

Biosorption of Cd(II) and Co(II) Ions from Contaminated Water onto Cyanophyta: Single And Binary Ion Exchange Isotherm

Salim Hrez Jessam Al-Khazraji

Al-Mussaib Technical Institute Al-Furat Al-Awsat Technical university 51009 Babylon Iraq

Salimhrez771@gmail.com

Abstract

This study used both single and binary biosorption of Cd(II) and Co(II) ions from a synthetic contaminated water onto a dead blue-green (Cyanophyta) algae \ as biosorbent of heavy metals. Experimental parameters included pH, initial metal concentrations, agitation speeds, contact time and temperatures were investigated. The uptake capacities were 38.4 and 23.5 mg/g for Cd (II) and Co(II), respectively. The best pH values were 5 for Co (II) and Cd (II), respectively, and the contact time was 1.5 hr. A sequence of batch experiments was performed in a batch device in order to get equilibrium isotherm data of single and binary metals solutions for biosorption. The ion exchange mechanism was the base absorption of these metals, along with the light metal release like sodium, magnesium, calcium and potassium therefore a model ion exchange had been found appropriate to describe the process of biosorption. However, the calculated affinity constant (K) sequence for both single and binary system was 2.33, 5.43 respectively, for Cd (II) and 1.87, 2.46 for Co (II) with less than 5% percentage error; these values remain in both systems that the Cd(II) was the strongest one. The affinity constant in the single and binary system was $K_{Cd} > K_{Co}$.

Keywords: biosorption, heavy metals, ions, single and binary, dead blue-green algal biomass, Cyanophyta

الخلاصة

تمت دراسة الامتزاز الحيوي المفرد والثنائي لمياه ملوثة بأيونات الكاديوم والكوبلت على الطحالب الخضراء المزرقمة الميتة (Cyanophyta). فقد اجريت التجارب المتضمنة على الدالة الحامضية، التركيز الاولي، سرعة الخلط، الوقت الامثل للامتزاز الحيوي ودرجة الحرارة. وقد تبين ان سعة الامتزاز للكاديوم هي 38.4 ملغم/غم وللکوبلت 23.5 ملغم/غم بوقت مثالي مقداره 1.5 ساعة. تم القيام بسلسلة من تجارب الدفعات (Batch experiment) للملوثات للحصول على مخططات التوازن للقرارات في حالة المفرد والثنائي. اعتمد الامتزاز الحيوي على التبادل الايوني والذي يعتمد على انبعاث وتحرير العناصر الخفيفة مثل البوتاسيوم، الصوديوم، الكالسيوم، والمغنيسيوم. حيث ان معامل الانجذاب المحسوب لكلا النظامين المفرد والثنائي كان 2.33 و 5.43 على التوالي للكاديوم وللکوبلت 1.87 و 2.46 بنسبة خطأ اقل من 5%. ان هذه القيم للكاديوم هي الاقوى في كلا النظامين ومعامل الانجذاب للكاديوم اكبر من الكوبلت

الكلمات المفتاحية: الامتزاز الحيوي، العناصر الثقيلة، ايونات، المفرد والثنائي، الطحالب الخضراء المزرقمة الميتة.

1. Introduction

Significant environmental problems are caused by the heavy metals presences in wastewaters. It is known that the heavy metals high concentrations are carcinogenic and toxic to living organisms. Even if the heavy metals with very low concentration are presented, bio-magnification could elevate these concentrations to some levels where they show toxic characteristics. For this reason, heavy metals are considered to be the main pollutants in lots of industrial wastewaters and toxic to both aquatic and

human life [Taghi, *et al.*, 2005]. The majority organic pollutants are susceptible to biological degradation, unlike heavy metal ions which will not go through a process of degradation into harmless end products. Heavy metal ions, like zinc, cadmium, lead, mercury, chromium, copper, and cobalt ions exist from different industrial activities in the waste streams, as, for example, from electroplating, petroleum refineries, electronics, petrochemical industries, mining operations, and tanneries [Cheueh, 2005].

For more than a decade, researchers have been searching for more effective, less and expensive methods to remediate heavy metal contaminated water and reduce the growing public health risks. Therefore, and as an alternative, researchers have introduced a low cost process of biosorption by using an adsorbent [Volesky, 2003]. Biosorption is a process of utilizing cheap dead biomass for the metals recovery and removal from aqueous solution [Romera *et al.*, 2007]. Removing metal ions from solutions that are contaminated by the use of this process is proven to be quite effective with low-cost and environment-friendly manner [Figueria, *et al.*, 2000]. In other words; the biosorption field first major challenge was selecting the most promising types of biomass from large inexpensive and available biomaterials. While this task has not been done, under various conditions an adequate number of biomass types have been tested for metal binding [Davis, *et al.*, 2003].

To clean the environment from metal ions, various biomasses such as bacteria [Ridha, 2011], activated sludge [Ali, 2011], yeast [Sulaymon, *et al.*, 2010], algae [Al-Hares, 2014], fungi [Brady, *et al.*, 1999] and plants [Melcakova, and Ruzovic, 2010] have been used. Algal biomasses are among the most promising classes of studied biosorbents [Romera, *et al.*, 2006; Figueria, *e al.*, 2000].

Green and blue-green algae in Iraq are available in large amounts, approximately in all marshes and surface water resources [Al-Hassany, 2003]. The growth of algae with other types of river plants causes many difficulties for networks and irrigation canals. Appropriate action should be taken in such circumstances. Algae change the taste and smell of water, clog filters, which may kill fish during its death and degradation (consume dissolved oxygen), reduce the beauty of the water surfaces, block aeration, prevent sunlight to reach the water surfaces, and hinder the process of photosynthesis, etc. Algae lead to problems in water pumping and irrigation canals and environmental problems caused by Algae death and decay, which cause pollution of water resources. The use of algae is to achieve the economical goal by using cheap materials for removing hazardous pollutants [Al-Hares, 2014]. The aim of using algae is to achieve the economical goal by using cheap materials for removing hazardous pollutants. In the current study, dead algal biomass was used for the competitive removal of heavy metals (Cd(II) and Co(II)) in batch reactors at changed operational situations.

