Evaluation of biomass type blue *Cyanophyta* algae for the sorption of Cr(III), Zn(II) and Ni(II) from aqueous solution using batch operation system: Equilibrium, kinetic and thermodynamic studies

Abbas S.H.[1],* and Ali W.H.[2]

[1]Department of Materials Engineering / Engineering Technical College / Middle Technical University/ Baghdad**,** Iraq

[2]Department of Mechatronic Engineering / Engineering Technical College / Middle Technical University/ Baghdad**,** Iraq

*to whom all correspondence should be addressed: e-mail: salman_abbas2001@yahoo.com

Abstract

The biosorption of Cr (III), Zn (II) and Ni (II) ions from aqueous solution by dead blue algal biomass (Cyanophyta) was investigated in single metal system and batch conditions. Experimental parameters included contact time (0-140 min), pH (2-8), sorbent dose (0.1-2.0 g), initial concentrations (10-120 mg/L), agitation speeds (50-300 rpm) and temperatures (298-232K) were investigated. The best values of pH were found 4 for Cr^{+3}, Zn^{+2} and 5 for Ni^{+2}, respectively. The biosorption process was relatively fast and equilibrium established after 90 min. Equilibrium isotherm experiments data were analyzed by Langmuir and Freundlich isotherm models and Langmuir isotherms gives the best fit to the experimental data. Biosorption kinetic models were used for the single metal system using the dead blue algal biomass, good matching was found between pseudo second order kinetic model and experimental data for Cr (III), Zn (II), and Ni (II) ions systems. Thermodynamic parameters included ΔG^o; ΔH^o and ΔS^o during the process were calculated, the results show that the biosorption process applied to remove Cr (III), Zn (II) and Ni (II) ions using blue algal biomass (Cyanophyta) is feasible, spontaneous and exothermic at 10 – 30 °C. The results indicated that blue algal biomass (Cyanophyta) could be used as a good sorbent for treatment of industrial effluents containing Cr (III), Zn (II) and Ni (II) ions in single metal system.

Keywords: Biosorption, Cr (III), Zn (II), Ni (II), Kinetic, Thermodynamic, Cyanophyta algae

1. Introduction

Environmental pollution of industrial aqueous streams caused by presence of heavy metals is the main problem today due to its high toxicity, mobility in the environment and harmful for living organisms (Li *et al.*, 2015), thus, the removal of heavy metals from wastewaters before its release to environment is important in terms of protection of public health and environment (Patel *et al.*,2016). Heavy metal ions are released by several industrial processes such as mining, pigments, plastics, fertilizers, textiles, dyes, surface finishing industry, electroplating, photography, paints, fuel production and leather industries (Naspu *et al.*,2014; Das *et al.*, 2012; Tantawy and El-Haddad, 2015).

Various traditional technologies such as ion exchange, membrane filtration, chemical precipitation, solvent extraction, reverse osmosis, evaporation, oxidation and adsorption have widely used to reduce the levels of metal ions from streams of wastewater (Monika *et al.*, 2014; Wang and Chen, 2009; Abdel-Aty *et al.*, 2013). Although these methods have been used for water treatment, but these processes have limitations and are not economical enough because of these methods are often expensive partially metal removal, needs high reagent, required high energy, low efficiency and production of the significant amount of toxic chemical sludge, which needs additional treatment (Sweetly *et al.*, 2014). Therefore, new economic, effective and safe technologies are recommended.

Biosorption method is a favorable alternative technology which is highly suggested for removing heavy metal ions at low concentrations and has an effective tool for the treatment of wastewater (Sari and Tuzen, 2009). Biosorption is the most promising technique containing several advantages such as easy to prepare, abundant in the nature, low operating cost, high efficiency in dilute effluents, short operating time, easy to handle, minimizing of chemical and biological sludge, no additional nutrient required, regeneration of biosorbent possibility of metal recovery, being eco-friendly and no production of secondary toxic compounds (Ning-Chuan *et al.*, 2009; Sudesh and Goyal, 2016) besides it can remove different kinds of contaminants (Hassan *et al.*, 2011).

Various types of biomass such as biological materials (fungi, algae, yeast, bacteria) and waste of agricultural products (corn stalk, wheat bran, oil palm fiber, banana bath, seeds, dried leaves, duck weed, sawdust, sugarcane bagasse, apple wastes), were investigated as biosorbent for removal of heavy metal ions (Yahaya and Don, 2014). Algal biomass was used as a promising type of biosorbent studied (El-Sayed *et al.*, 2011).

Algae have found to be more efficient, very fast growth, inexpensive biomass, large surface area and readily available worldwide. The cell wall of algae is responsible for the biosorption process, it contains many functional groups like hydroxyl, carboxyl, carbonyl, sulphate and amino which can bind with metal ions as binding sites (John *et al.*, 2011).

Green and blue green algae in Iraq are available in huge quantities, approximately in all surface water resources and marshes Bhatti *et al.*, 2011). The growth of algae with other kinds of river plants causes many difficulties for networks and irrigation canals. Appropriate action should be taken in such circumstances. Algae changes the taste and smell of water, clog filters, may kill fish during its death and degradation (consume dissolved oxygen) reduce the beauty of the water surfaces, blocking aeration, prevent sunlight to reach the water surfaces, and hinder the process of photosynthesis, etc. Algae cause problems in irrigation canals and water pumping as well as environmental problems caused by after death and decay, which cause pollution of water resources. The use of algae is to achieve an economical goal by using cheap materials for removing hazardous pollutants (Arshadi *et al.*, 2014).

In the present work, a dead blue *Cyanophyta* algal biomass were used as biosorbent material to study the effect of kinetics and thermodynamic parameters on the biosorption of heavy metal ions (Cr (III), Zn (II) and Ni (II)) from aqueous solutions in batch system process and evaluate the efficiencies at different operating conditions such as pH of the solution, initial concentration, biosorbent dosage, agitation speed and contact time.

2.   Kinetics Models and Thermodynamic Parameters

2.1 Kinetics Models

2.1.1 Intra-particle Diffusion Model

The intra-particle diffusion model proposed by Weber and Morris is given by following equation (Singh and Gupta, 2016):

$$q_t = k_{id} t^{0.5} + C \tag{1}$$

Where q_t is the amount of metal ion in (mg/g) adsorbed at time t in (min), K_{id} (mg /g min$^{0.5}$) is intra-particle diffusion rate constant. C is the intercept in (mg/g). Generally, if C is larger; concentration of surface sorption in the rate-controlling step is greater.

2.1.2 Fractional Power Kinetic Model

$$q_t = Kt^x \tag{2}$$

Where q_t is uptake capacity of metal ions in (mg/g) sorbed at time t in (min), *x* is the rate constant of power function. K is the constant of power function model. The model described the time-dependent metal on sorbent as the value of constant *x* was less than 1 (Sirvastava *et al.*, 2016)

The linear form of equation (2) becomes:

$$\ln(q_t) = \ln(K) + x \ln(t) \tag{3}$$

2.1.3 Pseudo-First-Order Kinetic Model

The general expression for pseudo-first order equation model is (Ho, 2004):

$$\frac{\partial q}{\partial t} = k_1 \left(q_{eq} - q_t\right) \tag{4}$$

Where q_{eq} (mg/g) and q_t are the sorption capacity of metal ions on biosorbent at equilibrium and at time *t*, respectively and k_1 is the Lagergren rate constant of pseudo first order biosorption (min^{-1}).

By taking the boundary conditions:

t=0 to t=t and q_t=0 to q_t=q_t, the linear form of the pseudo-first-order becomes

$$\log (q_{eq} - q_t) = \log q_{eq} - \frac{k_1}{2.303} t \tag{5}$$

The plots of log (q_e-q_t) against t (min) for different concentrations of heavy metals give straight lines.

From the plot, k_1 and q_e are determined from the slope and intercept respectively. The values of q are experimentally determined ($q_{e,exp}$) and calculated ($q_{e,calc}$).

