International Journal of Sciences

Research Article Volume 2 - October 2013 (10)

Biosorption of Cadmium (II), Lead (II) and Nickel (II) by Spirulina Maxima

Alma Rosa Domínguez-Bocanegra[1], Jorge Antonio Torres-Muñoz[3], Ricardo Aguilar López[2]

[1]Division de Química y Bioquímica, Tecnológico de Estudios Superiores de Ecatepec, Valle de Anahuac s/n, Ecatepec de Morelos, Estado de México, México
[2]Department of Biotechnology and Bioengineering, CINVESTAV-IPN
[3]Department of Automatic Control, CINVESTAV-IPN, Avenida Instituto Politécnico Nacional 2508, Col. Zacatenco 07300 D.F, MÉXICO

Abstract: Biosorption is the effective method for removal of heavy metal ions from wastewater. In this study *Spirulina maxima* was used as an inexpensive and efficient biosorbent for Cd (II), Pb (II), and Ni (II) at concentrations 5 mgL^{-1}, 10 mgL^{-1}, 20 mgL^{-1} from aqueous solutions. This work focuses mainly on the kinetics of biosorption which follows a first-order model and equilibrium is properly described by Langmuir isotherms. The maximal sorption coefficient (q_e) was 16.1, 36.2 and 12 for cadmium, lead and nickel respectively. Biosorption of lead was the most prominent, since even at 20 mgL^{-1} of initial concentration the equilibrium concentration was C_e = 4.8 mgL^{-1} at 240 min and a specific decay rate υ = 0.0062 min^{-1}, which together with its maximal adsorption capacity q_{max} = 46.9 (mgg^{-1}) and sorption rate constant k= 0.0081 min^{-1} attests for the quality of lead biosorption by living biomass of *Spirulina maxima*.

Keywords*: Spirulina maxima, biosorption kinetics, lead, cadmium, nickel*

Introduction

The study of biosorption is of great importance from an environmental point of view, as it can be considered as an alternative technique for removing toxic pollutants from wastewaters (Vieira and Volesky, 2000). In contrast with organic residuals, heavy metals can´t degrade neither by biological nor by chemical means in nature (Doshi *et al*., 2007). Therefore, when they are discharged into the environment, can only be distributed to air environments, water and soil, or incorporated into living organisms; even if they change its oxidation state. Although metal-containing compounds may be altered because of different factors, they may remain for long time in the nature. In some cases accidental reactions may lead to the most toxic metal states. It is worth noticing that heavy metal ions have high mobility in natural aquatic ecosystems, water networks in cities, etc. which together with its high toxicity really makes of them the most important inorganic contaminants in the environment (Cunningham 2001).

Among the different methodologies that address this type of toxic wastes by removing ions therein, we may mention: precipitation, ultrafiltration, nanofiltration, reverse osmosis, electrodialysis and electrolysis. Unfortunately, the high cost of installation and maintenance of these technologies is economically unviable for small Mexican firms. Consequently, the productive sector, handling heavy metals, is still discharging such kind of wastes into water bodies with severe damage to the environment. Besides the physical and chemical methods, alternative techniques based on natural materials have been addressed for the recovery of heavy metals (Volesky B., 1999).

On the issue of biotechnology, there are three major trends in the treatment of wastewater contaminated with toxic metals, namely, extracellular precipitation, uptake of purified polymers and biosorption. The latest is a physiological process that takes place at cellular level within living or dead species, which aims at the removal and recovery of heavy metals in aqueous media. In fact, it can be considered as an alternative to conventional methods for the treatment of contaminated effluents.

The biosorption capacity depends on both the composition of the cell wall and the conditions for growth of the biomass. Because of its abundance in nature, biomass or bio-based materials have been profusely studied for the removal of heavy metals, including fungi, bacteria, algae and microalgae. For instance, it is known that heavy metal polluting aquatic systems may be removed by algae phytoplankton. The algal cell wall consist of carbohydrates, pectin, xylans, mananes and alginic acid as well as lipids and proteins, which provide binding sites for metal ions. These compounds create

Alma Rosa Domínguez-Bocanegra (Correspondence)
adomin@cinvestav.mx
+

areas of high affinity for monovalent metal cations such as Ag (I), divalent and Hg (II), Pb (II), Cd (II), Ni (II) or trivalent as Al (III), Fe (III) and Au (III) , among others. More over, the cell wall of algae can reversibly absorb metals and act in a similar way as do ion exchange resins (Volesky B., 1999).

The importance of heavy metals, from a technological an economic point of view, had conducted to deep research studies on adsorption and heavy-metal recovery of such metals by a number of microorganisms. In this vein, different types of microbial biomass have been used for the uptake of such metals, among which we may mention: *Spirulina* sp (Chojnacka *et al.*, 2005), *Chlamydomonas reinhartdtii* (Bayramoğlu and Tuzun, 2006), *Spirulina* sp (Doshi *et al.*, 2007), *Chlorella vulgaris* (Nacorda *et al.*, 2007; Doshi *et al.*, 2008), *Saccharomyces cerevisiae* (Can and Jianlong, 2007), *Cladophora fascicularis (*Deng *et al.*, 2007*), Spirulina platensis*/ *Chlorella vulgaris* (Gokhale *et al.*, 2008), *Chlorella* sp. (Doshi *et al.*, 2008), *Spirogyra sp* (Gupta and Rastogi, 2008a), *Pseudomonas veronii* (Vullo *et al.*, 2008), *Nostoc commune* (Morsy et *al.*, 2011), *Isochrysis galbana* and *Tetraselmis chui* (Liu *et al.*, 2011), *Micrococcus luteus* (Puyen *et al.*, 2012).

The aim of this work is to analyze the biosorption process of heavy metals like cadmium, lead and nickel, by live biomass of *Spirulina maxima*. The analysis is carried out on the basis of the adsorption capacity, the adsorption isotherms and biosorption kinetics of the above mentioned metals. This study was conducted with the help of appropriate mathematical models of the kinetics of biosorption and adsorption isotherms, which are widely used in the literature of the subject (Volesky B., 1999).

Materials and Methods

Microorganism

Spirulina maxima (*Arthrospira*) is a native strain obtained from the Río de los Remedios, located in Ecatepec de Morelos State of Mexico.

Biosorption kinetics

Experiments were carried out in 1000 mL Erlenmeyer flask with 800 mL of modified Zarrouk medium (see, Table 1) and 10% of inoculums at exponential growth phase, then the seed was added respectively with 5 mgL^{-1}, 10 mgL^{-1} and 20 mgL^{-1} of cadmium, lead or nickel from aqueous solutions of cadmium acetate, lead bicarbonate or nickel chlorine, respectively. All cultures were incubated at room temperature (28 ± 2ºC), continuous aeration 0.5 vvm, continuous agitation 100 rpm, and natural photoperiod (day light). The pH of the medium was adjusted to pH 6.5 with 1M HCl or 1M NaOH. Samples of 10 mL were taken from the seed every 20 min during the first hour, every 30 min in the second hour and every 60 minutes in the third one until completing 8 hours, latest samples were taken every 24 h. Supernatant was analyzed to determine the residual concentration of each metal ions by atomic Absorption Spectrophotometry, model Varian 20 A plus.