2. Equilibrium Isotherm Batch Models for Biomass

A good modeling of a dynamic ion exchange system is required to be due to the proper choice of an equilibrium isotherm to characterize competitive ion exchange. Batch equilibrium studies have been granted a considerable attention.

Mathematical models, in principle, provide effective tools for performing design, prediction, forecasting, and sensitivity analysis on the different operational variables [Basheer, and Najjar, 1996].

Several processes are involved in the metal ion binding mechanism in biosorption, including ion exchange, physisorption, chemisorption, and complexation. Ion exchange identified as the principal mechanism of biosorption of metals by fresh

water algae and fungi [Fourest, and Roux, 1994; Crist, *et al.*, 1994]. Therefore, it is recommended to use the ion exchange reaction model for describing the isotherm process as an alternative to Langmuir or Freundlich relationships. As a result, lots of studies on biosorption have been done for developing a mathematical equilibrium sorption models and for verifying their suitability for the description of biosorption for heavy metals via green- blue algal biomass.

The biosorption mechanism that involves algal biomass is recognized as ion exchange response type among cations that have already been bound to the biomass and others existing in the aqueous solution [Diniz and Volesky, 2005; Yang, 2000]. Certainly, a model of ion exchange isotherm is an improved illustration of the process of biosorption on algae, since it reflects the fact that most algal biomass is either has light metal ions, like Ca(II), Mg(II), K(I), and Na(I) ions, that would be released after binding of a protonated or heavy metal cation [Davis *et al.*, 2003]. The following ion exchange reaction can describe the demonstration of the metals binding via algal biomass from aqueous solution [Kratochvil, 1997]:



Where M^{2+} and L^{2+} are the representations of the divalent metal cations released and sorbed from the biomass.

For all competing cations that represented by the total normality, which could be exchanged during the reaction, the total summation of the equivalent concentrations is the same as equilibrium level is reached; therefore, the total normality can be stated as:

$$c^0 = c_M + c_L \quad (2)$$

Where, c_M is the heavy metals total normality that remains in the liquid phase; c_L is the total normality of light metals released into the liquid phase, while the total normality of the solution is represented by c^0 .

Moreover, if ions exchange occurs during the process, the competing ions always employ the exchangeable binding sites; hence, in the solid phase of the elements involved, the sum of the concentrations is the total number of exchangeable binding sites (Q) and could be symbolized as follows:

$$Q = q_M + q_L \quad (3)$$

Where: q_M is the amount of adsorbed metal (meq/g), q_L is the released light metals to the solution due to biosorption of metal (meq/g).

For one component, the equivalent fraction in the solid phase (y_M, y_L) is the relation for its own concentration in solid phase divided by the total number of exchangeable binding sites (Q), while the equivalent fraction in the liquid phase (x_M, x_L) is the ratio between the total normality of the solution (c^0) and its own concentration in the liquid phase:

$$x_M = \frac{c_M}{c^0}, \quad x_L = \frac{c_L}{c^0} \quad (4)$$

$$y_M = \frac{q_M}{Q}, y_L = \frac{q_L}{Q} \quad (5)$$

In this case, the affinity constant ($K_{M,L}$) for a single system signifies the metal relative selectivity to the light ions and as explained in [Diniz, *et al.*, 2008]:

$$K_{M,L} = \frac{y_M \cdot x_L}{x_M \cdot y_L} \quad (6)$$

The light and heavy metal in the solution are referred via the subscript M and L.

Rearranging Eq. (6) by substituting the equivalent fraction of the light metal ($x_L=1-x_M$, and $y_L=1-y_M$), the equilibrium uptake model equation for a heavy metal ion presented in a binary system with light metals could be represented as shown in Eq.7:

$$y_M = \frac{K_{M,L} \cdot x_M}{1+(K_{M,L}-1) \cdot x_M} \quad (7)$$

For a single sorption system, ion exchange isotherm is shown in Eq. (7). The biosorption equilibrium data have been set for heavy metals as well as light metal, where the sorbing metal is indicated by the heavy metal, and total amount of the light metals is released because of metal biosorption is specified by the light metals.

We can calculate the x_M and y_M fraction from the experimental data and we can also use the software “STATISTICA version (6.0)” to calculate the affinity constant $K_{M,L}$ from Eq.(7). For binary systems, Eq.(8) is used [Diniz, *et al.*, 2008]:

$$y_{M1} = \frac{K_{M1,L} \cdot x_{M1}}{1+(K_{M1,L}-1) \cdot x_{M1} + (K_{M2,L}-1) \cdot x_{M2}} \quad (8)$$

3. Experimental Work and Materials

3.1 Materials

3.1.1 Adsorbate (Stock Solutions)

A solution of cadmium and cobalt ions of (1000 mg/L) concentration were prepared by the dissolvent of $Cd(NO_3)_2$ with an appropriate quantity of $Co(NO_3)_2$ (minimum purity 99.5%) in a liter of deionized water with 10 ml concentrated HNO_3 had been added [APHA, 1995]. For variable biomass weights, concentrations of 50 mg/l of both of those salts had been used as adsorbate. The active solutions were made by diluting the stock solution with distilled water to the desired concentration.

All the glassware used for experiments, storage and dilution were cleaned with extra detergent, carefully washed with tap water, soaked in a 20% HNO_3 solution overnight and finally, before the use it was rinsed with deionized water. The metal concentrations in solution before and after biosorption were measured by a flame atomic absorption spectrophotometer“(Buck, Accusys 211, USA).”

