Al-Nahrain Journal for Engineering Sciences (NJES) Vol.20 No.1, 2017 pp.298 - 310

Investigation of The Thermodynamic, Kinetic and Equilibrium Parameters of Batch Biosorption of Pb(II), Cu(II), And Ni(II) From Aqueous Phase using Low Cost Biosorbent

Mohanad J. Mohammed-Ridha
Environmental Eng. Dep.
University of Baghdad
muhannadenviro@yahoo.com

Ali Shihab Ahmed
Biotechnology Sci. Dep.
Al-Nahrain University
Alishihab@yahoo.com

Nagham Nafea Raoof
Environmental Eng. Dep.
University of Baghdad
agh90@yahoo.com

Abstract

In this study, low cost biosorbent−inactive biomass (IB) granules (dp=0.433mm) taken from drying beds of Al-Rustomia Wastewater Treatment Plant, Baghdad-Iraq were used for investigating the optimum conditions of Pb(II), Cu(II), and Ni(II) biosorption from aqueous solutions. Various physico-chemical parameters such as initial metal ion concentration (50 to 200 mg/l), equilibrium time (0-180 min), pH (2-9), agitation speed (50-200 rpm), particles size (0.433 mm), and adsorbent dosage (0.05-1 g/100 ml) were studied. Six mathematical models describing the biosorption equilibrium and isotherm constants were tested to find the maximum uptake capacities: Langmuir, Freundlich, Redlich–Peterson, Sips, Khan, and Toth models. The best fit to the Pb(II) and Ni(II) biosorption results was obtained by Langmuir model with maximum uptake capacities of 52.76 and 36.97 mg/g for these two ions respectively. While for Cu(II) the corresponding value was 38.07 mg/g obtained with Khan model. The kinetic study demonstrated that the optimum agitation speed was 400 rpm, at which the best removal efficiency and/or minimum surface mass transfer resistance (MSMTR) was achieved. A pseudo-second-order rate kinetic model gave the best fit to the experimental data ($R^2 = 0.99$), resulting in mass transfer coefficient values of 42.84×10^{-5}, 1.57×10^{-5} , and 2.85×10^{-5} m/s for Pb(II), Cu(II), and Ni(II) respectively. The thermodynamic study showed that the biosorption process was spontaneous and exothermic in nature.

Keywords: Biosorption, biomass, isotherm models, biosorption kinetics, biosorption thermodynamics

1. Introduction

Pollution of water resources is a widely recognized fact due to its common occurrence. In particular, the presence of heavy metals, even in trace amounts, is detrimental to both flora and fauna [1].

The damaging effects of heavy metals on humans are well known. Heavy metals are classified as carcinogens due to their ability to accumulate in living tissues, causing damages to these tissues with time [2]. Lead ions affect the liver, kidneys and cause mental retardation in children; copper ions result in liver and kidneys malfunctioning as well as induce nausea, vomiting, diarrhoea, intestinal cramps, and anemia; nickel ions affect skin sensitization and cause dermatitis, perinatal mortality [3].

The standard limitation for disposal of these heavy metal ions to the river environment according to the Iraqi Ministry of Environment is 0.1 mg/l for each of Pb(II), Cu(II), and Ni(II). While the limiting concentrations are less according to WHO being 0.03, 0.01, 0.04 mg/l for these three ions, respectively [4].

Expansion of various industries all over the word including energy and fuel, mining, fertilizer, surface finishing, pesticide, leather, electric appliance manufacturing, and photography has increased the disposal of organic and inorganic pollutants to the environment−representing major challenges to engineering [5]. This disposal increase also applies to heavy metals discharge, directly or indirectly, to the environment [6]. Several methods are being used to treat heavy metal ions effluents. The traditional methods of treating these pollutants including ion exchange, electrolysis, chemical precipitation, membrane technologies, activated carbon and adsorption are considered highly expensive and difficult to maintain, in addition to the problem of large amounts of sludge with high pollutant concentrations [7]. Furthermore, some of these methods are ineffective when heavy metal ions concentrations are lower than 50 mg/l [8]. This low concentration problem is aggravated in reality by the huge volumes of wastewater associated with it [9].