Results and discussion

Biosorption kinetics

The Figure 1 show the analysis in terms of the initial metal concentration (C_i), the concentration at equilibrium (C_e,) time (t_e), at which equilibrium is reached and the adsorption rate (υ); for simplicity such quantities are denoted together as (C_e, t_e, υ).

For an initial concentration of 5 mgL^{-1}, the following figures of (C_e, t_e, υ) were obtained; (0.16 mgL^{-1}, 240 min, 0.0168 min^{-1}) for Cd^{2+}, (0.85 mgL^{-1}, 240 min, 0.0079 min^{-1}) for Pb^{2+} and (0.56 mgL^{-1}, 240 min, 0.0141 min^{-1}) for Ni^{2+}. Notice that, the percentages of metal removal along the sorption process were 97% for Cd^{2+}, 83% for Pb^{2+} and 88% for Ni^{2+} see Figures 2. However, the uptake of lead requires a longer time resulting on a specific adsorption rate υ two times lower compared with those of Ni^{2+} and Cd^{2+}.

With cadmium, at 10 mgL^{-1} and 20 mgL^{-1} were obtained; (4.2 mgL^{-1}, 240 min, 0.0043 min^{-1}) and (17 mgL^{-1}, 90 min, 0.0019 min^{-1}), respectively (Figure 1a). Clearly there is a marked tendency to reduce the ability of metal uptake with removal percentages of 58% at 10 mgL^{-1} and 15% at 20 mgL^{-1}, which is accompanied by significant reductions in the adsorption rate at these concentrations with respect to that of 5 mgL^{-1}(Figure 2). Hence, at high metal concentrations, the cellular wall is trying to react quickly to metal uptake but finally undergoes a saturation effect of the sorption sites which is reflected by the significant reduction in the removal percentage. The process of metal adsorption at 5 mgL^{-1} and 10 mgL^{-1} took 120 min approximately which is similar to the time of contact between the metal and the cell wall as reported in (Aksu, 2002; Chojnacka *et al.*, 2005; Bayramoglu *et al.*, 2006; Gokhale *et al.*, 2008).

In the case of lead at 10 mgL^{-1} and 20 mgL^{-1}, the obtained values were as follows: (3.0 mgL^{-1}, 240 min, 0.0049 min^{-1}) and (4.8 mgL^{-1}, 240 min, 0.0062 min^{-1}), respectively (Figure 1b). Observe that, higher metal concentrations induces reduction of the adsorption rate with respect to that at 5 mgL^{-1} by a factor of about 0.6, as well as reaching the equilibrium takes longer, t_e is now 240 min. However, the removal percentage is kept at good levels, namely 64% and 76% for 10 $mgL^{-1}$and 20

mgL^{-1} respectively (Figure 2). This would mean that the combination of a largest equilibrium time with a decrease in the rate of removal will result in higher metal tolerance by the cyanobacteria. According to Chen and Pan, 2005, who studied the biosorption of lead (II) by biomass of *Spirulina*, biosorption is a very fast process, capturing 74% of the metal during the first 12 min of contact, reaching the 95% of metal absorbed at 24 hours, in our case the equilibrium is reached at about 240 min. Probably because the cell surface of the *cyanobacteria* shows many assets or trapping sites and thus has a high affinity for heavy metals, the active sites are due to certain functional groups such as carboxyl, hydroxyl, amino etc. found in the different constituents of the cell wall.

When dealing with nickel at 10 mgL^{-1} and 20 mgL^{-1}, the figures for were as follows; (6.35 mgL^{-1}, 90 min, 0.0045 min^{-1}) and (18.1 mgL^{-1}, 90 min, 0.0012 min^{-1}), respectively (Figure 1c). To higher initial concentrations will correspond lower equilibrium times, together with lower adsorption rates, this last were in a factor of 0.32 at 10 mgL^{-1} and 0.1 for 20 mgL^{-1} at 5 mgL^{-1}. Besides the former figures, the low removal percentages (26% at 10 mgL^{-1}, 19% at 20 mgL^{-1}), would testimony a low tolerance to high concentrations of nickel by *S. maxima* (Figure 2). Such situation is certainly due to the high electronegativity, low atomic weight, and low ionic radius of such heavy metal (Quintelas *et al.*, 2009). Now, according to the work of Pawan 2007, the metal quickly saturates the cell wall of microalgae, after the saturation time, the metal can penetrate the cell which produces an irreversible damage. Finally, observe that equilibrium is not really reached as far as oscillating values are present in the supernatant after 120 min.

The *blue-green algae Spirulina* genus was found to have a versatile metabolism it can grow either photoautotrophically, heterotrophically or mixotrophically (Vonshak, 1997). The cell wall of algal cells is surrounded by a porous three-dimensional macromolecular network. Important cell wall components are: peptydoglycan, teichuronic acid, teichoic acid, polysaccharides and proteins (Ting *et al.*, 1991), which display mainly carboxylic, hydroxyl and phosphate groups (Aksu, 2002). Most of these molecules are polyelectrolytes that carry charged groups, such as carboxyl, phosphate, hydroxyl or amine. The presence of anionic and cationic sites gives algal wall amphoteric properties and, depending on the pH, the groups are either protonated or deprotonated (Esposito *et al.*, 2002). The chemical composition of the cell wall, the presence and availability of metal-binding sites are not only associated with microbial species, but depend also on growth conditions, availability of nutrients, stress etc. *Spirulina* possesses a very high maximum biosorption capacity that depended on biomass growth conditions (Chojnacka *et al.*, 2005).

The pH of the solution is an important parameter affecting biosorption of heavy metals. At pH values higher than 9, different hydroxyl species of low solubility can be formed, i.e. Cd(OH)2 and Cd(OH)3. The cadmium, lead and nickel biosorption depends on the extent of protonation of these carboxyl groups are mainly protonated resulting in low cadmium, lead and nickel uptake. At pH values higher than pK_a, more functional groups carry negative charge and the positively charges cadmium, led and nickel ions will be bound increasing the cadmium, lead and nickel uptake (Lodeiro *et al*, 2005). Under these considerations the pH was regulated at 6.5 with 1M HCl or 1M NaOH as explained before.

The biosorption capacity q_t (mgg^{-1}) is typically defined as the amount of metal ion on the surface of the sorbent at time t, which is given by;

$$q_t = \frac{(C_i - C_t)\cdot V}{w} \qquad (1)$$

where C_i is the initial metal concentration (mgL^{-1}), C_t is the metal concentration at time t (mgL^{-1}), V is the volume of solution for biosorption (L) and w is the biomass dry weight (g). For conciseness, in what follows q_e will denote the biosorption capacity at the equilibrium state.