3.1.2 Biosorbent

3.1.2.1 Algal Biomass Collections

In this study, a blue-green (Cyanophyta) alga, as the biosorbent of heavy metals, has been used. In Iraq, several studies referred that algae can be blooming in the Tigris and Euphrates Rivers, and marshes water or elsewhere they accumulate in the aquatic environment [Al-Hassany, 2003; Najem, 2010]. Large quantities of algae have been observed along the Channels from Tigris River near Al- Sawira (South East Baghdad). 10 kg of fresh algae were collected from selected location in April 2016.

The algae analysis was done by using microscope after clean it from the inert material. These analyses were achieved according to the standard methods [APHA, 2005] in laboratories of Iraqi Ministry of Sciences and Technology/ Environment and Water Directorate. The results showed that their division genus, species, and percentage weight species were dominated: "Chlorophyta (Spirogyra aequinoctialis 1%, Oscillatoria Formosa 4%), Oscillatoria subbrevis 3%, Cyanophyta (Oscillatoria princeps 91%, and others 1%). Cyanophyta" (blue-green algae) species were dominated and had the highest percentage weight.

3.1.2.2 Preparation of Dead Blue Algal Biomass

The blue - green algae were cleaned by hand and washed few times with tap water as well as distilled water in order to remove the impurities, dirt, and other undesired components, then the water squeezed out. The washed algae were dried for 7 days in an aerated room and then dried in the oven at 60 °C for 48 h. The dried algal biomass was grinded and sieved [Al-Hares, H.S., 2014]. The average size of 200-300 μm particle diameters was used for biosorption experiments. The geometric mean diameter was given by $d_{gm} = (d_1 d_2)^{1/2}$ where d_1 is the diameter of the lesser sieve on which the particles were retained and d_2 was the diameter of the upper sieve through which the particles passed [Alexander, and Zayas, 1989]. The mean particle diameter of 0.245mm of dried sieved blue algal biomass. Physical properties of the particles such as surface area, voidage, and density were measured and listed in table(1). These measurements were using the multi-point-N₂-BET method and the Quanta chrome NovaWin2 system for measuring surface area and actual density respectively. The bulk density was determined using Hg-pycnometry analysis. Figure (1) showed scanning electron micrographs for dead green-blue algal biomass.

3.2 Biosorption Experiments

The batch experiments were executed: ion exchange equilibrium isotherms, series of experiments were done in an equilibrium set of data for biosorption of single and binary metals solutions for different parameters such as pH, biomass weight, temperature, initial concentration and agitation speed.

3.2.1 Batch Experiments

3.2.1.1 Equilibrium Isotherm Experiments at Different pH

Experiments set were done in conical flasks of 250ml volume with 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1 g of algal biomass and a volume of 100ml of each solution. However, all of those experiments were carried out at a (50 mg/L) as an initial concentration for each element. Different initial pH values (3, 4, 5 and 6) were used for each solution. The pH of the metal solutions was adjusted to the desired pH values using 0.1M NaOH or 0.1M HNO₃. The flasks were positioned in a shaker "(Edmund Buhler, 7400 Tubingen Shaker-SM 25, Germany)" for 1.5 h with continuous shaking rate of 200 rpm at room temperature. From each flask, 10 ml samples were taken and filtered by ashless filter paper (type: "WATMAN No.42, 7cm diameter, Germany)." To fix the heavy metals concentration during storage before analysis, few drops of 0.1M HNO₃ were added to the samples in order to decrease the pH value below 2 [APHA, 1995]. The residual concentration of cadmium, cobalt and light metal ions (magnesium) in the samples was fixed using AAS and the other light metals ions in the samples were fixed using flame photometer BWB-1(USA). The percentage removal efficiency was calculated also using the following equation:

$$\% \text{ Removal efficiency} = \frac{C_i - C_e}{C_i} * 100 \quad (9)$$

The equilibrium isotherm curves were plotted as percentage removal efficiency versus the green- blue algal biomass weight (w) for each pH value. Only, the equilibrium isotherms data at optimum pH for removal of each heavy metal were fitted with an ion exchange model

4. Result and Discussion

4.1 Factors Affecting Biosorption

4.1.1 Effect of pH

The solution pH effect on removal efficiency is achieved by a series of experimental sorption at different initial pH values as mentioned previously. The pH dependency of biosorption performance is clearly seen when plotting the percent removal efficiency versus blue-green algae weight at different pH values. According to the results that gathered, it has been found that the pH of the solution plays a significant role in the biosorption process [Schiewer, and Volesky, 1996; Herrero *et al.*, 2006].

Figures (2) and (3) show the initial pH solution influence on Co (II) and Cd (II) ions biosorption, respectively. From these figures, it can be noticed that the best pH value for removing is 5 for Cd(II) and Co(II), respectively. The active surface sites of the adsorbent at pH < 3 are either protonated [Lu, *et al.*, 2008] or dissociated [Lodeiro *et al.*, 2006], therefore, unfavorable curves are resulted for all two metals at pH value of 2.

The previous figures show that the pH value of 5 is the best for Cd(II) and Co(II) that can be taken in the single or mixing of two or more heavy metals so that this value will be fixed.

Coinciding with the previous experiments, it is noticed that the final or equilibrium pH solution is higher than the initial value figure (4). This can be the result of ion exchange mechanisms, as the heavy metals uptake is balanced by the observed release light metals [Schiewer, and Volesky, 1996; Kratochvil, 1997]. Generally, untreated algal biomass contains alkaline and alkali earth metals, like Na(I), K(I), Ca(II) and Mg(II) that are initially presented with fresh water. So that, when blue-green algal biomass reacts with the heavy metals bearing solution, the light metals released cause an increase in the pH due to the light metal alkalis formation 50 mg/L of biosorption of two heavy metals solutions onto algal biomass (1g) leads to the release of light metals amount, while the pH of heavy metal solutions remains fixed at the optimum value as figure (5) shows.

4.1.2 Effect of the Contact Time

The effect of contact time on efficiency of removal was investigated by using 0.6 g of blue-green algal biomass, mixing it with a concentration of 50 mg/L of Cd (II), and Co (II) ions at pH 5 and 100 ml of solutions with a single metal ion. These were kept at various time intervals. The results of the contact time of two metal solutions with the removal effectiveness were illustrated in figure (6). In order to achieve the equilibrium conditions for all heavy metals, it is possible to conclude that the contact time of 1.5h is adequate.