There is a new alternative for treating and removing heavy metal ions from aqueous solutions, which is the use of biomass [10]. The biosorbent materials which are easily available include three groups: algae, fungi, and bacteria, the former two perhaps giving broader choices. Waste materials or by-product biomass from large scale fermentation processes. Various types of biomasses have been reported to bind a variety of heavy metals to different extents. Some potential biomaterials with high metal binding capacity. Some types of biosorbents binding and collecting the majority of heavy metals with no specific priority, while others can even be specific for certain types of metals [11].Algae, fungi, and bacteria biosorbents have high uptake capacities for removing different organic / inorganic pollutants [12].

The main advantages of biosorption, in comparison with traditional treatment methods, include minimization of biological sludge and chemicals, low cost, high efficiency, and possibility of heavy metal recovery [13]. While the disadvantages of biosorption include: no potential for biologically altering the metal valency, fast saturation when metal ions interactive sites are occupied, metal desorption is necessary, the potential for biological process improvement is limited because cells are dead [14, 15].

The mechanism of metal ions biosorption is a complicated process [16]. Metal uptake by non-living cells is mainly in the passive mode [17]. Many researchers found that the metal uptake by microorganisms occurs in two stages: passive uptake which takes place immediately consider physical adsorption or ion exchange at the cell surface, this process takes 30-40 min., and active uptake which takes place slowly and is caused by complexation mechanism on the cell wall due to active functional groups [18].

A number of factors affect the biosorption process and the ability of the biomass to remove heavy metal ions form aqueous solution. These factors in the range of 20-35 ℃ are: biomass concentration, pH, initial metal ion concentration [19]. pH is considered as being the major important parameter in the biosorption process [20]. It affects the activity of the functional groups in the biomass and the solution chemistry of the metals [21].

The aim of this study is to determine the ability of using IB for removal of Pb(II), Cu(II) and Ni(II) from aqueous solution taking into account the physiochemical properties of these heavy metal ions and the characteristic of IB.

2. Materials and Methods

2.1.Adsorbent Preparation

The adsorbent, inactive biomass obtained from drying beds of Al-Rustomia Wastewater Treatment Plant, which is a mixed culture of: bacteria, fungus, and yeast. It was taken from a depth of one meter from the drying bed surface, then dried at ambient temperature for five days (40 - 45 ℃), crushed, and sieved to obtain the desired particle size of 0.433 mm. and then washed for three times with distilled water and dried at 70℃ for 6 hours, then kept in a closed container. Before each experiment, the IB was dried again at 70℃ for 2 hours to prevent any moisture intrusion. The characteristics of IB are listed in Table (1) and the scanning electron microscope (SEM) image for these particles is shown in Fig. (1) which shows the comparative between raw IB and Loaded with heavy metals ions

2.2.Chemicals

Heavy metal salts (BDH, England) were purchased from the local market. Three stock solutions, each with a concentration of 1000 mg/l of Pb(II), Cu(II) or Ni(II) were prepared from dissolution of 1.67, 56, or 79 g of $Pb(NO_3)_2$, $Cu(NO_3)_2$ or $Ni(NO_3)_2$ respectively with 99.5% purity (Merck Co.,Germany) in 1000 ml distilled water. Several drops of HNO_3 was add to each solution to keep its pH below 2 to prevent precipitation. The desired concentration was prepared from the stock solutions during all experiments. Each concentration was measured using atomic absorption spectrophotometer (AAS, GBC 933 plus, Australia) and was repeated three times. The characteristics of these there pollutants are listed in Table (2).