2.1.4 Pseudo-Second-Order Kinetic Model

The main assumption of pseudo-second- order kinetic model is based on that the rate-limiting step involves chemisorption. With the assumption that the measured concentrations are equal to the cell –surface concentrations (Ahmad *et al.*, 2016)

The pseudo-second order chemisorption kinetic rate of metal ions in solution is expressed as follows:

$$\frac{dq}{dt} = k_2 \left(q_{eq} - q_t\right)^2 \tag{6}$$

Where k_2 (g/mg min) is the constant of pseudo- second order rate, q_{eq} (mg/g) is the biosorption capacity at equilibrium, q_t (mg/g) is the biosorption capacity on the surface of the sorbent at any time, t

To obtain a linearized form of the pseudo-second-order model:

For the boundary conditions *t = 0 to t = t and q_t = 0 to q_t = q_t,* gives (Ho, 2006):

The integration form of Eq. (6) is:

$$\frac{1}{\left(q_{eq} - q_t\right)} = \frac{1}{q_{eq}} + k_2 t \tag{7}$$

Rearranging equation (7):

$$q_t = \frac{t}{\left(\frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}\right)} \tag{8}$$

Linearization of equation (8) gives:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}\right) \tag{9}$$

When plotting t/q_t against t, we get the values of constants (slope & intercept) experimentally. The initial sorption rate can be written as:

$$h = k_2 q_{eq}^2 \tag{10}$$

2.1.5 Elovich Kinetic Model

Elovich equation can be used to express the kinetics of chemisorption of heavy metal ions in the solution as follows (Sirvastava *et al.*, 2016; Ho, 2006):

$$\frac{dq}{dt} = a\, exp(-b\, q_t) \tag{11}$$

Where the parameter *a* is regarded as the initial rate while parameter b is related to the extent of surface coverage and activation energy for chemisorption.

By taking the boundary conditions:

At t = 0, q = 0, the integrated form of equation (11) is:

$$q_t = \left(\frac{1}{b}\right) \ln(t+t_0) - \left(\frac{1}{b}\right) \ln t_0 \tag{12}$$

Where $t_0 = 1/ab$. If $t \gg t_0$, equation (12) can be rearranged as:

$$q_t = \left(\frac{1}{b}\right) \ln(ab) + \left(\frac{1}{b}\right) \ln t \tag{13}$$

2.2 Thermodynamic Parameters

The effect of temperature on biosorption process must be needed to study three main thermodynamic parameters such as free energy change ΔG^0, enthalpy change ΔH^0, and entropy change ΔS^0. The biosorbent contains more than one type of sites for metal binding so; the effect of temperature on each site is different and contributes to overall metal uptake. The thermodynamic parameters can be estimated by the following equations (Colak *et al.*, 2009)

$$\Delta G^\circ = -RT\ln(k_c) \tag{14}$$

Where

$$K_c = \frac{C_{ad}}{C_e} \tag{15}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{16}$$

Where K_c is the equilibrium constant, C_{ad}/C_o is the "biosorption affinity". C_{ad} is the concentration of metal ion in a solid biosorbent in (mg/L), C_o is the equilibrium concentration of metal ions in liquid phase in (mg/L). Free energy changes ΔG° can be obtained from equation (14), while the changes of enthalpy ΔH° and entropy ΔS° for the biosorption process can be obtained by plotting the $\ln K_c$ against $1/T$ (Zubeyde *et al.*, 2009).

3. Experimental Work and Materials

3.1 Preparation of Materials

3.1.1 Adsorbate

Stock metal solutions (1000 mg/L) of chrome, zinc and nickel ions as a single metal ion system were prepared by dissolving an appropriate quantity of $Cr(NO_3)_3$, $Zn(NO_3)_2$ and $Ni\ NO_3)_2$ in a liter of deionized water (APHA, 2005). The desired concentrations were prepared by diluting the stock solution with distilled water. Heavy metals were treated in separate solutions. Metal ion concentrations were measured before and after biosorption using Atomic Absorption Spectrophotometer (Buck scientific model Accusys 211, USA).

3.1.2 Biosorbent

3.1.2.1 Algal Biomass Collections

The biosorbent of heavy metals used in this study is a Blue-green (Cyanophyta) algae. In Iraq, several studies referred that algae can be blooming in the Tigris, Euphrates Rivers, and marshes water or else where they accumulate along the aquatic environment (Yahaya and Don, 2014; Najem, 2010). Large quantities of algae have been observed along the Channels from Tigris River near Salman Pac (South East Baghdad). 10 kg of fresh algae were collected from selected location in April 2016.

The algae were analyzed by using microscope after cleaning it from 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 are two dominated: Cyanophyta (Oscillatoria princess 90%, Oscillatoria sub braves 4%, Oscillatoria Formosa 4%), and Chlorophyta (Spirogyra aequinoctialis1%, and others1%). Cyanophyta (blue algae) species are dominated and have the highest percentage weight.

3.1.2.2 Preparation of Dead Blue Algal Biomass

The blue-green algae were cleaned by hand and washed several times with tapered and distilled water in order to remove the impurities, dirt, and other unwanted materials, then water squeezed out. The washed algae were dried for 7 days in an aerated room and then dried in the oven at 65 °C for 24 h. The dried algal biomass was ground and sieved. The average size of 150-300 μm particle diameters was used for biosorption experiments.

**Table 1.** Properties of the dead algal biomass

| Particle size (mm)	0.15-0.3
Color	Dark-Green
Appearance	Granular or Powder
Solubility	Insoluble in Water
Durability	Excellent
Bulk density (kg/m³)	199.3
Real density (kg/m³)	1495
Surface area (m²/g)	3.692
Bed porosity	0.866

The geometric mean diameter is given by $d_{gm} = (d_1 d_2)^{1/2}$ where d_1 & d_2 are the diameters of lower sieve (retained particles) and upper sieve (Passed particles) respectively (Alexander and Zayas, 1989). The mean

particle diameter of 0.212 mm of dried sieved blue algal biomass.

Physical properties of the particles like surface area, density, and void age were measured and listed in Table (1)
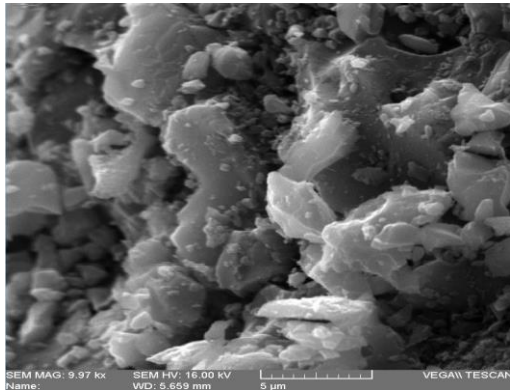
using the multi-point-N_2-BET method and the Quanta chrome NovaWin2 system for measuring surface area and actual density respectively. The bulk density was determined using Hg-picnometry analysis. Figure (1) shows scanning electron micrographs for dead blue algal biomass.
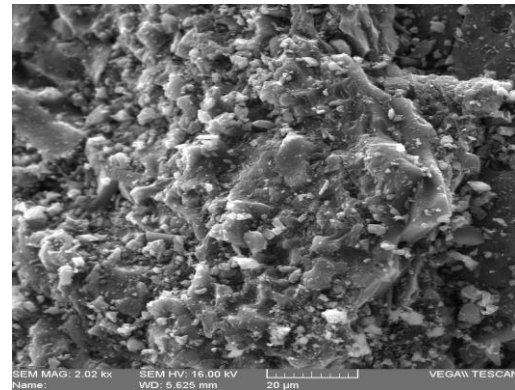
Figure1. Scanning electron micrographs for dead algal biomass

3.2 Biosorption Experiments

Biosorption experiments were carried out using a batch system for different parameters such as, pH, initial concentration, biomass dose, contact time, and temperature. Experiments were performed under thermodynamic and kinetic parameters.

3.2.1 Batch Biosorption Studies

Batch biosorbent experiments were carried out in 250 ml conical flask containing the desired amount of biosorbent of algal biomass (0.1- 2.0 g) mixed with 100 ml of each solution containing metal ions at initial concentrations (10-120 mg/). The effect of solution pH was studied in the range of (2.0-8.0). pH was adjusted by using a dilute solution of 0.1 N HCL or 0.1 N NaOH. The flasks were placed in a shaker (Edmund Buhler, 7400 Tubingen Shaker-SM 25, Germany) at 200 rpm agitation speed for 180 min at room temperature (250 °C) to attain the equilibrium. For equilibrium studies, 25 mL polyethylene centrifuge tubes were used.