4.1.3 Effect of Initial Heavy Metal Concentration

Concentrations of 10, 50, 90 and 120 mg/L were chosen for studying the removal efficiency variation with various initial concentrations at room temperature and at the fixed weight of blue-green algae biomass (0.6g). The pH of heavy metal solutions was specified at 5 for each heavy metal, and the speed of agitation of the shaking process was 200 rpm for 1.5h [figure (7)]. It was noticed that there was no great alteration in the percentage removal if the increment of concentration was from 10-50 mg/L, this happened due to that 0.6g of algae could include sufficient exchangeable sites for this concentration range, nevertheless, when the concentrations increment was 90 and 120 mg/L the exchangeable sites in 0.6 g were not going to be sufficient to accumulate those concentrations. Therefore, it was obvious that the percentage removal was reduced.

4.1.4 Effect of Temperature

The temperature effect on the capacity of equilibrium sorption for Cd(II) and Co(II), ions was examined, the temperature was set between 10-50°C (283-323°K) while other parameters were taken as mentioned previously. The variations in the percentage removal efficiency with temperature will be shown in figure (8). It is well known that increasing temperature leads to raising the adsorbate molecules rate for diffusion in the pores as a consequence of the decrement in solution viscosity. This, for a certain adsorbate, will change the adsorbent equilibrium capacity [Saleem, *et al.*, 2007].

An additional increase in temperature (above 30 °C) resulted in decreasing the efficiency of percentage removal. This reduction in the efficiency of biosorption might be attributed to many reasons: weakness of biosorption forces between the active sites of the sorbents and the sorbate species and as well as among the adjacent molecules of the sorbed phase, increasing in the relative escaping tendency of the heavy metals from the solid phase to the bulk phase, [Meena, *et al.*, 2005] or the biosorbent surface deactivation or destruction of some active sites on the biosorbent surface because of bond ruptures [Sari, and Tuzen, 2008].

A conclusion could be made from figure (8), that the change of temperature from 10-30 °C (283-303 °K) has small or no significant influence on the process of biosorption, and, hence, the experiments of biosorption could be executed at room temperature with no modification to be made.

4.1.5 Effect of Agitation Speed

The effect of agitation speed on removal efficiency of Cd(II) and Co(II) ions was studied by varying the speed of agitation (50,100,150,200 and 250rpm) and keeping other parameters equal to best ones obtained in the previous steps. Figure (9) shows that if the shaking rate is increased, the removal efficiency is increased as well. When agitation speed was increased, the metal ions uptakes were increased gradually. The 200rpm shaking was enough to make sure that all the surface binding sites were available for metal uptake, as the results indicated that.

4.2 Equilibrium Isotherms in Single System

In this section, algal biomass biosorption performance was for the uptake of 38.4, 23.5 mg/g for Cd(II) and Co(II) ions respectively and these were evaluated by determining the respective biosorption isotherms for optimum pH values. Ion exchange model was used for expecting the theoretical isotherms data at optimum pH.

A biosorption isotherm model was considered by specific constant values, which expressed the affinity of the biosorbent and surface properties, it also could be used for the comparison of the biosorptive capacities of the biosorbent for various pollutants [Dursun, *et al.*, 2005]. Previously, the mechanism of ion exchange was demonstrated as the main mechanism that the heavy metal uptake involved by blue-green algal biosorbent materials. So that confirmed this phenomenon in the current work, an isotherm outcome at optimum situations obtained for the single system, were carried out consistently with ion exchange model constraints by finding the light metals concentration which unconfined because of the biosorption of heavy metal. Then the equilibrium isotherm data at best pH were fixed with ion exchange models (Eq. 7).

An ion exchange constraint (affinity constant, K_M) was determined by fitting the model to experimental data using a non-linear regression option in "STATISTICA software, version 6." The results were shown in figures (10) and (11) for the biosorption of Co(II) and Cd(II) ions, respectively. These figures showed that an ion exchange isotherm model fitted fine for wholly heavy metals experimental data due to great values of regression constants (R^2) that were obtained.

The values of biomass affinity constant gave a useful sign to understand the metals biosorption capacity [Kratochvil, 1997]. These values of affinity constant reflected the relative affinities of the metals towards the binding groups in the algal biomass. The calculated affinity constants were 2.33, and 1.87 for Cd (II), and Co (II), respectively. Therefore, the metals could be sorted in the order of descending affinity according to the values of the equilibrium constants as the following sequence: Cd (II) > Co(II).

As in [Hashim *et al.*, 1997], the reason behind the biomass showing a high affinity for a given metal than other was may be related to the degree of affinity of specific biomass for each metal (affinity constants). Although the dependence of the total amount of metal anchored on the adsorbent surface would also be on the number of active sites presented and how easily they could be accessed by metal [Sulaymon, *et al.*, 2010].

4.3 Equilibrium Isotherms of Binary System

Usually, heavy metals binary mixtures were current in different industries discharges. As previously shown, the pH of combinations in binary systems was set at 5 as a value that corresponds for all metal removal. These data were fitted with an ion exchange model of each system (Eq.8). For each model, the parameters were got from non-linear STATISTICA fitted the experimental data.

Figures (12 and 13) displayed an ion exchange equilibrium isotherm for Cd(II) and Co(II) in binary systems. It was clear that the biosorption of Cd(II) with Co(II) was the highest biosorption rate than Co(II) in a binary system for algal biomass ($K_{CdCo} > K_{CoCd}$), therefore, the lower affinity Cobalt ions had less strength of covalent binding than cadmium ions.