At a given concentration of 5 mgL^{-1} of lead, cadmium and nickel, fifty percent of the metal uptake happened in similar conditions, namely, for lead at t = 40 min with a biosorption capacity $q_t = q_{40}$ = 4.3 mgg^{-1}; then for cadmium and nickel at t = 60 min with biosorption capacities q_{60} = 6.2 mgg^{-1} and q_{60} = 6.57 mgg^{-1}, respectively. In turn, 90% of the metal uptake took place at 180 min for cadmium and lead, and between 90min-120min for nickel. Indeed, equilibrium values for nickel and lead were very close, i.e q_e = 12.3 mgg^{-1} and q_e = 11.7 mgg^{-1} respectively; while for cadmium was qe = 14.5 mgg^{-1} (see, Figure 3).

The figure 3a shows the kinetic behavior for cadmium (II) by *S. maxima*. Sorption of metal at 10 mgL^{-1} initial concentration was similar to that of 5 mgL^{-1}, since registered sorption capacity q_t was q_{60} = 7.9 $mgg^{-1}$and q_{180} = 15.4 mgg^{-1}at 60 min and 180 min respectively, which represents 50% and 90% of the equilibrium value. Sure, such figures represent a modest improvement in the adsorption capacity. On the contrary, at 20 mgL^{-1}, a significant decline in the adsorption capacity was observed with q_{40} = 3.3 $mgg^{-1}$and q_{90} = 9 mgg^{-1} at 40 min and 90 min, respectively; such figures represent 50% and 90% of the equilibrium value.

The figure 3b shows the adsorption of Pb (II) by *S.*

maxima. The kinetic behavior at 10 mgL^{-1}or 20 mgL^{-1} showed dilation in time with respect to 5 mgL^{-1}, in both cases 50% and 90% of the metal uptake took place at 90 min and 180 min, respectively. Indeed, the figures were q_{90}=10.6 mgg^{-1} and q_{180} = 16 mgg^{-1} when dealing with 10 mgL^{-1}. However, the maximum removal capacity is obtained with 20 mgL^{-1} of Pb^{2+}, indeed q_{90}=18.7mgg^{-1} and q_{180} = 36.3 mgg^{-1}. In turn, the equilibrium value of q_e for 20 mgL^{-1} is four times larger than that for 5 mgL^{-1}. It is worth noticing that the process seemed to run even after 240 min.

Finally, the variation in adsorption of Ni^{+2} with respect to time is given in Figure 3c). The concentration of 5 mgL^{-1} was the only one tolerated by microalgae biomass; figures for 10 $mgL^{-1}$and 20 mgL^{-1} are shown for completeness, it makes no sense to try to adjust pseudo-linear equations (1), (2) due to data dispersion. It seems that a rapid uptake of metal by *S. maxima* may cause high toxicity to this microalga, (Meenakshi *et al.*, 2007).

Kinetic model analysis

Kinetic models, based on the capacity of the adsorbent, have been largely employed, among which the first-order equation of Lagergren and the pseudo second-order equation are the most widely used to describe the biosorption process (Wang J.L. and Chen C., 2009) (Ho, 2006). Formally, they are expressed as,

$$\frac{dq_t}{dt} = k \cdot (q_e - q_t)^n \qquad (2)$$

where k (min^{-1}) is the sorption rate constant, q_t (mg/g) is the amount of metal ion on the surface of the sorbent at time t, q_e (mgg^{-1}) is the amount of sorbed metal ions at equilibrium.

In expression (2), when $n=1$ and $q_t = 0$ at $t = 0$ and q_t at time t, one gets:

$$\ln(q_e - q_t) = \ln q_e - k \cdot t \qquad (3)$$

or in the case $n=2$,

$$\frac{t}{q_t} = \frac{1}{k \cdot q_e^{\,2}} + \frac{1}{q_e} \cdot t \qquad (4)$$

which actually are the pseudo-linear equations of first order ($n=1$) or second order ($n=2$), respectively. The constant parameters k and q_e can be determined from experimental data by plotting $\ln(q_e - q_t)$ against t for equations (3) or t/q_t against t in the case of equation (4). The first order equation was chosen since it matched better the experimental data.

The Figure 3 show the first-order approximations to the experimental data for concentrations of 5 mgL^{-1}, 10 mgL^{-1} and mgL^{-1}20 of cadmium, lead and nickel, respectively.

As it may be observed, the biosorption kinetic parameters for cadmium, lead or nickel are pretty similar at low metal concentrations (5 mgL^{-1}). The biosorption capacity was of 11.44 mgg^{-1} for lead and 14.47 mgg^{-1} for cadmium with a constant of biosorption ranging from 0.0135 min^{-1} for lead and 0.0167 min^{-1} for cadmium.

Cultures with 10 mgL^{-1} of cadmium with respect to the case of 5 mgL^{-1}, exhibited a reduction of 25% in the sorption rate k, followed by an increase of around 11% in the metal uptake q_e ; the conjunction of both factors represent a real effort of the microorganism to maintain the relative number of sorption sites, i.e. the microalgae are still able to handle reasonably the sorption of this Cd^{2+} at these concentrations. In contrast, with 20 mgL^{-1} of cadmium, there was a reduction of the sorption capacity q_e = 8.95 mgg^{-1} together with an increase in the sorption rate k = 0.0181 min^{-1}, which mean that sorption process is trying to run faster followed of a saturation of the sorption sites according to reduction of q_e, such scenario would imply high toxicity to *S. maxima* (Meenakshi *et al.*, 2007).

In cultures containing lead, 10 mgL^{-1} or 20 mgL^{-1}, there was a net improvement in the biosorption (uptake of metals q_e and sorption rate k) with respect to 5 mgL^{-1}: cultures at 10 mgL^{-1} increased 56% in q_e and the 29% decrease k, while at 20 mgL^{-1} produced a 200% increase in q_e and a 25% reduction in k. The above values represent a good tolerance to high metal concentrations, but the price to pay is to have longer times in the adsorption of metal (see Table 2). It is clear that the reduction in the rate of sorption time corresponds well to longer times of metal uptake; in fact 50% of the metal adsorption took place at 40 min for 5 mgL^{-1} and between 90 to 120 minutes for 20 mgL^{-1}. In summary, biosorption kinetics analyzed in view of the parameters of the first order equation (2) was as follows. At low metal concentration 5 mgL^{-1}, biosorption of cadmium, lead or nickel had exhibited similar kinetic properties. Moreover, uptake kinetics was kept on good values when faced to 10 mgL^{-1} of cadmium and lead. When handling higher concentrations, 20 mgL^{-1} for instance, combining an increase of the sorption rate k with a reduction of the sorption capacity is linked to a rapid reaction of the microalgae which produces a saturation of the sorption sites on the cellular wall having a toxic effect on it. In contrast, when combining a diminution of the sorption rate k with an increase of the sorption capacity is clear that heavy metal sorption might be highly efficient, as was the case of *S. maxima* in presence of 20 mgL^{-1} of lead.