After centrifugation at 4000 rpm for 10 min, the liquid phase was separated by taking samples of 10 ml from each tube and filtrated using a filter paper (type: WATMAN No.42). In order to fix the concentration of the metal ions during storage before analysis, few drops of 0.1M HNO_3 were added to the samples to decrease the pH value below 2 [26]. The residual concentration of zinc, chrome, nickel and light metal ions (magnesium) in the samples was determined using AAS and other light metals ions in the samples were determined using flame photometer BWB-1(USA). All biosorption experiments were carried out in duplicate at room temperature and the mean values of results were used for further calculations.

The adsorbed amount and removal efficiency were calculated as follows:

$$q_e = \frac{V}{W}(C_o-C_e) \tag{17}$$

$$\%Removal = \frac{C_o-C_e}{C_o} \times 100 \tag{18}$$

Where q_e is the biosorption amount at equilibrium (mg/g), Co and C_e is the initial and final metal concentration (mg/L) in the solution respectively, v is the volume of solution (L) and w is the sorbent dosage (g).

3.2.2 Thermodynamic Parameter of Biosorption

The effect of temperature on removal of Cr (III), Ni (II) and Zn (II) using dead blue algal biomass was studied by mixing 0.5 g of dead algal biomass with 100 ml (50 mg/l) from metal ion solutions; the mixture was shaken at 200 rpm for 90 min maintained at different temperatures from 283 to 323K. After mixing period, (10 ml) of filtrate samples was analyzed using Atomic Absorption Spectrophotometer

3.2.3 Kinetic Studies

A 2000 ml Pyrex beaker with a magnetic stirrer was used. The beaker was filled with 1000 mL of 50 mg/L of known pollutant concentration, and the agitation started before adding the adsorbent. At zero time optimum weight of algal biomass of particle size 0.150-0.300 mm for each metal was added to the solutions and stirred with the different agitation speeds at room temperature. Samples were taken for different time intervals (1, 2, 3, 5, 10, 15, 20, 30, 40, 50, 60, 80, 100, 120, and 140 min.) during the experiment. These samples were filtered and analyzed.

The optimum agitation speed was obtained by repeating the experiments for each solute with variable speeds (300, 400, 500, and 600 rpm). The uptake capacity of each solute was measured by monitoring the solute concentration with time using AAS device, and then the concentration time decay curves were obtained by plotting the percentage remaining versus time. The optimum weight of algal biomass (w) to reach an equilibrium concentration of $C_e/C_o=0.1$ (90% removal efficiency) was obtained from the curves of removal efficiency versus weight of algal biomass (w).

4.   Results and discussion

4.1 Effect of pH

pH of the solution is considered one of the major parameter affecting the biosorption process due to its effects: the solubility of the metal ions, concentration of the counter ions on the functional groups of the biosorbent and the degree of ionization of the biosorbate. The effect of solution pH on removal efficiency is achieved by a series of experimental biosorption at different initial pH values.

The pH dependency of biosorption performance is clearly seen in Figure 2. According to the results that gathered, it has been found that the pH of the solution played a significant role in the biosorption process. Also, this fact is well documented in bibliography (Li *et al.*, 2014; Esposito *et al*, 2002).

Adsorption was carried out over the range of pH 2 to 8. Figure (2) shows the influence of 50 mg/L of different initial pH solutions at 25 °C on biosorption of Cr (III), Zn (II), and Ni (II) ions respectively. From this figure, it can be seen that the best pH value for removal were 4 for Zn^{+2}, Cr^{+3} and 5 for Ni^{+2} respectively. It is evident that, as the pH increases from 2 to 5, adsorption capacity increases and the maximum removal of 94.5%, 88.2% and 82.1% for Cr (III), Zn (II) and Ni (II) respectively are observed at pH 4, 5. It may safely be stated that the removal of metal ions was mostly due to adsorption and not precipitation as a result of the acidity of medium which affect the uptake capacity of the metal ions on the sorbent process where the hydrogen ions was found and could compete with metallic ions for active sites on the biosorbent surface.
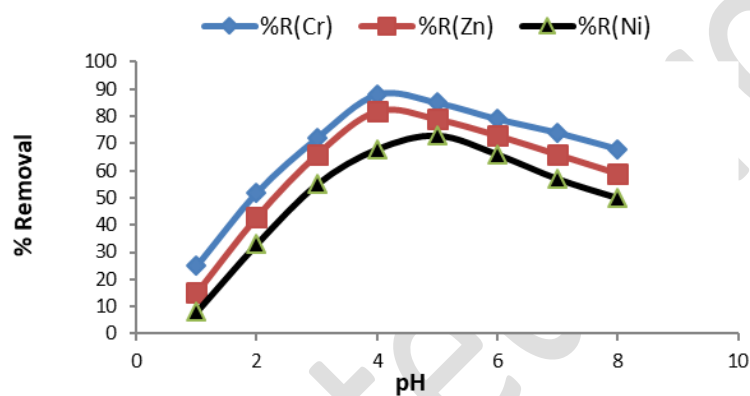

Figure 2. Effect of pH on biosorption of Zn(II), Cr(III) and Ni(II) by algae biomass

At pH higher than 5, the adsorption capacity decreases due to the formation of hydroxyl complexes of metal ions which leading to precipitation of ions.

When pH below 3; Active sites of the adsorbent were either protonated (Lu *et al.*, 2008) or dissociated (Hamdaoui, 2006), so unfavorable curves resulted for all three metals at pH value of 2. So heavy metal cations are completely released under extremely acidic conditions.

Above figure showed that the best value of pH is equal 4 for Cr(III) and Zn(II) while it is equal 5 for N(II) but there is very little difference in results with pH 4 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 was noticed that the final or equilibrium pH solution was higher than the initial value as shown in Figure (3).
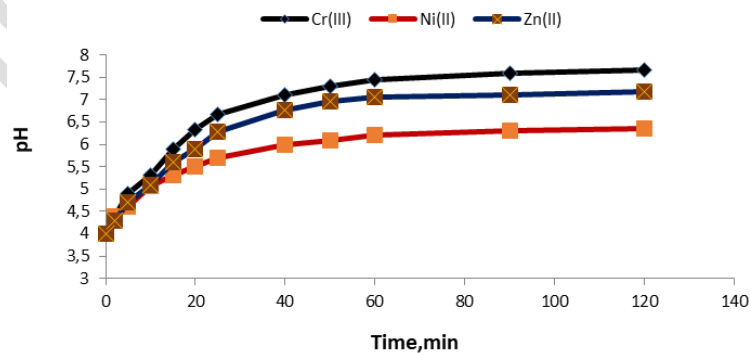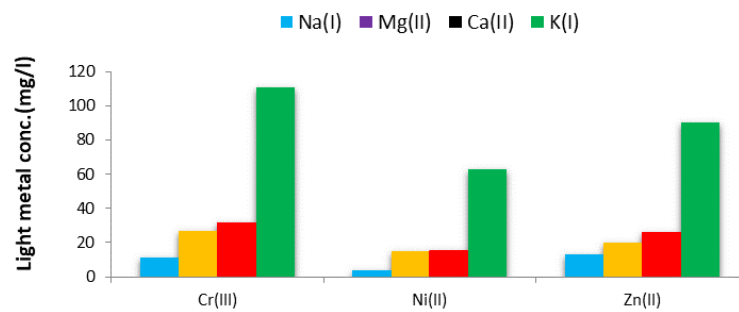

Figure 3. pH evolution as a function of time of Cr (III), Zn (II), and Ni (II) ions biosorption

**Figure 4.** Quantity of light metal ions released due to the uptake of heavy metal ions

This can be attributed to the mechanisms of ion exchange happened between light metals released and heavy metals, so, balance case will be happened between the release of light metals such as K (I), Na (I), Ca (II) and Mg (II) which are originally presented from fresh water and the uptake of heavy metals because untreated algal biomass is generally contained alkali and alkaline earth metals (Li *et al*, 2014; Latinwo *et al.*, 2015). So that, when blue algal biomass reacts with the heavy metals bearing solution, the light metals released cause an increase in the pH due to the formation of light metal alkalis.