The calculated affinity constants for all heavy metals in single and binary systems were listed in table (2). Because of the competition among metals for binding sites presented in wall of algal biomass, there was a decrease of biosorption capacity in binary system when it's compared to the single metal biosorption of two metals. A decrement was occurred by the metal biosorption capacity when the number of metals was increased and, thus, at binary system the lowest biosorption capacity was got compared with the other systems. These results finding were in good agreement with [Schiewer and Volesky, 1996].

5. Conclusions

This study revealed the following conclusions, concerning the batch for algal biomass, of Cd(II), and Co(II) ions:

1. The biosorption of those metals onto algal biomass is an ion exchange mechanism with accompany of the light metals release like potassium, calcium, magnesium, and sodium.
2. Potassium is high release than the other of light metals.
3. Optimum pH is 5 for Cd(II) and Co(II) respectively with contact time 1.5h and agitation speed 200 rpm in biosorption process onto dead algal biomass.
4. For describing the biosorption process, an ion exchange model is found to be appropriate; approximately less than 5% percentage error was obtained due to fitting theoretical and experimental data for each metal in binary and single systems.
5. For the single system, the affinity constant sequence is $K_{Cd} > K_{Co}$.
6. It can be noticed that there is no significant change in the percentage removal when the concentration increases from 10-50 mg/L, this behavior is because dead algal biomass might has sufficient exchangeable sites for this range of concentration, while when the concentrations are increased to reach 100 and 150 mg/L the exchangeable sites in biomass will not be sufficient to accumulate these concentrations and, therefore, the percentage removal reduction is clear.
7. Compared of two metal percentage removal efficiencies with their values in the single system, the biosorption capacity of two metals present clear reductions in the binary system. However, this is because of the existence of more than one metal which will improve the competitive struggling race to occupy a particular site, while the weakest metal will be restrained.
8. Due to the competitive effect of two metal mixtures with each other to occupy the available sites of the algal biomass in the binary system, Cd(II) ions offer the strongest component compared with the weakest adsorbed component, Co(II).

6. References

- Alexander, P.M., and Zayas, I., 1989, "Particle size and shape effects on adsorption rate parameters", *Environ. Eng.*, 115(1), 41–55.
- Al-Hares, H.S., 2014, "Competitive Adsorption of Heavy Metals onto Algae and (Fe_3O_4) Nanomaterial", Ph.D. Dissertation, University of Baghdad, College of Engineering.
- Al-Hassany, J.S., 2003, "A study of the ecology and diversity of epiphytic algae on some aquatic plants in Al-Hawizah marshes, southern Iraq", M.Sc. Dissertation, College of Science for Women, University of Baghdad.
- Ali, A.H., 2011, "Performance of Adsorption/Biosorption for Removal of Organic and Inorganic Pollutants", Ph.D. Thesis, University of Baghdad, College of Engineering.
- APHA, 1995, "Standard methods for the examination of water & wastewater", 19th Edition, *American Public Health Association*, Washington, DC.
- APHA, 2005, (American Public Health Association), "Standard Method for the Examination of Water and Wastewater", 20th edition, *American Public Health Association*, Washington, DC.
- Basheer, I. A. and Najjar, Y. M., 1996, "Predicting dynamic response of adsorption column with neural nets", *J. Computing in Civil Engineering*, 10(1), 31-39.

- Brady, J.M., Tobin J.M., and Roux J., 1999, "Continuous fixed bed biosorption of Cu^{2+} ions: application of a simple two parameters mathematical model", *J. Chem. Technol. and Biotechnol.*, 74,71-77.
- Cheueh, I. Z., 2005, "Ion Exchange Modeling of Silicotitanate Column for Chromium Removal from Argentine Waste", *Wisting house Savannah River Company, USA*.
- Crist, R.H., Martin, J.R., Carr, D., Waston, J.R., Clarke, H.J., and Crist, D.R., 1994, "Interaction of metals and protons with algae", *Environ. Sci. Technol.*, 28, 1859-1866.
- Davis, A., Volesky, B., Mucci, A., 2003, "A review of the biochemistry of heavy metals biosorption by brown algae", *Water Research*, 37, 4311-4330.
- Diniz, V., and Volesky, B., 2005, "Biosorption of La, Eu and Yb using *Sargassum* biomass", *Water Research*. 39(1), 239-247.
- Diniz, V., Weber, M.E., Volesky, B., and Naja, G., 2008, "Column biosorption of lanthanum and europium by *sargassum*", *Water Research*. 47, 363-371.
- Dursun, D., Cicek, H., and Dursun, A.Y., 2005, "Adsorption of phenol from aqueous solution by using carbonized beet pulp", *Hazard. Mater.* , 125,175-182.
- Figueria, M.M., Volesky, B., Ciminelli, and V.S.T., Roddlick, F.A., 2000, "Biosorption of metals in brown seaweed biomass", *Water Research*, 34, 196-204.
- Fourest, E. and Roux, J.C., 1994, "Improvement of heavy metal biosorption by mycelial dead biomass (*Rhizopus arrhizus*. *Mucor miehei* and *Penicillium chrysogenum*): pH control and cationic activation", *FEMS Microbiol. Rev.* 14, 325-332.
- Hashim, M.A., Chu, K.H., Phang, S.M., and Ong, G.S., 1997, "Sorption equilibrium of Cadmium on algal biomass", *Sorption Sci. Technol.* ,15(6), 445-453.
- Herrero, R., Cordero, B., Lodeiro, P., Rey-Castro, C., and Vicente, M.E., 2006, "Interactions of Cadmium(II) and protons with dead biomass of marine Algae *Fucus Sp.*", *Marine Chemistry*, 99, 106-116.
- Kratochvil D., 1997, "A study of the Metal Biosorption Process Utilizing *Sargassum Seaweed Biomass*", Ph.D. Thesis, Department of Chemical Engineering, McGill University, Montreal, Canada.
- Lodeiro, P., Herrero, R. and Sastre de Vicente, M.E., 2006, "Batch desorption studies and multiple sorption regeneration cycles in a fixed-bed column for Cd(II) elimination by protonated *Sargassum muticum*", *Journal of Hazardous Materials*, B137,1649-1655.
- Lu, D., Cao, Q., Li, X., Cao, X., Luo F., and Shao, W., 2008, "Kinetics and equilibrium of Cu(II) Adsorption onto Chemically Modified Orange Peel Cellulose Biosorbents", *J. Hydrometallurgy*, available online at: <[http: doi: 10.1016/j. hydromet.2008.05.008](http://doi:10.1016/j.hydromet.2008.05.008)>.
- Meena, A.K., Mishra, G.K., Rai, P.K., Rajagopal. C., and Nagar, P.N., 2005, "Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent", *Hazard. Material*, 122, 161–170.
- Melcakova, I., and Ruzovic, T., 2010, "Biosorption of Zinc from Aqueous Solution Using Algae and Plant Biomass", *Nova Biotechnologica*, 10(1), 33-43.
- Najem, A.M., 2010, "Antagonistic Activity Evaluation of Some Plants in Control of Algae", M.Sc. Dissertation, College of Science, University of Baghdad.
- Ridha, M.J., 2011, "Reactor", Ph.D. Thesis, University of Baghdad, College of Engineering".
- Romera, E., Gonzalez, F., Ballester, A., and Blazquez, M.J., 2006, "Biosorption with algae: statistical review", *Crit. Rev. Biotechnol.*, 26, 223-235.
- Romera, E., Gonzalez, F., Ballester, A., and Blazquez, M.J., 2007, "Comparative study of heavy metals using different types of algae", *Bioresource Tech.*, 98, 3344-3353.