2.3. Biosorption Isotherm Models

Different empirical models for representing the behavior of biosorption of heavy metal ions onto biomass can be used to find the maximum uptake capacity and identify how much sorbate can be attracted and conserved in a fixed form onto IB in a single batch system. The experimental uptake of a solute by a biosorbent can be found using Eq. (1) [22].

$$q_{exp.=}\frac{(C_0-C_e\,)\,V}{W_b} \quad \text{……………………..(1),}$$

where $q_{exp.}$ is the experimental uptake capacity (mg/g), C_0 and C_e are the initial and equilibrium metal ion concentrations, respectively (mg/l), W_b is the biomass dose (g), and V is the solution volume (ml). Six mathematical models describing the biosorption equilibrium and isotherm constants were tested: Langmuir, Freundlich, Redlich–Peterson, Sips, Khan, and Toth models, using nonlinear regression by Statistica software program version 9.

2.4. Biosorption Kinetic Models

Various models were tested by researchers in this regard; all have attempted to quantitatively describe the kinetic behavior during the biosorption process. Each model has its limitation depending on the experimental conditions applied. The two common models used in the kinetic studies are pseudo-first order and pseudo‒second order rates which are given in Eq.(2) and Eq.(3) [22].

$$q_t = q_e(1-\exp(-K_1\,t)) \quad \text{………….. (2)}$$

$$q_t = q_e\left(1-\frac{1}{1+q_e k\,t}\right) \quad \text{………….(3)}$$

where q_e is the equilibrium amount of sorbed solute (mg/g); q_t is the amount of solute sorbed at time t (mg/g); k_1 is the first order rate constant at equilibrium (min^{-1}) and k_2 is the second order rate constant in equilibrium (g/mg min).

2.5. Surface Mass Transfer Coefficient

External mass transfer coefficient was determined from the batch experiment time decay curve at optimum agitation speed. It was determined from the average of many values of K_f calculated by Eq. (4) in the first 15 min from the beginning of the experiment. For accurate estimation of K_f, samples were taken after 3, 6, 9, 12, 15 min and analyzed [22, 17, 15]

$$k_f = -\frac{R_p \rho_p V_L}{3 W_b\, t} \ln\left(\frac{C_t}{C_0}\right) \quad 0 < {C_t}/{C_0} < 1 \; \text{….(4),}$$

where R_p is the radius of particle (m), W_b is the mass of biomass (kg), ρ_p is the particle density (kg/m^3), V is the volume of solution (m^3), t is the time (s), C_0 and C_e are the solute concentrations at time 0 and at time t (kg/m^3).

2.6. Thermodynamic Analysis

Thermodynamic parameters for the biosorption such as enthalpy (ΔH), free energy (ΔG) and entropy (ΔS) were calculated using Eq. (5) to Eq. (7). The equilibrium constant can be found using the following equations. [23, 15]

$$\Delta G = -RT \ln \pi \,(K_c) \qquad \text{..(5)}$$

$$\Delta G = \Delta H - \Delta S\, T \qquad \text{…(6)}$$

$$K_c = \frac{C_{ad}}{C_e} \qquad \text{… (7),}$$

Where C_{ad} is the adsorbed concentration onto IB surface (mg/), ΔS is the change in entropy (kg/mol), ΔH is the change in enthalpy (kg/mol), ΔG is the standard Gibbs free energy change (kg/ mol).

2.7. Effect of pH

The effect of pH value on Pb(II), Cu(II) and Ni(II) biosorption onto IB was investigated. One gram of IB was mixed with 100 ml of a single metal ion solution of Pb(II), Cu(II) or Ni(II) having a concentration of 50 mg/l. The experiment was repeated for pH values of 2, 3, 4, 5, 6,7, 9 and controlled using 0.1 M NaOH or HNO_3 solution. Conical flasks (250 ml) were placed on an incubator orbital shaker (Lab S1-600R, Korea) at a temperature of 25℃, agitation speed of 200 rpm for a period of 3 h. Samples of 10 ml were taken with 2 drops of 0.1 M HNO_3 added to each sample.