Figure (4) shows the quantity of light metal ions released due to heavy metal biosorption using 50 mg/L of Zn (II), Cr (III) and Ni (II) solutions onto 1 g of algal biomass

4.2 Effect of Sorbent Dosage

Metal ion solutions at a concentration (50 mg/l) were added to a various amount of the algal biomass dosage in the range of 0.1 – 2.0 g/100 mL, the mixture was put in 250 ml conical flasks and agitated for 2 hr on a shaker (200 rpm) at 25±1°C. The content of the glass bottles was filtered and analyzed. Figure (5) shows the effect of variation in biomass dosage on the uptake capacity and metal removal efficiency.

The adsorption of Cr (III), Zn (II) and Ni (II) ions was observed to increase as the percentage removal is increased sharply from 50.22 to 90.75% for Cr(III), 30.75 to 77.75% for Zn(II) and 25.22 to 62.15% for Ni (II) respectively with an increase in sorbent dose from 0.1 to 0.6 g. The large surface area and rapid increase in a number of available vacant sites for the sorption of Cr^{+3}, Zn^{+2} and Ni^{+2} will play an important role [Al-Qodah,2006]. So, a higher quantity of metal ions will attach the surface of the biomass. Therefore, the maximum ions of heavy metals will be adsorbed when using 0.6 g of the adsorbent. When it used a further increase in the quantity of the adsorbent up to 2 g, no more effect to the adsorption rate, then, the rate of adsorption remains approximately constant. From Figure (5): the adsorption capacity of Cr (III), Zn (II) and Ni (II) ions decreased from 25.11 to 7.56mg/g; 15.37 to 6.47 mg/g and 12.61 to 5.18 mg/g respectively, with an increase in sorbent dose from to o.1 to o.6 gm. When the adsorbent load was increased from 0.6 to 2.0 g, the quantity of metal ions adsorbed onto the unit weight of the adsorbent cuts down as can be seen from the declining curve of uptake capacity (*q*) versus dose of sorbent (*w*) as shown in the same Figure. This may be attributed to the aggregation of adsorption sites, which leads to a decrease in total available adsorbent surface area and an increase in diffusion path length.
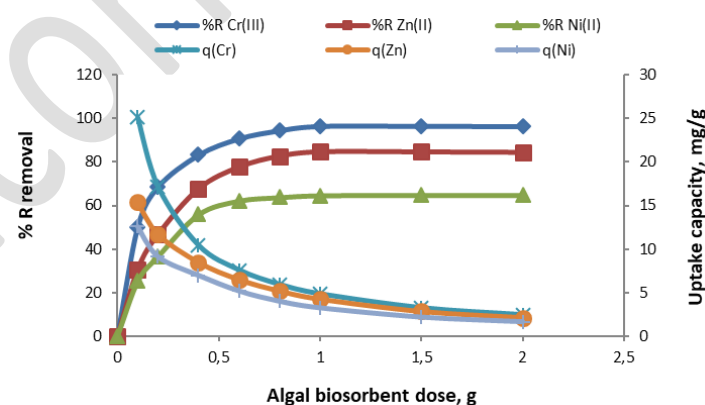
Figure 5. Effect of mass of algae on uptake capacity & percentage removal of Cr(III), Zn(II) and Ni(II) ions at optimum pH =4, I.C.=50 mg/L, Temp= 25 °C

4.3 Effect of Contact Time

The effect of contact time on removal efficiency was studied by using 0.6 g of blue algal biomass at pH 4. Different time intervals like 5, 10, 20, 30, 40, …, 140 min were used. Figure (6) shows the results of removal

efficiency with the contact time of three metal solutions. At the beginning, the rates of adsorption of all the metal ions are higher and the percentage of metal ions removal increases with an increase in contact time (Dorris *et al.*, 2000). The uptake of all used metal ions is rapid for the first

60 min because, this phenomenon is related to: In the initial stages of contact, a large number of vacant sites are available, and hence the uptake is faster. After 90 min, a number of metal ions adsorbed are almost constant. Then, the slowing down of metal uptake later is due to difficulty in occupying the remaining vacant sites. Repulsive forces between the adsorbed metal ions and aqueous metal ions also contribute in slowing down the uptake of metal at equilibrium. As a result, 90 min contact time is sufficient to reach equilibrium conditions for all heavy metals.
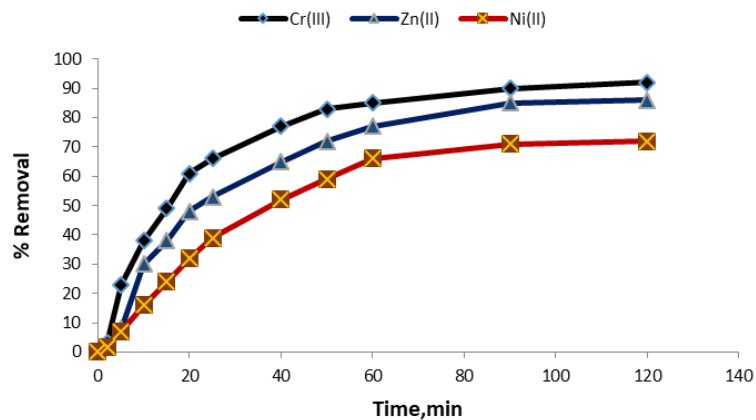

Figure 6. Variation of biosorption efficiency with the contact time

4.4 Effect of Initial Heavy Metal Concentration

Different concentrations of 10 to 120 mg/L using fixed algal biomass dose (0.6 g) at room temperature with pH equal 4 for each heavy metal ions and agitation speed of the shaker was 200 rpm at 1.5 h were used to study the effect of initial concentrations on the biosorption capacity and removal efficiency. Figure (7) shows that the initial concentration had an important effect on uptake capacity, but percentage removal not changed greatly when the concentrations increased from 10 mg/L to 60 mg/L. this is due to contain enough exchangeable sites for this concentration range and then a large driving force was found between the biosorbent and biosorbate (Aksu and Akpiner,2000), where an increase in initial concentrations will decrease all the other mass transfer resistances, but when the concentrations increase from 60 mg/L to 90 and 120 mg/L, the exchangeable sites in 0.6 g will not be enough accumulate these concentrations , it is observed a decrease in percentage removal of Cr(III), Zn(II) and Ni(II) ions with an increase in the initial concentration from 60 to 120 mg/L.
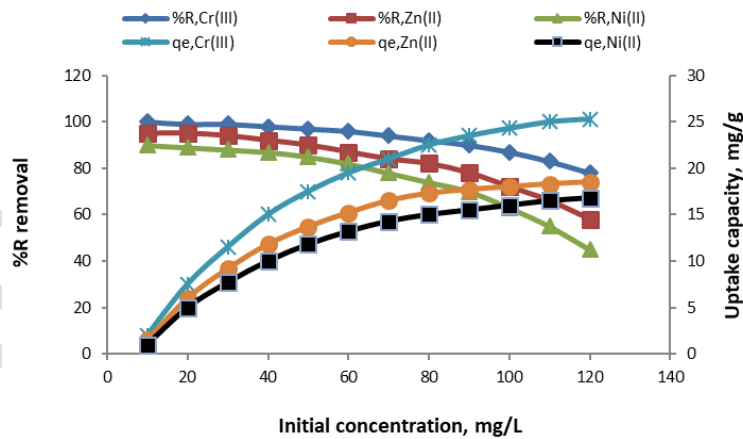

Figure 7. Effect of metal initial concentrations on sorption capacity and percentage removal
using blue algal biomass as biosorbent

