values (θ) against metal ions concentration. Figure 7 showed that increase in initial metal ion concentration for C reticulata, P. granatum, D. carota and M. charantia biomass increased the surface coverage on the biomass until the surface was nearly fully covered with a monomolecular layer. Further examination of Figure 7 revealed that the surface coverage ceases to vary significantly with concentration of metal ions at higher levels.

Conclusion

The results of this study indicated that the biomass of C. reticulata, P. granatum, D. carota and M. charantia are suitable for the development of an efficient metal removal system for the removal of cations and anions from waste water. Biosorption of these metals on the biomass was pH-dependent and the maximum biosorption was obtained at pH 5.0. The adsorption sites on the algal biomass showed a higher affinity for Cu^{2+} compared to Ni^{2+} and Mn^{2+}. The experimental data were described by the Freundlich adsorption isotherm model. Although all four biomass well performed under randomly controlled experimental conditions, further research is required to investigate the optimum conditions to get the best performance.

REFERENCES

American Public Health Association, (1998). Standard Methods for the Examination of Water and Wastewater, 20th ed. APHA, Washington, DC.

APHA (1992). Standards methods of water and waste water examination. Am. Public Health Association, USA.

Bender J, Ieanusi V (1987). Effects of supplements on the bioaccumulation of lead in Anabaena spp., Bull. Environ. Contam. Toxicol. 34: 209-213.

Chamberlian AHL (1992). The role of adsorbed layers in bacterial adhesion, in Biofilms-Science and technology (Eds: L. F. Melo, T.R. Bott, M. Fletcher, B. Capadeville), Kulwer Academic Publisher, Dordrechet, pp. 59-67

Chan WC, Chiang CY (1995). Flocculation of clay suspension with water insoluble starch grafted acrylamide/sodium allylsulphonated copolymer powder. Appl Polym. Sci. 69: 45.

Chang JS, Hong J (1994). Biosorption of mercury by the inactivated cells of Pseudomonas aeruginosa PU21 (Rip64), Biotechnol. Bioengineering, 44: 999-1006.

Gaddie LJ, Sutherland WI (1993). Uptake metals by bacterial polysaccharides. J. Appl. Bacteriol. 74: 467-472.

Gourden R, Bhende S, Rus E, Sofer SS (1990A). Comparison of cadmium biosorption by Gram-positive and Gram-negative bactaria fron activated sludge. Biotechnol. Lett. 12(1): 839-842.

Hanif MA, Nadeem R, Bhatti HN, Ahmad NR, Ansari TM (2007). Ni (II) biosorption by Cassia fistula (Golden Shower) biomass. J. Hazard. Mater. 139(2): 345-355.

Jalali R, Ghafourian H, Asef Y, Davarpanah SJ, Sepehr S (2002). Removal and recovery of lead using nonliving biomass of marine algae. J. Hazard. Mater. B92: 253-262.

Nassar MM, Hamoda MF, Radwan GH (1995). Adsorption equilibria of basic dyestuff onto palm-fruit bunch particles. Water Sci. Tech. 32: 27-32.

Senthikumar S, Varatharajan PR, Porkodi K, subburaam CV (2005). Adsorption of methylene blue carbon onto jute fibre carbon, Colloid. Inerface Sci. 284: 79

Swift DT, Forciniti D (1997). Accumulation of lead by Anabaena cylindrical: mathematical modeling and dispersive X-ray study. Biotechnol. Bioengineering, 55: 408-419.

Ting YP, Laeson F, Prince IG (1989). Uptake of cadmium and zinc by the alga Chlorella vulgaris: part 1. Individual ion species. Biotechnol. Bioengineering, 34: 990

Volesky B (1990). Removal and recovery of heavy metals by biosorption, in Biosorption of Heavy Metals (Ed: B. Volesky), CRC Press, Boca Raton, pp. 7-44.