- Saleem, M., Pirzada, T., and Qadeer, R., 2007, "Sorption of acid violet 17 and direct red 80 dyes on cotton fiber from aqueous solutions". *Colloids Surf. A: Physicochem. Eng. Asp.* 292, 246–250.
- Sari, A., and Tuzen, M., 2008, "Biosorption of cadmium (II) from aqueous solution by red algae (*Ceramium virgatum*): Equilibrium, kinetic and thermodynamic studies", *Hazardous Materials*, 157, 448–454.
- Schiewer, S., and Volesky, B., 1996, "Modeling Multi-Metal Ion Exchange in Biosorption", *Environ. Sci. Technol.*, 30, 2921-2927.
- Sulaymon, A.H., Ebrahim, S.E., Abdullah, S.M., and Al-Musawi, T.J., 2010, "Removal of Lead, Cadmium, and Mercury Ions Using Biosorption", *Desalination and Water Treatment*, 24, 344-352.
- Taghi, g., Khosravi, M., and Rakhshae, R., 2005, "Biosorption of Pb, Cd, Cu and Zn from the wastewater by treated *Azolla filiculoides* with $H_2O_2/MgCl_2$ ", *International Journal of Environmental Science & Technology*, 1(4), 265-271.
- Volesky, B., 2003, "Sorption and biosorption", *BV-Sorbex, Inc.*, Montreal, Canada, 103,316.
- Yang, J., 2000, " *Biosorption of uranium and cadmium on sargassum Seaweed Biomass*", Ph.D. Thesis, Department of Chemical Engineering, McGill University, Montreal, Canada.

Table (1): Particles properties of green-blue algal biomass used in batch experiments

Particle diameter 0.2-0.3 mm	
Color	Dark-Green
Appearance	Granular or Powder
Solubility	Insoluble in Water
Durability	Excellent
Bulk density (kg/m³)	187.1
Real density (kg/m³)	1387
Surface area (m²/g)	3.272

Table (2): Values of the R² and affinity constant for each metal in binary and single systems

System	Metal	Affinity constant (K)	R²
Single	Cd	2.33	0.988
	Co	1.87	0.977
Binary	Cd	5.34	0.952
	Co	2.46	0.981

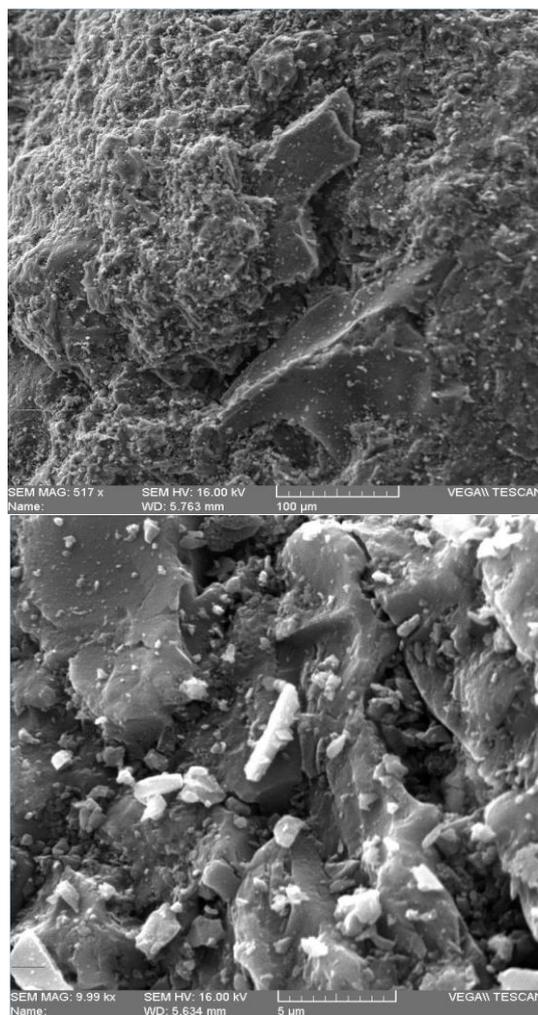


Figure (1): Scanning electron micrographs for dead algal biomass.