Adsorption isotherms

The so-called adsorption isotherm curves provide a way to describe the thermodynamic distribution of a substance in one phase on the surface of another along the adsorption process as the system reaches the equilibrium (Lodeiro *et al.*, 2005). Langmuir´s model was chosen, it is a hyperbolic equation that

can be expressed in its linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} \cdot b} + \frac{C_e}{q_{\max}} \qquad (5)$$

or also as:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} \cdot b \cdot C_e} \qquad (6)$$

where $q_{\max}$ denotes the maximal capacity of sorbate adsorption (mgg^{-1}), it represents the total number of adsorption sites on the adsorbent; b is the Langmuir constant related to the bond strength between metal and adsorbent (mgg^{-1}). From one side a high value of $q_{\max}$ is desirable as it represents total number of adsorption sites on the adsorbent. On the other side, a high value of b is a good sign of the isotherm reflecting a high affinity of the bisorbent for the sorbate.

The Langmuir-type linear parameters are reported in Table 3, where we observed that the approximations are reasonably good according to R^2 values. In terms of equations (5), (6), the maximal adsorption capacity for lead was q_{max} = 46.9 mgg^{-1}together with a sorbent/sorbate affinity parameter b= 3.18. In second place we found the biosorption of cadmium with computed values of q_{max} = 8.63 mgg^{-1} and b= 1.05, which compared with the previous case may suggest that the cadmium biosorption processes by *S. maxima* are not suitable. However, in terms of kinetics parameters of Table 2 a high capacity of cadmium uptake for concentrations 5 mgL^{-1}or 10 mgL^{-1} has been concluded. Among all the trials, cultures with nickel reached the lowest figures (q_{max} = 3.38 $mgg^{-1}$and b = 0.55) which means that biosorption process was successful just for the concentration of 5 mgL^{-1}. Langmuir´s model assumes a fixed number of adsorption sites, in each site can be only one molecule of sorbate, which mean that all sites are equivalent, and possible interaction between absorbed molecules cannot take place. Such analysis is in harmony with a number of reported results, just to mention a few of them, Vullo *et al.*, (2008) considered *Pseudomonas veronii* in the biosorption of Cd^{2+}, (Yin *et al.*, 1999) with *Rhizopus arrhizus* and (Solisio *et al.*, 2008) with *Spirulina platensis*, all of them reported Langmuir´s model as the best one fitting the experimental data.

A comparison of the biosorption capacity of *Spirulina maxima* with respect to other biosrobents is presented here, see Table 4. In the case of cadmium, the metal uptake capacity is comparable to those reported for *P. stutseri* (Hassan *et al.*, 2009) and for *Spirogyrainsignis* (Romera *et al.*, 2007). In this study, the amount of absorbed lead was the most important and it ranges between that reported for *Caulerpalentilifera* (Pavasant *et al.*, 2006) and the one for *Gelidium algae* (Vilar *et al.*, 2005). Finally, when dealing with Nickel, the biosorption capacity is really compared with the one reported for *Chlorella vulgaris* (Akzu, 2002). Despite the differences with respect other approaches (live or dead biomass, amount of dried biomass, etc) the result reported in this work are comparable with those on the literature, see Table 4.

Conclusions

Effective biosorption by *S. maxima* required a maximal contact time of 90 min at (5, 10 mgL^{-1}) of nickel, then 180 min at (5, 10, 20 mgL^{-1}) of cadmium and 240 min at (5, 10, 20 mgL^{-1}) of lead.

Biosorption at 5 mgL^{-1} exhibited similar kinetics for all the metals. While at 20 mgL^{-1}, increase of k (sorption rate) with diminution of q_e (sorption capacity) characterized cell toxic effect.

In contrast, a diminution of k with an increase of q_e is linked with a highly efficient metal sorption, *i.e* 20 mgL^{-1} of lead was effectively biosorbed by live *S. maxima*.

Acknowledgements

The authors gratefully acknowledged the partially support given by the French-Mexican Joint International Unit UMI-LAFMIA 3175 CNRS-CINVESTAV.

References

1. Aksu, Z., 2002. Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel (II) ions onto *Chlorella vulgaris*. Process Biochemistry 38, 89–99.
2. Bayramoğlu,G.,Tuzun,I. ,2006. Biosorption of mercury (II), cadmium(II) and lead(II) ions from aqueous system by microalgae *Chlamydomonas reinhartdtii* immobilized in alginate beads. Int J Miner Process.81, 35-43.
3. Can H., Jianlong W., 2007. Influence of metal ionic characteristics on their biosorption capacity by *Saccharomyces cerevisiae.* Appl Microbiol Biotechnol, 74,911–917
4. Chen H.,Pan S., 2005. Bioremediation potential of *Spirulina* : toxicity and biosorption studies of lead. J Zhejiang University SCIENCE.6B(3): 171-174.
5. Chojnacka, K., Chojnacki,A., Gorecka,H., 2005. Biosorption of Cr^{3+},Cd^{2+} ,Cu^{2+} ions by blue-green algae *Spirulina sp.*: kinetics, equilibrium and the mechanism of the process.Chemosphere.59,75-84.
6. Cunningham W.P., Saigo B. W., 2001. Environmental Science: a global concern. Sixth edition. McGraw – Hill. New York.
7. Deng L., Su Y., Su H., Wang X., Zhu X., 2007. Sorption and desorption of lead (II) from wastewater by green algae *Cladophora fascicularis.* J. Hazardous Materials 143, 220–225.
8. Doshi H., Ray A., and Kothari I. L., 2007. Bioremediation Potential of Live and Dead *Spirulina*: Spectroscopic, Kinetics, and SEM Studies. Biotechnol Bioengineer 96,1051–1063.
9. Doshi H., Ray A., and Kothari I. L., 2008. Bioremediation Potential of *Chlorella*: Spectroscopic, Kinetics, and SEM Studies. Int J Phytoremediation, 10,264–277
10. Esposito, A., Paganelli, F., Veglio, F., 2002. pH related equilibria models for biosorption in single metal systems. Chem. Eng. Sci. 57, 307-313.
11. Fan T., Liu Y., Feng B., Zeng G., Yang C., Zhou M.and Zhou H., Biosorption of Cadmium(II), Zinc(II) and Lead(II) by Penicillium simplicissimum: Isotherms, Kinetics and Thermodynamics, J. Hazard. Mater. 2008, 160, 655–661.
12. Gokhale S.V., Jyoti K.K., Lele S.S., 2008. Kinetic and equilibrium modeling of chromium (VI) biosorption on fresh and spent *Spirulina platensis/Chlorella vulgaris* biomass Bioresour