2.8. Biosorption Experiments

Different weights (0.05, 0.1, 0.15, 0.2, 0.25, 0.5, 0.75, 1 g/100 mml) of dry IB were used (Electrical balance, Sartorius BL 210S, Germany). These IB weights were placed in 250 ml conical flasks, to each of which 100 ml of 50 mg/l solution concentration of Pb(II), Cu(II), or Ni(II) was add. pH was adjusted to the desired value 5 using 0.1 M NaOH or HNO_3, then placed on a shaker and agitated continuously for 3 h at 200 rpm. Each experiment was repeated to investigate the effects of other parameters (contact time, particles diameter, temperature, initial metal ion concentration, agitation speed) on the biosorption process by fixing the best result of the preceding run for the succeeding run.

3. Result and Discussion

3.1. Effect of pH

The pH of the solution plays a very important role in the biosorption process [2, 15]. Fig. (2) shows that the removal efficiency enhanced significantly from 25, 60 and 80 to 70, 95 and 90 percent for Ni(II), Cu(II) and Pb(II), respectively, when the pH was raised from 2 to 5 this result is due to that the pH effect the dismantling degree of functional groups located on the surface of IB and the metal solubility. pH value of 5 was used in the next experiments to avoid the effect of precipitation at pH values of above 7. These findings well agreed with results obtained by Sulaymon et al., 2013 [17].

3.2. Effect of Contact Time

The contact time is an important parameter for increasing the removal efficiency of heavy metal ions by IB to make physiochemical binding with active sites on the cell wall of the IB. Fig. (3) shows that the removal efficiency enhanced from 0 to 90, 60, and 35 percent during the first 40 minutes for Pb(II), Cu(II) and Ni(II) respectively. Then the removal efficiency increased to 95, 74, 50 percent after 180 minutes. The results indicate that the biosorption process is a rapid phenomena and that the main mechanism is adsorption on the external surface of the biomass. The removal of Pb(II) is better than the other two heavy metals ions (Cu(II) and Ni(II)) due to the physicochemical properties of Pb(II). Lead ion has the highest molar mass (331.2 g/mol) and the highest standard atomic mass (207.2) as well as the lowest solubility in water at 20 °C (52 g/100 ml) among the three ions.

3.3. Effect of Biomass Concentration

Biomass concentration affects the removal of heavy metal ions by providing more active sites. low values of biomass concentration lead to interference between the binding sites and uptake capacity resulting in a decrease of the removal efficiency [15, 17]. Fig. (4) shows the removal efficiency increased from 50, 20, 18 percent to 100, 90, 60 percent when the biomass dosage increased from 0.05 to 0.2, 0.5, 0.1 g/100 ml for Pb(II), Cu(II) and Ni(II). To obtain better removal efficiency for Ni(II) biomass dosage must be increased above 0.1 g/100 ml.

3.4. Effect of Initial Metal Ion Concentration

As the concentration of a metal ion increases, more surface sites will be covered and the capacity of the adsorbent becomes exhausted due to non − availability of the sites [3, 7]. It is therefore obvious that at low concentrations of Pb(II), Cu(II) and Ni(II) the percentage of adsorption was high because of the availability of more active sites on the surface of IB and vice versa. Fig (5) shows that the removal efficiency decreased from 95, 93, 97 percent to 75, 63, 45 percent as the initial heavy metal concentration for Pb(II), Cu(II) and Ni(II) increased from 10 to 200 mg/l. this may be attributed to the increase of driving force between the liquid and solid phases with increasing heavy metal ions concentration.

3.5. Effect of Agitation Speed

Agitation speed is an important parameter in the biosorption of Pb(II), Cu(II) and Ni(II) onto IB , which has an earnest action on the distribution of the solute in the bulk solution and formation of the external boundary film [3, 15]. Increasing the agitation speed decreases the resistance in the liquid−solid interface phase which leads to better removal efficiency and lower equilibrium time. Fig. (6) shows that the removal efficiency increased significantly from 35, 32 and 28 percent to 95, 93, 88 percent when the agitation speed increased from 50 to 200 rpm, thus confirming that the influence of external diffusion on the sorption kinetic control plays a significant role [5, 16].