4.5 Effect of Shaking Speed

Agitation speed is considered an important factor in biosorption phenomena which promotes mass transfer by affecting the liquid film thickness surrounding the solid particle and distribution of the solute in the bulk solution. Figure (8) shows the effect of batch agitation speed on Zn (II), Ni (II) and Cr (III) adsorption by dead algal biomass using initial concentration (50 mg/L) at different shaking speeds (50–300 rpm) with in contact time of 2 h, dose biomass is 0.6 g and pH of solution was adjusted to desired value. From this figure, it is clear that with increasing agitation speed from 50 to 200 rpm, the percentage removal of metal ions enhanced from41.3 to 92.3% for Cr (III); 37.2 to 89.1% for Zn (II) and 33.08 to 85.95 %.for Ni (II) respectively. The increase in removal percentage can be described by the fact that increasing agitation speed reduces the film thickness surrounding particles, then the

maximizes the mass transfer rate of metal ion to the surface of the biosorbent, therefore increasing external film transfer coefficient, then improves the diffusion of metal ions towards the surface of the biosorbent (Al-qodah, 2006). However, when increasing agitation speed from 200 to 250 rpm, the sorption will be reduced, this is

due to the high turbulence occurs where the bonding between the metal ions and the biosorbent gets broken resulting in the metal ions desorbing from the surface sites. So maximum adsorption occurred at 200 rpm and this speed will be constant and adopted in all experiments.
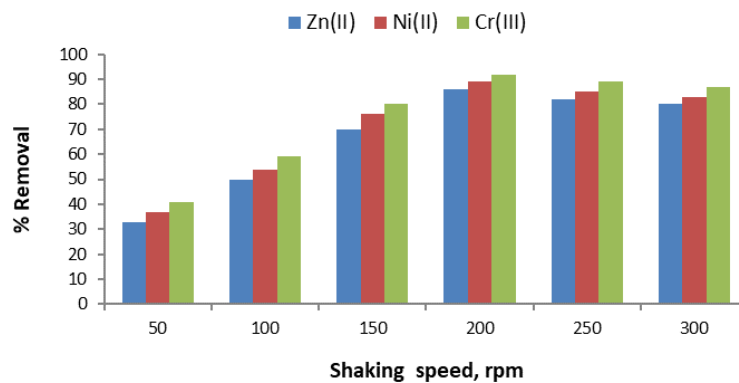

Figure 8. Effect of shaking speed on the removal of Zn (II), Ni (II) and Cr (III) from aqueous solution using dead algal biomass

4.6 Effect of Solution Temperature

Effect of temperature on the equilibrium sorption capacity for Cr (III), Zn (II) and Ni (II) ions has been investigated at temperature ranges between 10-50 °C as shown in Figure (9). Increasing temperature is well known to increase the diffusion rate of adsorbate molecules within the pores as a result of decreasing solution viscosity. This will modify the equilibrium capacity of the adsorbent for a particular adsorbate (Ning-chun *et al.*, 2009). Maximum biosorption of Cr (III), Zn (II) and Ni (II) ions occurred at 10-30 C and then decreased gradually.

At higher temperature (above 30 °C) leads to decrease the percentage removal efficiency, it has a negative effect on the biosorption efficiency for Cr (III), Zn (II) and Ni (II) biosorption, where the thickness of the boundary layer decreases due to increased tendency of metal ion to escape from the biomass surface to the solution phase (Arshadi *et al.*, 2014), so the decrease in equilibrium uptake capacity indicates that lower temperature favor the adsorption of metal ions from aqueous solution. (Sari and Tuzen, 2008).
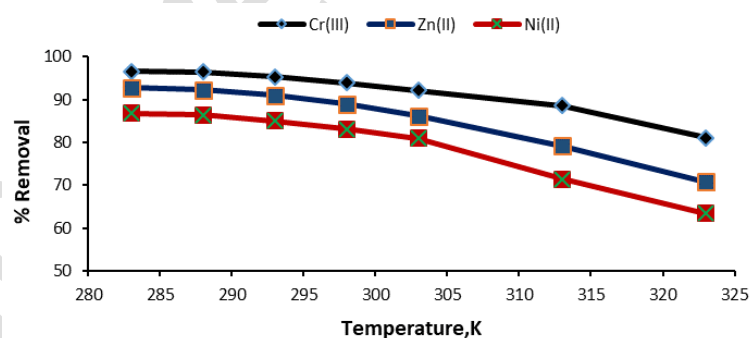
Figure 9. Effect of temperature on the biosorption of Zn (II), Ni (II) and Cr (III) by dead algal biomass

4.7 Adsorption Isotherms

The adsorption isotherm discussed the way of distributes the adsorption molecules between the liquid phase and solid phase at equilibrium stage of adsorption process. Several isotherm models were found to analyze isotherm data that can be used for design purpose. Langmuir and Freundlich isotherm were used in our work. The applicability of these equilibrium models was estimated by the correlation coefficients, R^2 value, so the better fit to the model gives the higher value of R^2.

4.7.1 Langmuir Isotherm

This model has been widely used to describe the experimental data of adsorption process based on the assumptions: 1) the adsorption energy is constant, 2) no interactions happen between adsorption molecules, and 3) maximum adsorption occurs when the surface is covered by a monolayer adsorbate (Malik, 2004), Langmuir isotherm equation can be expressed as:

$$q_e = \frac{q_m \, b \, C_e}{1 + b \, C_e} \tag{19}$$

Where q_m is the maximum amount adsorbed per unit mass of adsorbent (mg/g), b is the constant related to the affinity of binding sites, q_e is the amount adsorbed at equilibrium time (mg/g) and C_e is the equilibrium concentration of the adsorbate (mg/L).

Linearized form of above equation can be used to determine the values of q_m and b as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m}(C_e) + \frac{1}{q_m b} \qquad (20)$$

By plotting of C_e/q_e versus C_e will obtain a straight line with a slope of $1/q_m$ and an intercept of $1/q_m b$.

Separation factor or equilibrium parameter (R_L) is used to express the essential features of Langmuir adsorption isotherm, which is defined as:

$$R_L = \frac{1}{1 + b\, C_o} \qquad (21)$$

Where C_o, is the initial concentration of metal ion (mg/g). The value of R_L indicates the shape of the isotherm, the favorable shape value is $(0 < R_L < 1)$ (Malik, 2004).

4.7.2 Freundilch Isotherm

This isotherm model can be used for non-ideal sorption involving heterogeneous surface energy systems. Freundlich isotherm equation can be expressed as (Malik, 2004):

$$q_e = k_f C_e^{1/n} \qquad (22)$$

Where q_e is the amount of metal ion adsorbed at equilibrium, C_e is the concentration of metal ion solution at equilibrium (mg/L), k_f is the adsorption capacity of the adsorbate (mg/L) $(L/mg)^{1/n}$, $1/n$ represents the adsorption intensity, a favorable value of adsorption condition will happen when n>1. It will be noticed that the adsorption capacity will be increased when the value of k_f increased

Freundlich equation can be linearized as follows;

$$\log q_e = \frac{1}{n}\log C_e + \log k_f \qquad (23)$$

By plotting *log q_e* versus *log C_e* will give a straight line with slope of *1/n* and an intercept of log k_f

Table (2) summarized the Langmuir and Freundlich isotherm model parameters using non-linear regression analysis. The accuracy of models was determined by calculating the correlation coefficients (R^2) as listed in Table (2). According to the values of R^2, the Langmuir isotherm model shows the best fit to the equilibrium of metal ions biosorption data compared with Freundlich isotherm model. The values of R^2 lie in acceptable range ($R^2 > 0.90$). Langmuir isotherm behavior indicates the homogeneous nature of the surface of the biosorbent used and the molecules of each metal ion on the surface of biosorbent has equal biosorption activation energy, also Langmuir isotherm model suggests monolayer coverage of metal ion molecules on the surface of biosorbent. The maximum biosorption capacity of Ni(II), Zn(II) and Cr(III) are 19.43, 4.79 and 23.15 mg/g respectively. The values of R_L showed in the Table $(0 < R_L < 1)$ for all ions, that indicates the biosorbent Algae was favorable for adsorption of Ni(II), Zn(II) and Cr(III) solutions according to the values of R_L.