Technol 99,3600–3608
13. Gupta V. K., Rastogi A., 2008a. Equilibrium and Kinetic Modelling of Cadmium (II) Biosorption by Nonliving Algal Biomass *Oedogonium sp.* from Aqueous Phase, J. Colloid Interface Sci., 153, 759–766.
14. Gupta V. K., Rastogi A., 2008b. Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: Kinetics and equilibrium studies, J. Hazardous Materials 152, 407–414.
15. Hassan S. H. A., Kim S. J., Jung A. Y., Joo J. H., Oh S. E and Yang J. E., 2009. Biosorptive Capacity of Cd(II) and Cu(II) by Lyophilized Cells of *Pseudomonas stutzeri*, J. Gen. Appl. Microbiol, 55, 27–34.
16. Ho Y. S., 2006. Review of second-order models for adsorption systems. J Hazard Mater. 136,681–9.
17. Liu G, Chai X, Shao Y, Hu L, Xie Q, Wu H., 2011. Toxicity of copper, lead, and cadmium on the motility of two marine microalgae *Isochrysis galbana* and *Tetraselmis chui*. J Environmen Sciences 23(2), 330-335
18. Lodeiro, P., Cordero, B., Barriada, J. L., Herrero, R., and Sastre de Vicente, M., 2005. Biosorption of cadmium by biommas of brown marine macroalgae. Bioresour Technol, 96, 1796-1803.
19. Meenakshi C., Umesh K. , Mohammed A., Sunaina Z., Tasneem F., 2007. Effect of heavy metal stress on proline, malondialdehyde, and superoxide dismutase activity in the cyanobacterium *Spirulina platensis*-S5. Ecotoxicology and Environmental Safety 66, 204–209.
20. Morsy F.M., Hassan S.H.A., and Koutb M. 2011. Biosorption of Cd(II) and Zn(II) by Nostoc commune: Isotherm and Kinetics Studies. Clean – Soil, Air, Water, 39 (7), 680–687.
21. Nacorda J.O., Martinez-Goss M.R., Torreta N.K., Merca F.E., 2007. Metal resistance and removal by two strains of the green alga, *Chlorella vulgaris* Beijerinck, isolated from Laguna de Bay, Philippines. J Appl Phycol 19,701-710.
22. Pavasant P., Apiratikul R., Sungkhum V., Suthiparinyanont P., Wattanachira S., Marhaba T.F., 2006. Biosorption of Cu2+, Cd2+, Pb2+, and Zn2+ using dried marine green macroalga *Caulerpa lentillifera*, Bioresour. Technol. 97 (18), 2321–2329.
23. Puyen Z.M., Villagrasa e., Maldonado J., Diestra E., Esteve I., Solé A. 2012. Biosorption of lead and copper by heavy-metal tolerant Micrococcus luteus DE2008. Bioresour Technol 126. 233-237
24. Pawan Raj Shakya., 2007. Nickel Adsorption by Wild type and Nickel Resistant Isolate of *Chlorella* sp. Pak. J. Anal. Environ. Chem. 8(1), 86 – 90.
25. Quintelas C., Rocha Z., Silva B., Fonseca B., Figueiredo H, Tavares T.,2009. Removal of Cd(II), Cr(VI), Fe(III) and Ni(II) from aqueous solutions by an *E. coli* biofilm supported on kaolin. Chem. Eng. J. 149,319–324.
26. Romera E., Gonzalez F., Ballester A., Blazquez M. L. and Munoz J. A., Comparative Study of Biosorption of Heavy Metals Using Different Types of Algae, Bioresour. Technol. 2007, 98, 3344–3353
27. Solisio C., Lodi A., Soletto D., Converti A.,2008. Cadmium biosorption on *Spirulina platensis* biomass. Bioresour Technol 99,5933–5937
28. Ting, Y.P, Lawson, F., Price, I.G., 1991. Uptake of cadmium and zinc by the alga *Chlorella vulgaris* : part II. Multi – ion situation. Biotechnology and Bioengineering 37, 445- 455.
29. Wang JL, Chen C.,2009. Biosorbents for heavy metals removal and their future: a review. Biotechnol Adv. 27,195-226.
30. Yin P., Yu Q., Jin B., Ling Z.,1999. Biosorption removal of cadmium from aqueous solution by using pretreated fungal biomass cultured from starch wastewater. Water Res. 33 (8), 1960–1963.
31. Vieira, R.H.S.F., Volesky, B., 2000. Biosorption: a solution to pollution? Int. Microbiol. 3 (1), 17–24.
32. Vilar V.J.P., Botelho C.M.S., and Boaventura R.A.R. 2005. Influence of pH, ionic strength and temperature on lead biosorption by *Gelidium* and agar extraction algal waste, Process Biochem. 40 (2005) 3267–3275.
33. Volesky, B., 1999. Biosorption for the next century. Chemical Engineering Department. Mc Gill University, Canadá. Ed. CRC PRESS.
34. Vonshak, A., 1997. *Spirulina platensis*. Physiology, Cell-biology and Biotechnology.
Taylor & Francis, New York.
35. Vullo D., Ceretti H., Daniel M.A., Ramírez S. y Zalts A., 2008. Copper, cadmium and zinc biosorption by *Pseudomonas veronii* 2E, Bioresour Technol 99,5574-5581

LIST OF FIGURES AND TABLES

Figure 1. Biosorption kinetics of cadmium (1a), lead (1b) and nickel (1c) by live biomass of *Spirulina maxima*, (♦) 5 mgL^{-1}, (■) 10 $mgL^{-1}$and (▲) 20 mgL^{-1} respectively.

Figure 2. Percentages of metal removal.

Figure 3. Variation in the biosorption capacity of cadmium (3a), lead (3b) and nickel (3c) by *Spirulina maxima*, experimental versus model data (continuous or dashed lines); (♦) 5 mgL^{-1}, (■) 10 mgL^{-1} and (▲) 20 mgL^{-1} respectively

Figure 4. Isotherms of adsorption for different metals: (■) cadmium, (♦) lead and (▲) nickel.