3.6. Effect of Temperature

The effect of temperature on biosorption of Pb(II), Cu(II) or Ni(II) onto IB was investigated under isothermal conditions for temperatures of 20, 30, 40, and 50 °C. The results of Fig. (7) indicate that when the temperature was raised from 20^oC to 50^oC, the removal efficiencies of heavy metal ions onto IB increased from 60 to 80 percent for Ni(II). The removal efficiency for Pb(II) was wobbling from 90 to 85 percent. While for Cu(II) the removal efficiency slightly increased from 90 to 95 percent. Therefore, higher temperature facilitated the adsorption of Ni(II) onto IB. Generally, previous reported studies results showed that temperature plays a minor role on the mechanism of removing heavy metal ions from wastewater.

3.7. Equilibrium Isotherm Models

Equilibrium isotherm models are usually classified into empirical equations and mechanistic models. The mechanistic models are based on the mechanism of metal ion biosorption. They are able not only to represent but also to explain and predict the experimental behavior [7, 17]. The empirical models do not reflect any mechanism of sorbate uptake and hardly have a meaningful physical interpretation for biosorption. [8]

Fig (8) shows the relationship between Pb(II), Cu(II), and Ni(II) uptake with effluent concentration. These results indicate that the biosorption of Pb(II) and Ni(II) obey the Langmuir isotherm model, while biosorption of Cu(II) obeys Khan isotherm model. The maximum uptake capacities were found to be 52.76, 27.78 and 36.97 mg/g for Pb(II), Cu(II), and Ni(II) respectively. Table (3) shows the equilibrium parameters for the different isotherm models for biosorption of metal ions onto IB. To further quantify the adsorption properties of the Langmuir isotherm, a dimensionless separation factor (R_L) was used. R_L is a dimensionless constant, shown in Eq. (8). The favourability of the isotherm can be considered by the following: the isotherm is unfavourable if $R_L > 1$; linear if $R_L = 1$; favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$. The experimental results show that the type of biosorption is favourable for all three heavy metal ions.

$$R_L = \frac{1}{1+bC_0} \quad \text{…..(8)}$$

3.8. Kinetic Modeling and Concentration Time Decay in A Batch System

Kinetic models can be helpful to comprehend the mechanism of metal adsorption and estimate the performance of adsorbents for metal removal [12]. They offer information on the rate of metal uptake, together with the hydrodynamic parameters, for biosorption process design [1, 13]. Numerous kinetic models have been suggested to describe the reaction order of adsorption systems based on solution concentration. Kinetic models based on the capacity of the adsorbent have also been presented, such as the Lagergren's first-order equation and Ho's second−order expression. [1, 2, 19]. Table (4) which was obtain from applying Eqs. (2) and (3) the pseudo second-order equation fitted the data very well (above R^2= 0.90). The results were 20.53, 4.69, and 0.79 mg/g for Pb(II), Cu(II) and Ni(II) respectively. The process of sorption of Pb(II), Cu(II), and Ni(II) appeared to include surface chemisorption at the boundary layer between particles. Fig(9) shows the matching between the pseudo-second order kinetic model with experimental results for biosorption of Pb(II), Cu(II), and Ni(II) onto IB.

Figs. 10 to 12 show the time concentration decay curves, which were obtained from different dosages of IB (2.8, 11.8, and 37.4 g/l). These weights were determined from C/Co= 0.05 to obtain 0.95 removal efficiency by equivalent Eq.(1) with Langmuir isotherm model for each Pb(II) and Ni(II) . While for Cu(II) with Khan isotherm model. The agitation speed was varied as 200, 300, 400, 500, and 600 rpm. The external mass transfer coefficient (k_f) was calculated from the average results obtained from Eq. (4) based on samples taken at 3, 6, 9, 12 min with the optimum agitation speed of 400 rpm. The k_f values were 42.84×10^{-5}, 1.57×10^{-5} and 2.85×10^{-5} m/s for Pb(II), Cu(II) and Ni(II) respectively.