For Freundlich isotherm, the experimental data can be fitted well only for Cr(III) compared with Ni(II) and Zn(II) due to the R^2 value (0.963 for Cr(III)) which lies in acceptable range ($R^2 > 0.9$), while R^2 for Ni(II) and Zn(II) are 0.881 and 0.8640 respectively which shown a poor agreement with Freundlich isotherm.
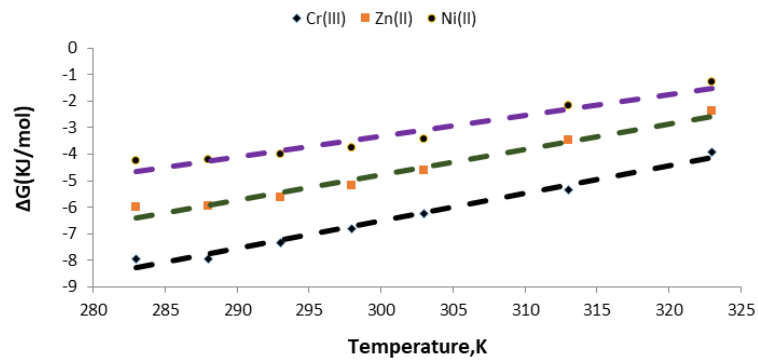
Table 2. Isotherm parameters of the adsorption of heavy metal ions onto Algae

Metal Ions	Langmuir Constants				Freundlich Constants		
	q_m(mg/g)	b(L/mg)	R^2	R_L	K_f(mg/g)	n	R^2
Ni(II)	19.43	0.0931	0.9961	0.176	3.5250	2.5252	0.881
Zn(II)	4.79	0.1745	0.9941	0.102	6.8052	3.7551	0.864
Cr(III)	23.15	0.5529	0.9856	0.034	18.5412	12.516	0.963

4.8 Thermodynamic Parameters

Thermodynamic parameters were obtained by varying temperature conditions over the range 10-50°C (283-323°K) by keeping other variables constant. The values of the thermodynamic parameters such as ΔG°, ΔH° and ΔS°, describing chrome, nickel and zinc ions uptake by dead blue algal biomass, were calculated using the thermodynamic equations. The negative values of ΔH° reveal the biosorption is exothermic.

Figure (10) and Table (3) show the thermodynamic constants obtained of Cr (III), Zn (II) and Ni (II) for biosorption onto dead blue algal biomass.

Table (3) shows the negative values of enthalpy ΔH° was -37.69, -33.54 and -26.82 kJ.mo1^{-1} for Cr (III), Zn (II) and Ni (II) ions respectively, indicate the nature of adsorption is exothermic. This is also supported by the decrease in the values of uptake capacity of biosorbents with the increase in temperature. The values of entropy ΔS° was -0.104, -0.096 and -0.078 J.mol^{-1} K^{-1}, reflect the biosorption affinity of Cr(III), Zn(II) and Ni(II) ions to be sorbed onto algal biomass. The increase in the value of the free energy ΔG° positively with the increase in temperature indicates that the biosorption process is exothermic. The negative values of ΔG° which show that the spontaneity of the biosorption process reduces with increase in temperature and it is thereby favored with decrease in temperature, thus, the process is better carried out at a low temperature (Lokeshwari and Keshava, 2008).

Figure 10. Variation in free energy with temperature for the biosorption of Cr (III), Zn (II), and Ni (II)

Table 3. Thermodynamic parameters for the adsorption of Cr (III), Zn (II) and Ni (II) onto dead algal biomass

Metal	Temperature (K)	ΔG^o (kJ.mol^{-1})	ΔH^o (kJ.mol^{-1})	ΔS^o (J.mol^{-1}K^{-1})	R^2
	283	-7.9325			
	288	-7.9560			
	293	-7.3529			
Cr(III)	298	-6.8171	-37.69	-0.104	0.981
	303	-6.2219			
	313	-5.3360			
	323	-3.9114			
	283	-6.0148			
	288	-5.9474			
	293	-5.6360			
Zn(II)	298	-5.1799	-33.54	-0.096	0.974
	303	-4.6151			
	313	-3.4793			
	323	-2.3785			
	283	-4.2268			
	288	-4.2202			
	293	-4.0191			
Ni(II)	298	-3.7585	-26.82	-0.078	0.937
	303	-3.4489			
	313	-2.1825			
	323	-1.2726			

4.9 Kinetics Experiments

4.9.1 Best Amount of Biomass

In order to determine the best amount of biomass used for each solute, several methods can be used to get that, one of these methods, a relationship from the equilibrium related concentration of (C_e/C_o=0.1) with mass balance in one liter of solution was used. Also, as shown in Figure (5), the best weights of biomass for each solute were found to be 0.60*10^{-3}Kg for Cr (III), Zn (II) and Ni (II) ions.
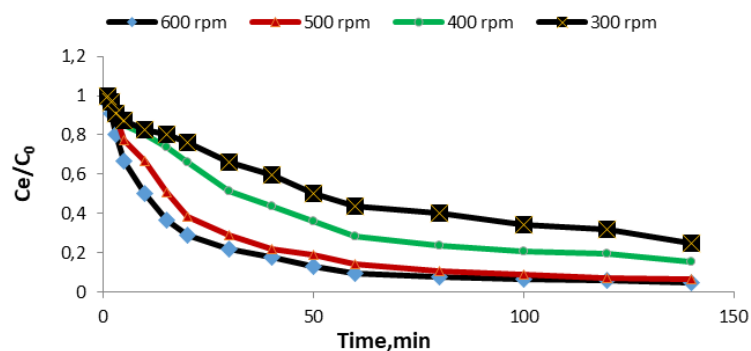

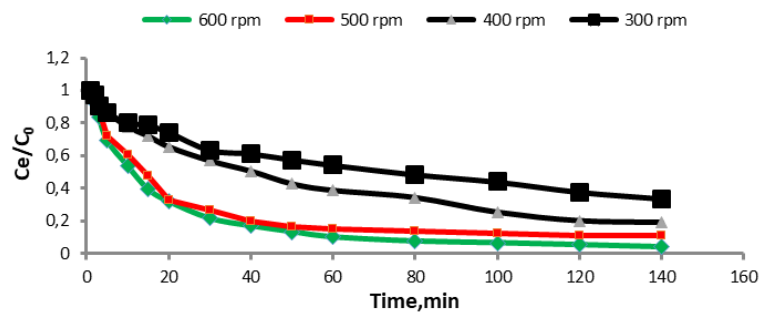**Figure 11.** Concentration-time decay curve for Cr(III) onto biomass at different agitation speeds

Figure 12. Concentration-time decay curve for Zn (II) onto biomass at different agitation speeds
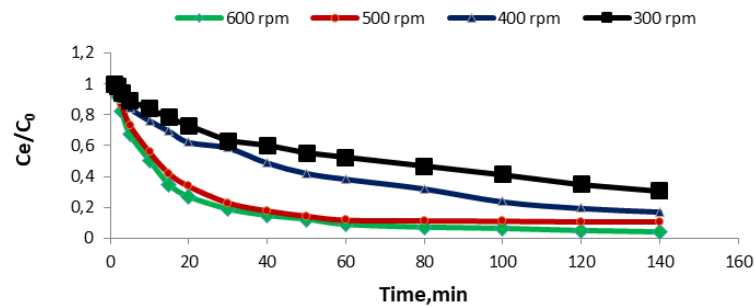

Figure 13. Concentration-time decay curve for Ni (II) onto biomass at different agitation speeds

4.9.2 Best Agitation Speed

Figures (11-13) represent concentration-time decay curves of Cr (III), Zn (II) and Ni (II) ions using various agitation speeds of 300, 400, 500 and 600 rpm. The best agitation speed needed to achieve $C_e/C_o = 0.1$ was found to be 500 rpm.

In order to minimize the mass transfer resistance, an appropriate agitation speed can be used. So, increasing in agitation rate will give a considerable turbulence causing a decrease in the thickness of the liquid boundary layer, as a result, a higher diffusion rate of a solute from the bulk liquid to the liquid boundary layer surrounding particles can be get, then the value of the external diffusion coefficient becomes larger (Vijayaraghavan and Yun, 2008).