Table 1. Composition of Zarrouk´s modified medium

Table 2. Kinetic parameters in the adsorption process of cadmium, lead, or nickel by *Spirulina maxima*

Table 3. Adsorption parameters from Langmiur´s linear model for cadmium, lead and nickel

Table 4. Comparison of maximum biosorption capacities obtained in this study with other values reported in the literature

Figure 1a

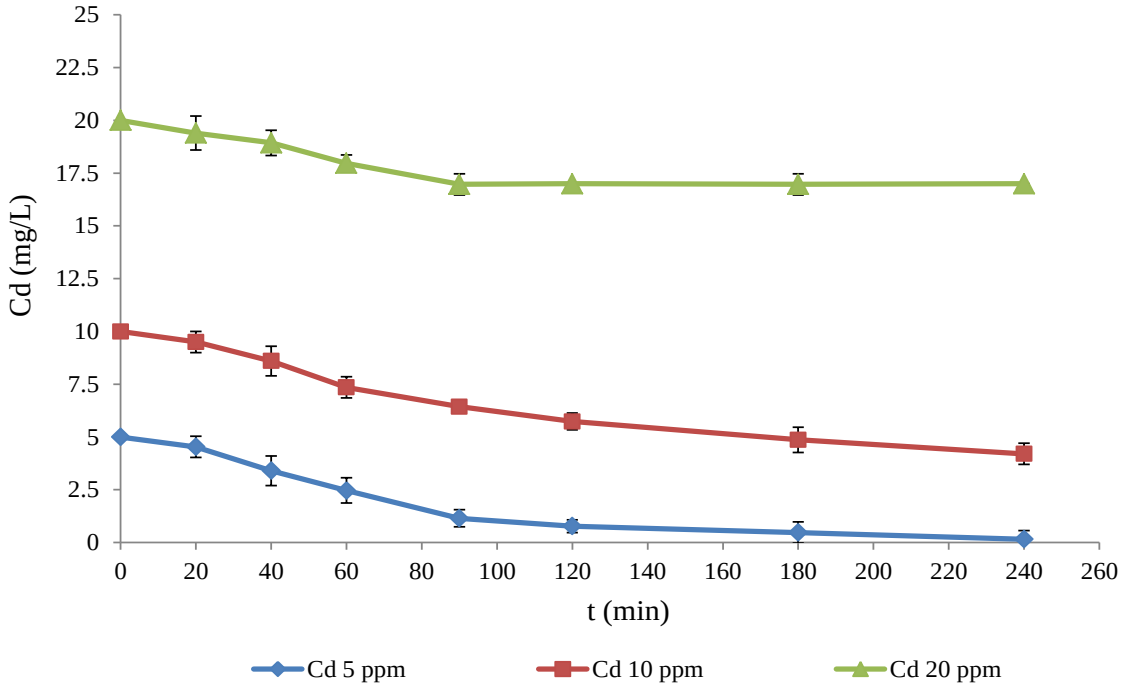

Figure 1b

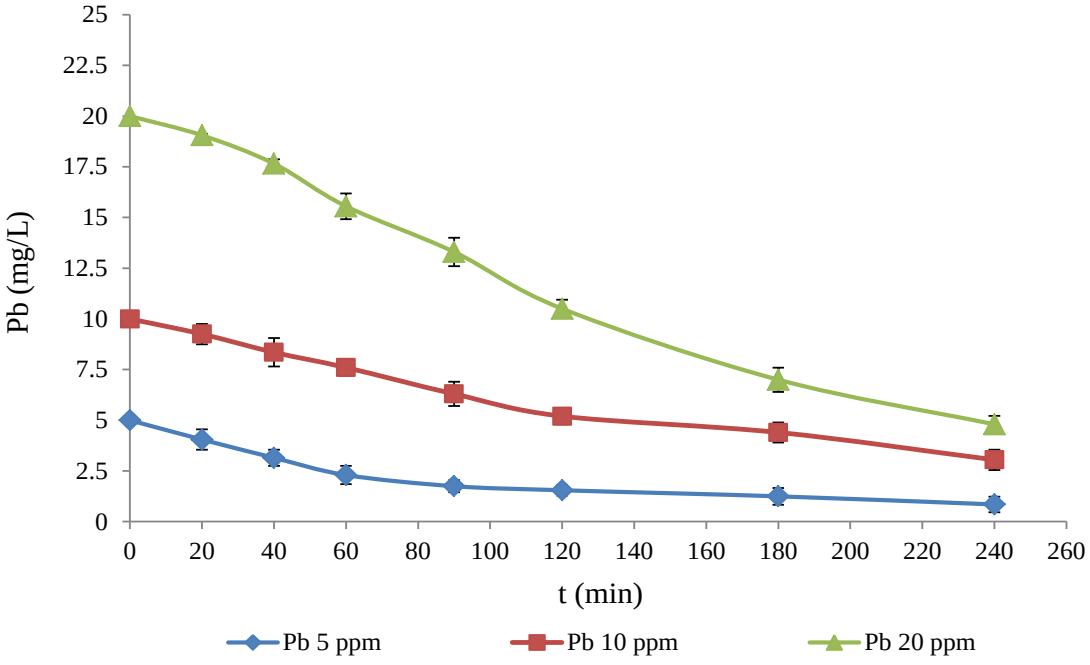

Figure 1c

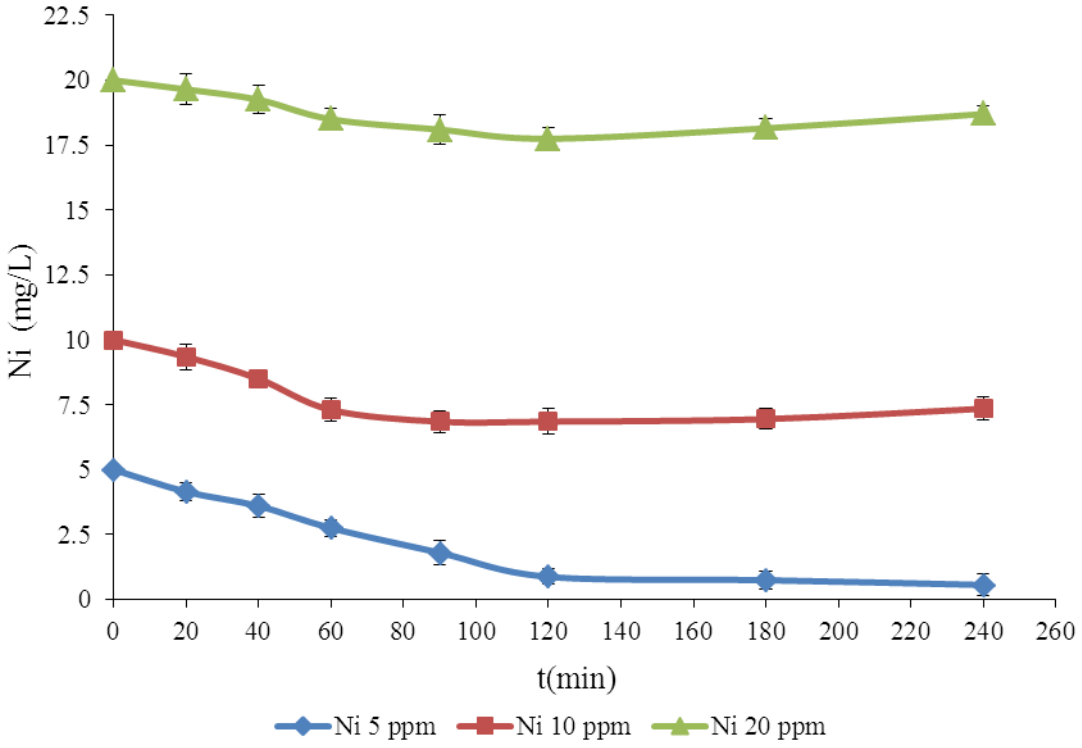

Figure 2

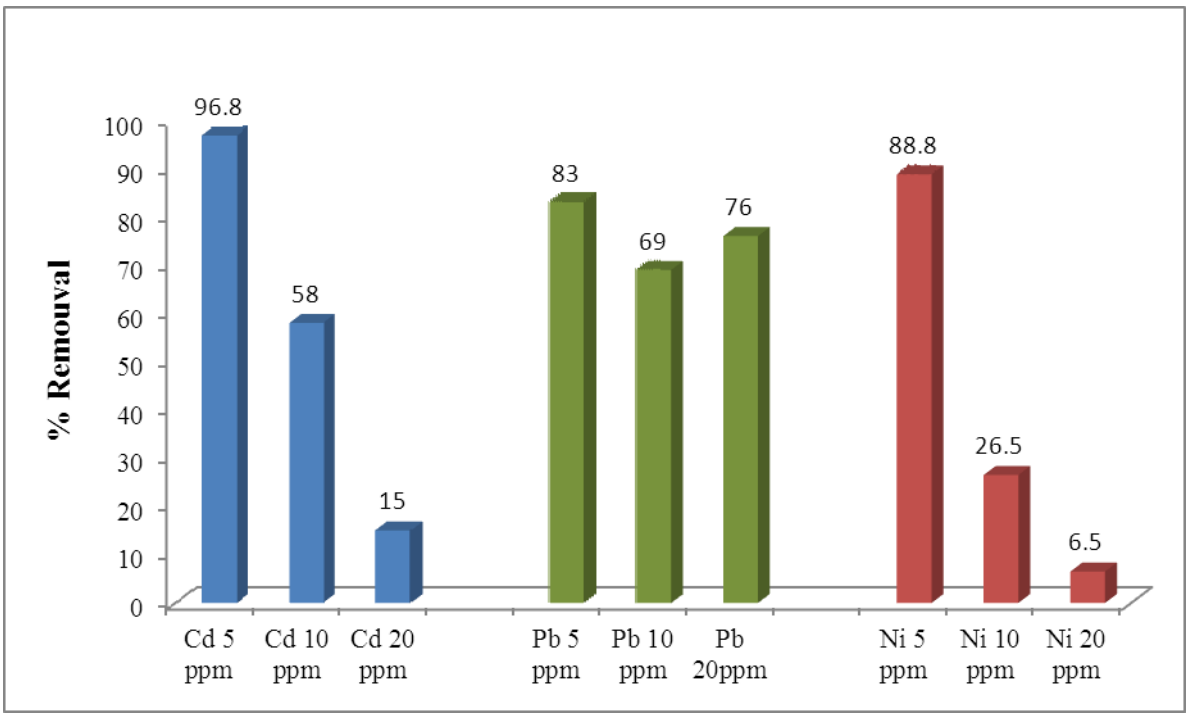

Figure 3a

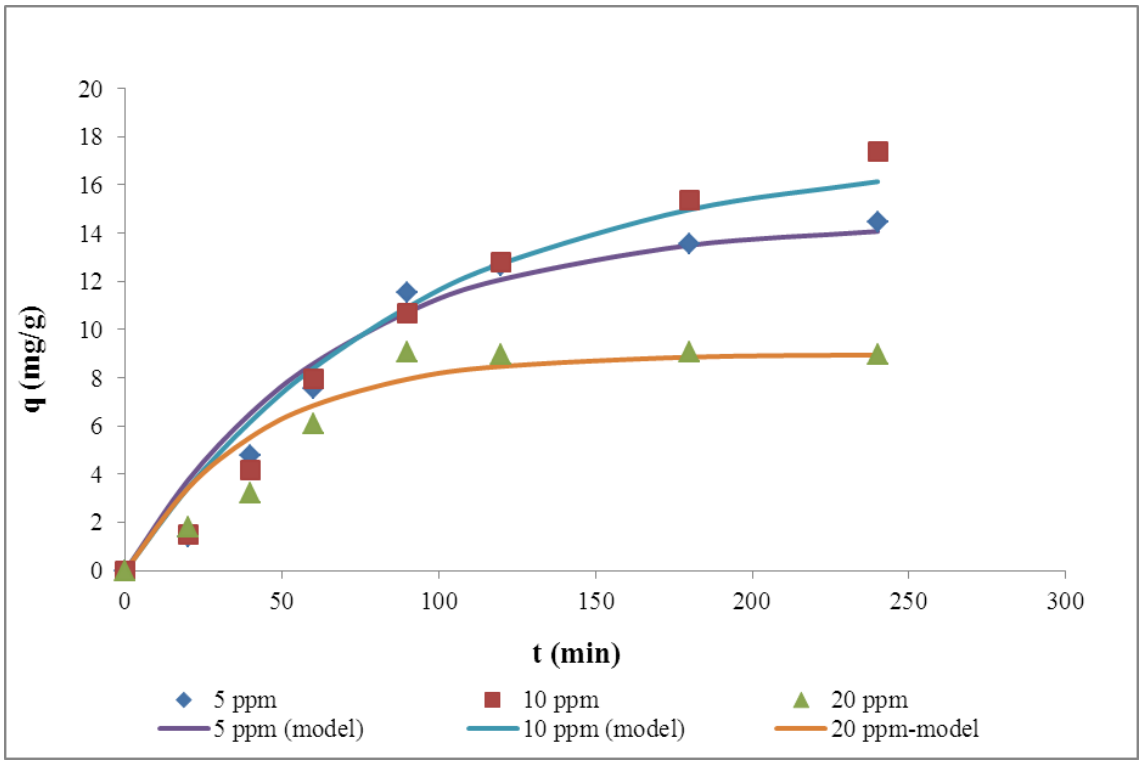