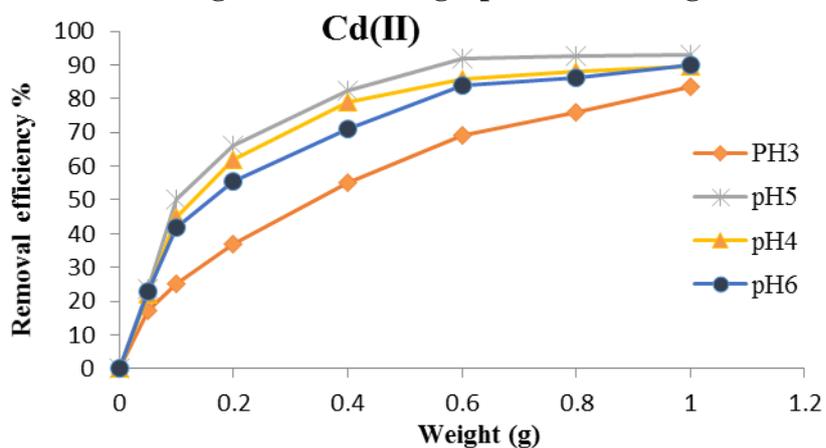


Figure (2): Biosorption of Cd(II) ions at different pH solution.

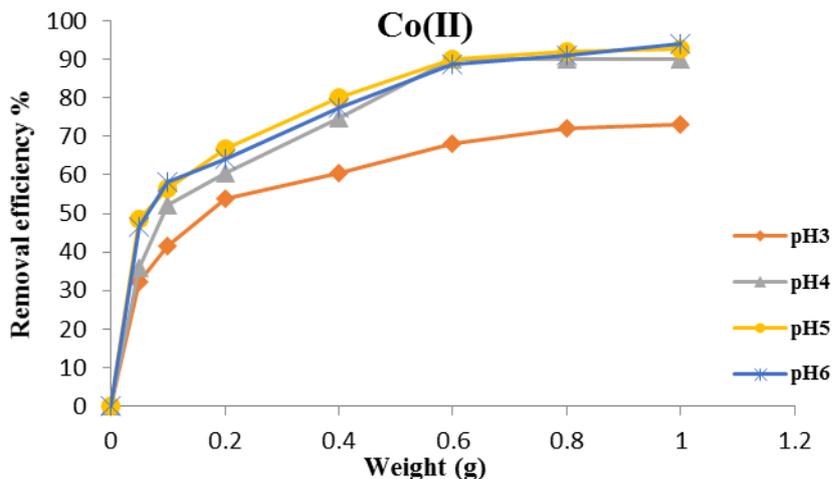


Figure (3): Biosorption of Co(II) ions at different pH solution.

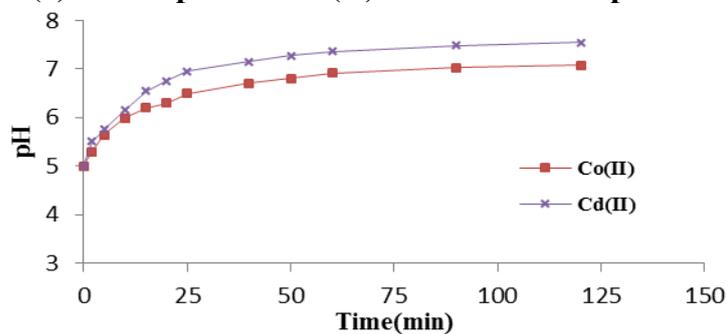


Figure (4): pH evolution of Cd(II) and Co(II) as a function of time, ions biosorption.

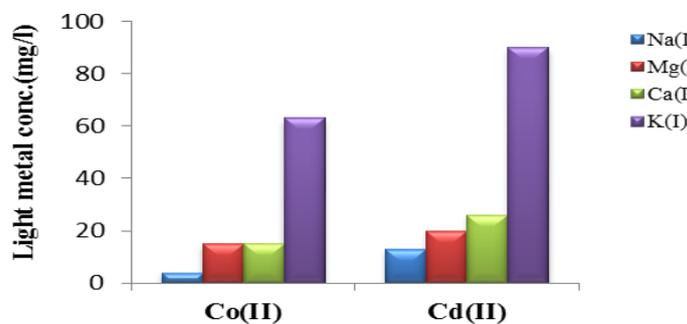


Figure (5): Light metals amount released due to biosorption of heavy metal.

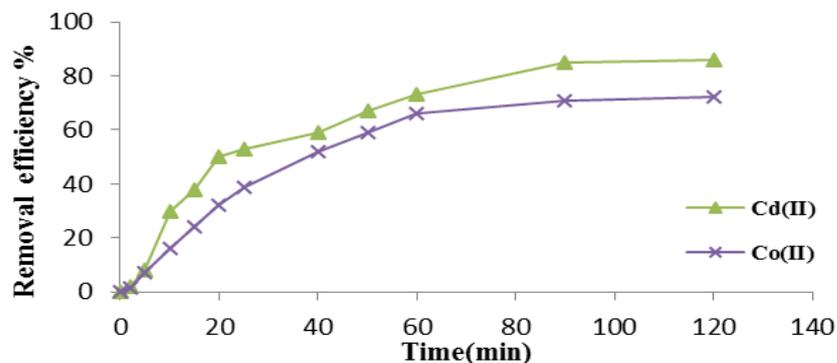


Figure (6): Variation of biosorption efficiency with the contact time.

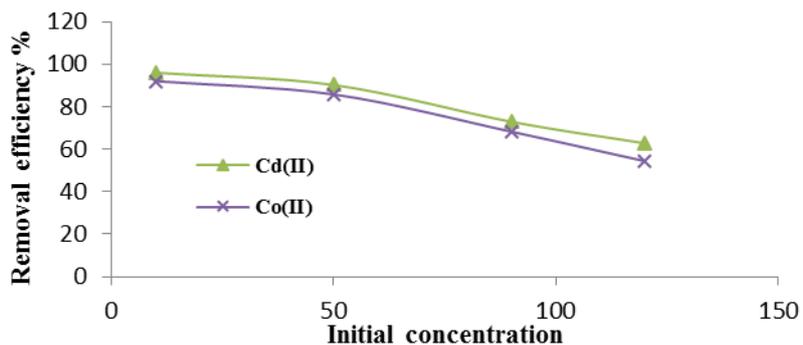


Figure (7): Percentage removal of biosorption with variation of the initial concentration.