4.9.3 Kinetics Models

The kinetics of chrome, zinc, and nickel ions biosorption onto dead blue algal biomass was analyzed using Fractional power. Pseudo-first-order, Elovich, Pseudo-second-order [Ho,2006] and intra-particle diffusion [Singh and Gupta, 2016] kinetics models. Table (4) and Figures (14 to18) demonstrate the results of these models. The data obtained separately for each of the kinetic models from the slopes of plots show a good compliance with the pseudo second-order equation, the correlation coefficient values for the linear plots being higher than 0.977 with biosorption uptake equal to 34.5, 12.87, and 9.124 mg/g, for Cr (III), Zn (II) and Ni (II) ions, respectively, obtained from the best agitated speed of 500 rpm.

Table 4. Kinetic model parameters for Cr (III), Ni (II), and Zn (II) ions biosorption

| Model	Parameters	Cr(III)	Zn(II)	Ni(II)
Intraparticle diffusion (Equation 1)	C (mg/g)	5.394	1.604	1.37
	K_{id} (mg/g.min$^{0.5}$)	2.663	0.992	0.701
	R^2	0.816	0.83	0.801
Fractional power (Equation 3)	K, (mg/g)	2.76	0.802	0.632
	x,(min^{-1})	0.576	0.627	0.601
	R^2	0.845	0.851	0.836
Pseudo-first-order (Equation 5)	q_e(mg/g)	40.88	8.38	6.2
	k_1(min^{-1})	0.062	0.036	0.042
	R^2	0.744	0.974	0.951
Pseudo-second-order (Equation 9)	qe cal. (mg/g)	34.5	12.87	9.124
	k_2(mg/g.min)	0.002	0.0044	0.007
	h_o	2.438	0.722	0.581
	R^2	0.988	0.977	0.978
Elovich (Equation 13)	a_E(mg/g.min)	6.69	2.36	1.858
	$ß_E$(g/mg)	0.151	0.407	0.569
	R^2	0.975	0.977	0.97
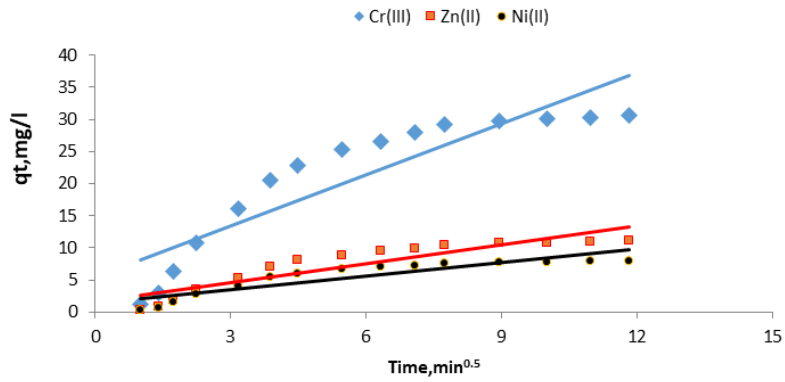
Figure 14. Intraparticle diffusion model for biosorption of Cr (III), Ni (II) and Zn (II)
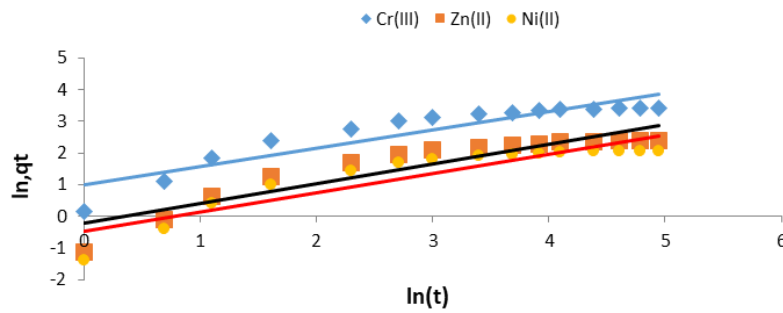

Figure 15. Fractional power model for biosorption of Cr (III), Ni (II) and Zn (II)
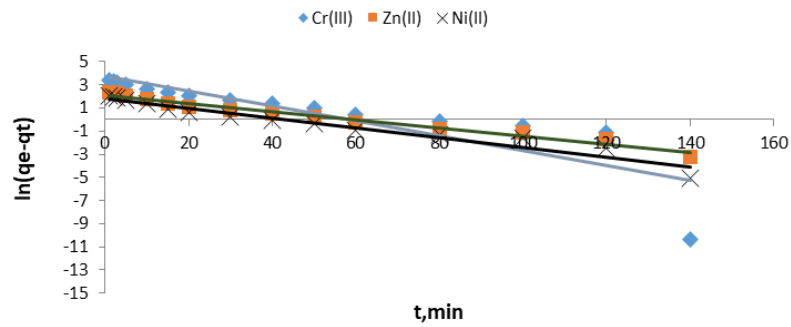

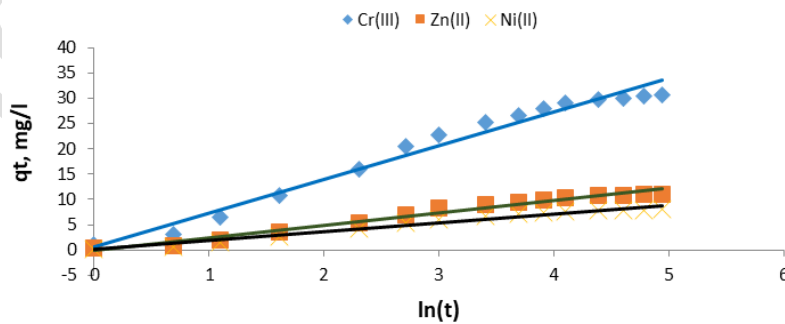**Figure 16.** Pseudo first order model for biosorption of Cr (III), Ni (II) and Zn (II)

Figure 17. Elovich model for biosorption of Cr (III), Ni (II) and Zn (II)
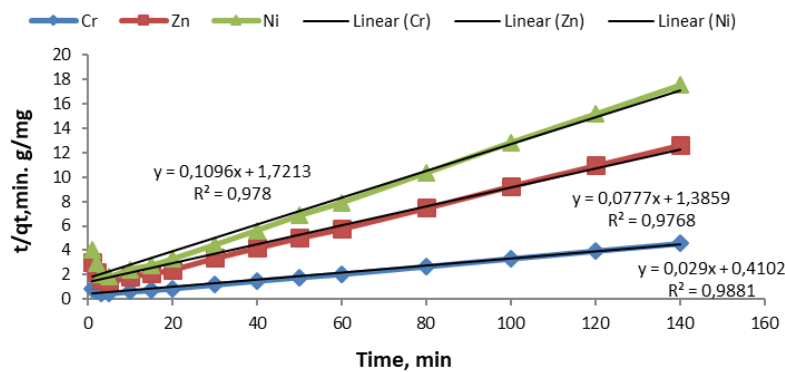
Figure 18. Pseudo second order model for biosorption of Cr (III), Zn (II) and Ni (II) onto dead algal biomass

5. Conclusions

The results of this study show that the mechanism of biosorption of Cr (III), Zn (II) and Ni (II) ions onto algal biomass is an ion exchange due to release of light metals such as calcium, magnesium, potassium, and sodium. The ions of potassium are high release compared with the other light metals. The optimum pH was 4 for Chrome and Zinc ions, while equal 5 for Nickel ions (II) respectively with contact time 1.5 h in biosorption process onto dead blue algal biomass. Also, it can be observed that; when the concentration increased from 10-50 mg/l, the percentage removal was not changed greatly because a lot of active sites was found on the surface of dead blue algal biomass, but when the concentrations increase to 100 and 120 mg/l the active sites in biomass will not be enough to accumulate these concentrations so that the depletion in percentage removal was obvious. The values of thermodynamic parameters indicate that all biosorption processes are exothermic, and this is in agreement with the stability of biosorption capacity with temperature. Kinetic measurements showed that the process was rapid and the biosorption of the three metals are well fitted the pseudo-second order kinetics model. Finally, compared of three metal percentage removal efficiencies with their values in single system, Cr (III) ions offer the strongest component compared with the others, and Ni (II) was the weakest sorbed component**.** It is concluded that the dead blue algal biomass can be used effectively as a low-cost and efficient biosorbent for removal of heavy metals from industrial effluents.