Figure 3b

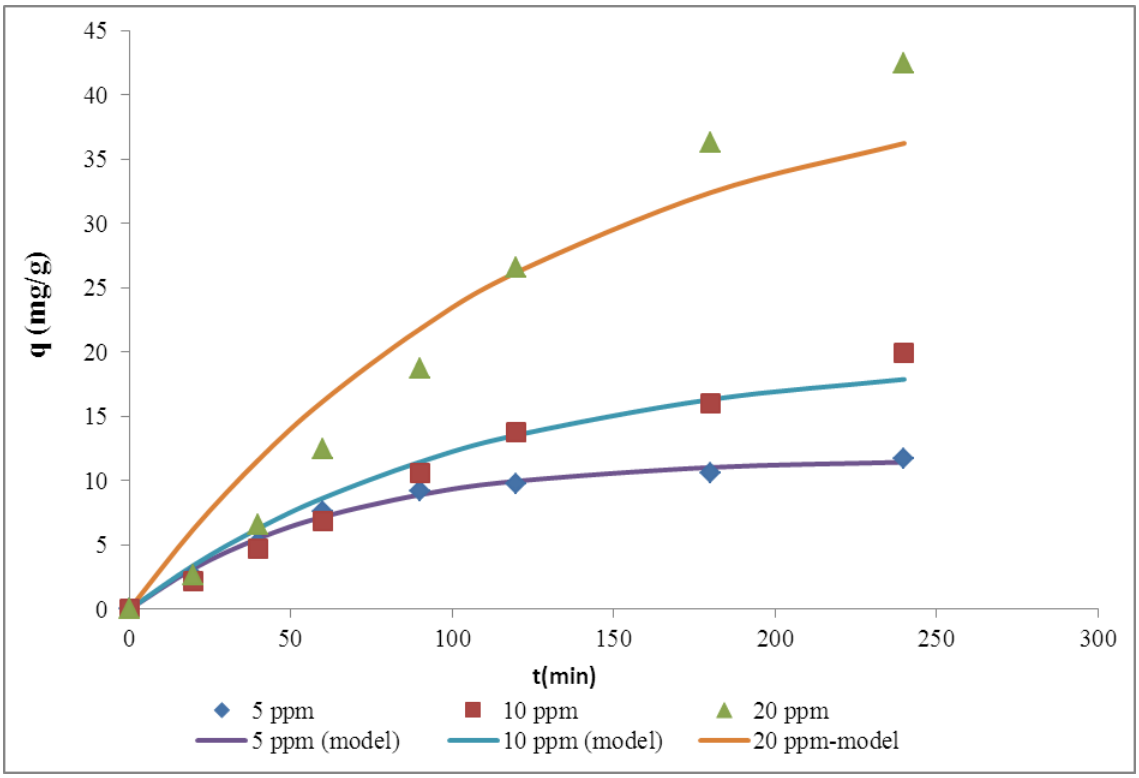

Figure 3c

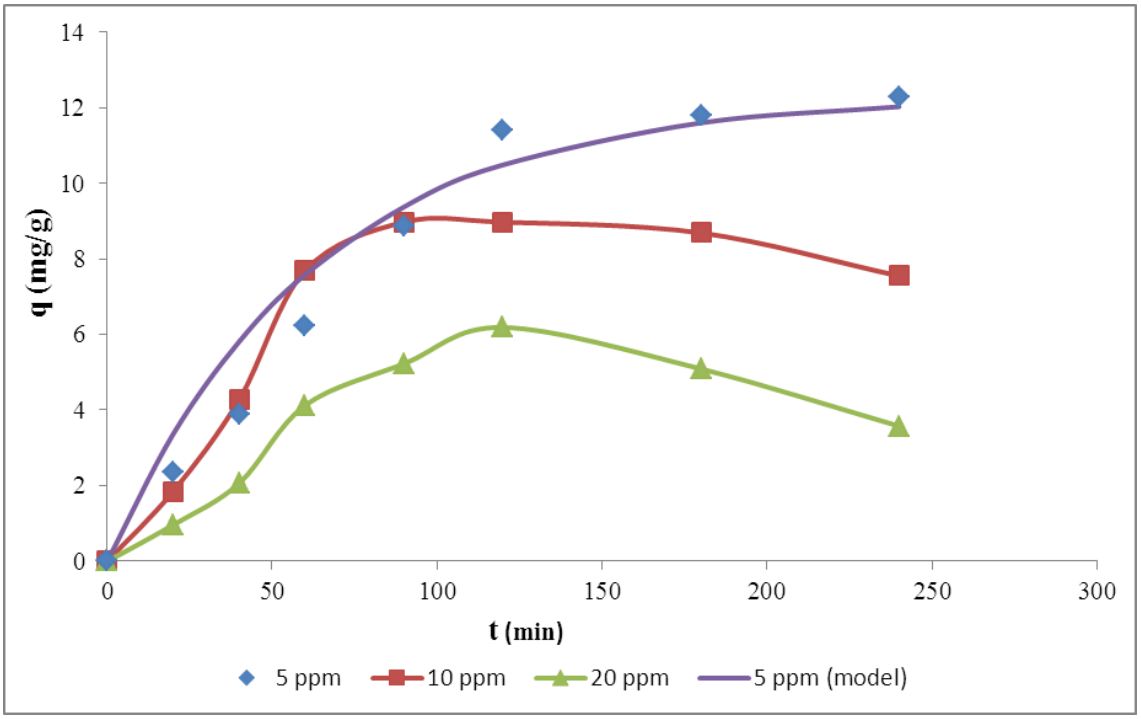

Table 1

Compounds	gL^{-1}
$NaHCO_3$	8
K_2HPO_4	0.5
$NaNO_3$	2.5
K_2SO_4	1
NaCl	1
$MgSO_4.7H_2O$	0.2
$CaCl_2$	0.04
$FeSO_4$	0.01
EDTA	0.08

Table 2

		Kinetic parameters		
		r^2	q (mgg^{-1})	k (1/min)
Cadmium	5 mgL^{-1}	0.97	14.47	0.0167
	10 mgL^{-1}	0.99	16.14	0.0124
	20 mgL^{-1}	0.91	8.95	0.0181
Lead	5 mgL^{-1}	0.97	11.44	0.0135
	10 mgL^{-1}	0.99	17.88	0.0096
	20 mgL^{-1}	0.96	36.23	0.0081
Nickel	5 mgL^{-1}	0.95	12.02	0.0196

Table 3

	LINEAR PARAMETERS		
	q_{max}(mgg^{-1})	b (mgg^{-1})	R^2
Cd^{2+}	8.63	1.05	0.9986
Pb^{2+}	46.9	2.61	0.8949
Ni^{2+}	3.38	0.55	0.9562

Table 4

Metal	Biosorbent	Amount Adsorbed (mg/g)	Reference
Cd (II)	*P. stutzeri*	21.3	Hassan *et al.*, 2009
	Oedogoniumsp	88.2	Gupta and Rastogi, 2008 (a)
	P. simplicissium	52.5	Fan *et al.*, 2008
	Spirogyrainsignis	22.9	Romera *et al.*, 2007
	Nostoc commune	126	Morsy *et al.*, 2011
	Spirulina maxima	16.1	This work
Pb (II)	*Caulerpalentilifera*	28.7	Pavasant *et al.*, 2006
	Gelidium algae	64	Vilar *et al.*, 2005
	Spirogyra sp	140	Gupta and Rastogi, 2008(b)
	Spirulina maxima	36.2	This work
Ni (II)	*Chlorella vulgaris*	48	Akzu, (2002)
	Spirulina maxima	12	This work