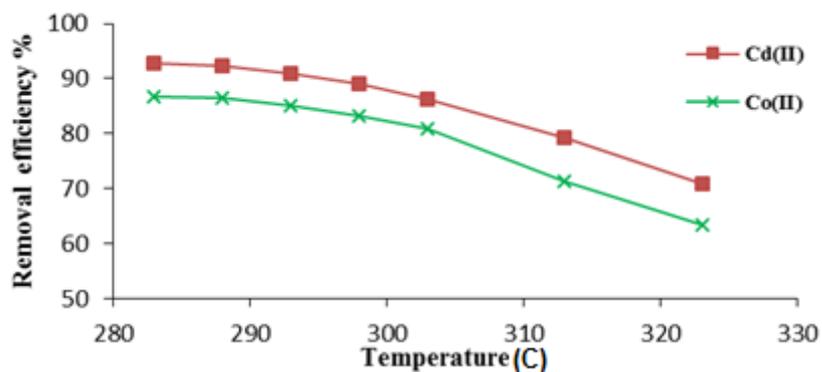


Figure (8): Variation of removal ratio with solution temperature.

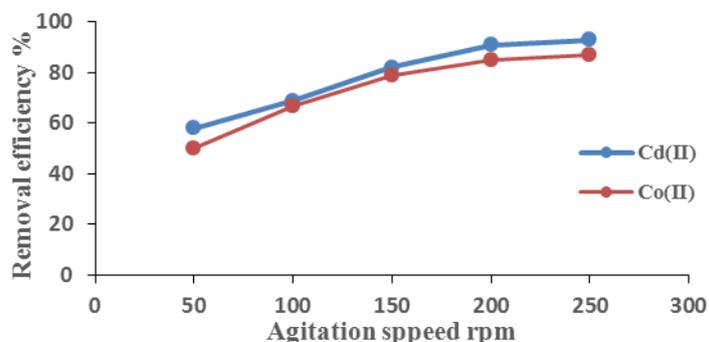


Figure (9) Effect of agitation speed on removal efficiency of Cd(II) and Co(II)

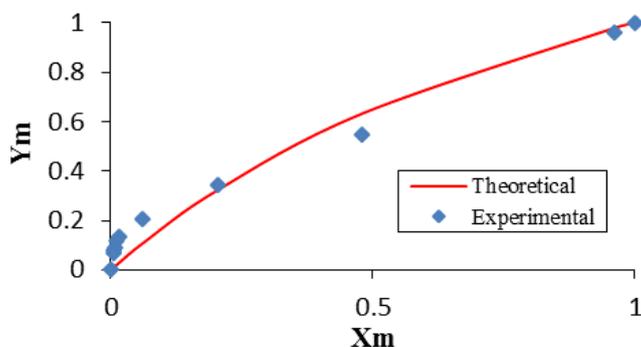


Figure (10): Single Ion exchange equilibrium isotherm for Co(II)

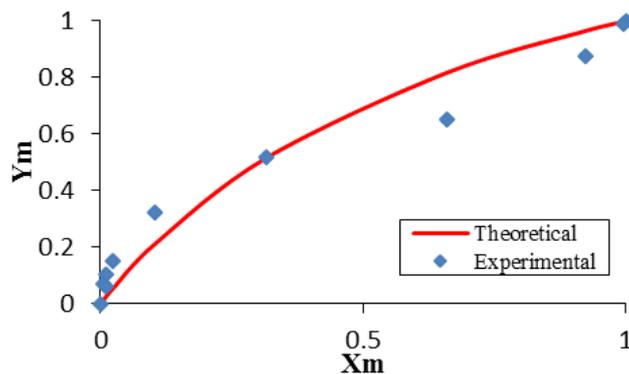


Figure (11): Single Ion exchange equilibrium isotherm for Cd(II)

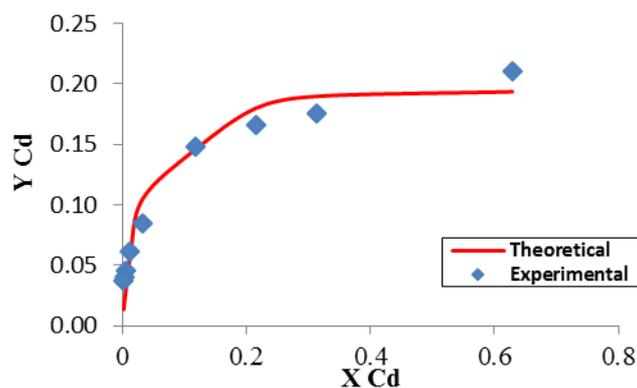


Figure (12): Binary system Ion exchange equilibrium isotherm for Cd(II) with Co(II)

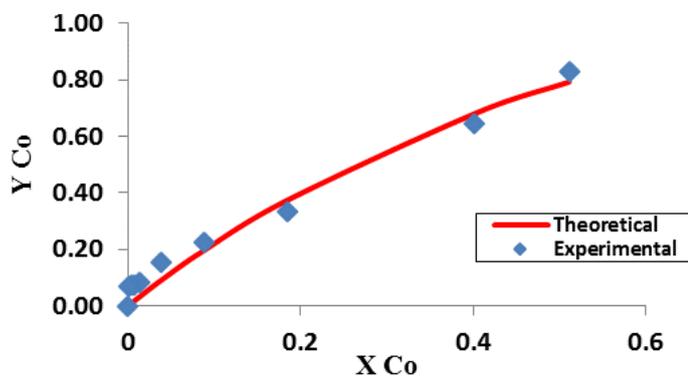


Figure (13): Binary system Ion exchange equilibrium isotherm for Co(II) with Cd(II)