References

Abdel-Aty A.M., Ammar N.S., Abdel Ghafae H.H. and Ali R.K. (2013), Biosorption of cadmium and lead from aqueous solution by fresh water alga *Anabaena spphaerica* biomass, *Journal of advanced research*, **4**, 367-374.

Ahmad S., Ali A. and Ashfaq A. (2016), Equilibrium, Kinetic and Thermodynamic Study of Pb(II) ions from Aqueous Solution by Using Fired Ceramic, *IJSRME*, **1**(1), 231-345.

Aksu Z and Akpinar D. (2000), Modeling of simultaneous sorption of Phenol and Nickel(II) onto dried aerobic activated sludge, *Separation and Purification Technology,* **21**(1-2)*,* 87-99.

Alexander P.M. and Zayas I. (1989), Particle size and shape effects on adsorption rate parameters, *Environ. Eng.,* **115**(1), 41–55.

Al-Qodah Z. (2006), Biosorption of heavy metal ions from aqueous solutions by activated sludge, *Desalination,* **194***,* 164-176.

APHA (2005), Standard methods for the examination of water & wastewater, 19th Edition, American Public Health Association, Washington, DC.

APHA (American Public Health Association), 2005, Standard Method for the Examination of Water and Wastewater, 20th edition, American Public Health Association, Washington, DC

Arshadi M., Amiri M.J. and Mousavi S. (2014), Kinetic, equilibrium and thermodynamic investigations of Ni(II), Cd(II), Cu(II) and Co(II) adsorption on barley straw ash, *Water resources and industry*, **6**, 1-17.

Bhatti H.N., Hafiz R. and Hanif M. A. (2011), Adsorptive removal of chromium ions from synthetic effluents by *Mentha arvensis* biomass: kinetic and equilibrium modeling, **2**(4), 261-266.

Colak F., Atar N. and Olgun A. (2009), Biosorption of acidic dyes from aqueous solutionby Paenibacillus macerans: kinetic, thermodynamic and equilibrium studies, *Chem. Eng. J.*, **150**(1), 122–130.

Das, S. (2012), Biosorption of chromium and nickel by dried biomass of cyanobacterium *Oscillatoria late-virens, International journal of Environmental Sciences*, **3**(1), 341-352.

Dorris K.I., Yu Y., Zhang A. and Shukla S.S. (2000), The removal of heavy metal from aqueous solutions by sawdust adsorption removal of copper, *Journal of Hazardous Materials* B, **80**, 33-42.

El-Sayed G.O., Dessouki H.A. and Ibrahiem S.S. (2011), Removal of Zn(II), Cd(II) and Mn(II) from aqueous solutions by adsorption on maize stalks, *The Malaysian Journal of Analytical Sciences*, **15**(1), 8-21.

Esposito A., Pagnanelli F. and Veglio F. (2002), pH-related equilibria models for biosorption in single metal systems, *Chem Eng. Sci.*, **57**(3), 307-313.

Hamdaoui O. (2006), Removal of rhodamine B from aqueous solutions by tea waste, *Journal of Hazardous Materials*, **135**, 264-273.

Hassan H.S., El-Toony M.M. and El-Kamash A.M. (2011), Sorption potential of epoxy/pac composite for removal of Cs^{+} ion from aqueous solutions, *Journal of Environmental and Analytical Toxicology*, **1**(1), 1-8.

Ho Y.S. (2004), Citation review of Lagergren kinetic rate equation on adsorption reactions, *Science to metrics*, **59**, 171–177.

Ho Y.S. (2006), Review of second-order models for adsorption systems, *J Hazard Mater* B, **136**, 681–689.

John A.C., Lara I.O. Victor A. and Oladunni O. (2011), Equilibrium and kinetic studies of the biosorption of heavy metal

(Cadmium) on *Cassia siamea* bark, *American-Eurasian Journal of Scientific Research*, **6**(3), 123-130.

Latinwo G.K., Jimoda L.A., Agarry S.E. and Adeninan J.A. (2015), Biosorption of Some Heavy Metals from Textile wastewater by Green seawood Biomass, *Universal Journal of Environmental Research and Technology*, **5**(4), 210-219.

Li Y.X, Wang Y. and Zhao F.J. (2015), Kinetic and equilibrium studies of chromium(VI) biosorption by spent macroalgae *Polysiphonaia urceolata* and *Chondrus ocellatus*, *Biotechnology and biotechnological equipment*, **29**(3), 498-505.

Li Y.X, Wang Y. and Zhao F.J. (2014), Biosorption of chromium (VI) from aqueous solutions by *Sargassum thunberggii* kuntze, *Biotechnology and Biotechnological Equipment*, **28**(2), 259-265.

Lokeshwari N. and Keshava J. (2009), Biosorption of Heavy Metal (Chromium) Using Biomass, *Global Journal of Environmental Research*, **3**(1), 29-35.

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*, doi:10.1016/j.hydromet.2008.05.008>.

Malik P.K. (2004), Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics, *Journal of Hazardous Materials* B, **113**, 81-88.

Monika B., Alka S. Srivastava J.K. and Palsania J. (2014), Biosorption of heavy metals from wastewater by using microalgae, *International Journal of Chemical and Physical Sciences*, **3**(6), 67-81.

Najem A.M. (2010), Antagonistic Activity Evaluation of Some Plants in Control of Algae, M.Sc. Dissertation, College of Science, University of Baghdad.

Naspu A.S.M., Kamal M.L. and Hasan S. (2014), Adsorption-desorption study of metal ions on brown macro algae *Padina sp.*, *Journal of Applied Science Agriculture*, **9**(11), 1-8.

Ning-Chuan F., Xue-Yi G. and Sha L. (2009), Kinetic and thermodynamic studies on biosorption of Cu (II) by chemically modified orange peel, *Transactions of Nonferrous Metals Society of China*, **19**, 1365-1370.

Patel G.G., Doshi H.V. and Thakur M.C. (2016), Biosorption and equilibrium study of copper by marine seaweeds from north west coast of India, *Journal of Environmental Science, Toxicology and Food Technology*, **10**(7), Ver II, 54-64.

Sari A. and Tuzen M. (2008), Biosorption of cadmium (II) from aqueous solution by red algae (Ceramium virgatum): Equilibrium, kinetic and thermodynamic studies, *Journal of Hazardous Materials*, **157**, 448–454.

Sari A. and Tuzen M. (2009), Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amantia rubescens*) biomass, *Journal of Hazardous Materials*, **164**, 1004-1011.

Singh N .and Gupta S.K. (2016), Adsorption of Heavy Metals: A review, *IJIRSET*, **5**(2), 2267-2281.

Sirvastava S.K., Tyagi R. and Pant N. (1989), Adsorption of heavy metals on carbonaceous material developed from the waste slurry generated in local fertilizer plants, *Water Research*, **45**, 654-664.

Sudesh and Goyal V. (2016), Cr (VI) removal from synthetic textile effluent using *Tamarindus Indica Bark*: a kinetic and thermodynamic study, *Current science*, **110**(3), 392-398.

Sweetly D.J., Sangeetha K. and Suganthi B. (2014), Biosorption of heavy metal lead from aqueous solution by non-living biomass of *Sargassum myriocystum*, *International Journal of Application or Innovation in Engineering and Management*, **3**(4), 39-45.

Tantawy S.T.A. and Elhaddad E. (2015), Equilibrium and kinetic studies of biosorption of Cr (III) and Cd (II) by activated carbon prepared from Spirulina algal, *Journal of Biodiversity and Environmental Sciences,* **7**(3), 132-140.

Vijayaraghavan K. and Yun Y.S. (2008), Bacterial biosorbents and biosorption, *Biotechnology Advances*, **26**, 266–291.

Wang L. and Chen C. (2009), Biosorbents for heavy metals removal and their future: A review, *Biotechnol Adv.*, **27**, 195–226.

Yahaya Y.A. and Don M.M. (2014), *Pycnoporus sanguineus* as potential biosorbent of heavy metal removal from aqueous solution: A review, *Journal of Physical Science*, **25**(1), 1-32.

Zubeyde B., Ercan C. and Mehmet D. (2009), Equilibrium and thermodynamic studies on biosorption of Pb(II) onto *Candida albicans* biomass, *Hazardous Materials*, **161**, 62–67.