3.9. Biosorption Thermodynamic Study

Thermodynamic parameters such as the free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS), were calculated from the variation of the thermodynamic equilibrium constants with temperature. The negative values of ΔG indicate the spontaneous nature of Pb(II), Cu(II), or Ni(II) sorption onto IB. Fig. (13) and Table (5) show that the magnitude of ΔG, increased from 4.58, 6.47, and 1.38 to 5.50, 7.81, and 1.97

kJ/mol for Pb(II), Cu(II), and Ni(II), respectively with increasing temperature, revealing that the degree of spontaneity increased at higher temperatures. The positive values of ∆S reflect an increased degree of disorderliness at the solid/liquid interface during the adsorption of Pb(II), Cu(II), or Ni(II) onto IB. The exothermic nature of heavy metal ions sorption by IB was confirmed by the positive values of ∆H. For chemical sorption, values of enthalpy change range from 83 to 830 kJ /mol, while for physical sorption they range from 8 to 25 kJ/ mol. The low values of ∆H: 4.09, 7.07 and 4.5 kJ/ mol for Pb(II), Cu(II), and Ni(II) respectively give clear evidence that the interaction between these heavy metal ions and IB was weak. On this basis we concluded that Pb(II), Cu(II), and Ni(II) sorption by IB is a physical adsorption process. Table (6) shows comparison of results obtained in this study with other studies for removal of heavy metals ions using different biomass.

4. Conclusions

This study shows that IB has a promising equilibrium adsorption capacity to uptake heavy metal ions from aqueous solution with order of Pb(II) > Cu(II) > Ni(II). The experimental results were well representative by Langmuir isotherm model for Pb(II) and Ni(II); by Khan isotherm for Cu(II). The kinetic study showed that an adsorption kinetic rate could be simulated better by a pseudo-second-order model. The k_f values were 42.84×10^{-5}, 1.57×10^{-5} and 2.85×10^{-5} m/s for Pb(II), Cu(II) and Ni(II) respectively at the best agitation speed of 400 rpm. The equilibrium sorption time was 180 min. The better removal efficiencies were obtained at pH of 5 for the three heavy metal ions. Thermodynamic study showed that the nature of Pb(II), Cu(II), or Ni(II) sorption onto IB was spontaneous and exothermic indicating a physical process.

Acknowledgements

The authors wish to thank the Environmental Engineering Department / College of Engineering / University of Baghdad for their support. The authors would like to express sincere gratitude to all technicians in the Environmental Engineering Laboratory (Baghdad University) for their help.

5. References

1- K. Vijayaraghavan, Y. Yun, “Bacterial biosorbents and biosorption” Biotechnology Advances, V(26), 266 – 291, 2008
2- O. Abdia, M. Kazemia “A review study of biosorption of heavy metals and comparison between different biosorbents” Journal Material Environmental. Science , V(6) , No.(5), 1386-1399, 2015
3- H. Bulut “ A kinetics and thermodynamics study of methylene blue adsorption on wheat shells”, Desalination, V(194), 259–267, 2006
4- H. Hu, Y. Liu, Z. Huang, “Screening of bacterial strain XP05 and its properties adsorbing Pt4”, Journal of Xiamen University (Natural Science) V(42) No. (2), 233 e237, 2003.
5- B. Zubeyde, C. Ercan¸ B. Yasemin, A. Huseyin ,D. Mehmet ” Equilibrium and thermodynamic studies on biosorption of Pb(II) onto Candida albicans biomass” Journal of Hazardous Materials, V (161), 62–67, 2009
6- S. Iram, S. Abrar “Biosorption of Copper and Lead by Heavy Metal Resistant Fungal Isolates” International Journal of Scientific and Research Publications, V(5), No(1), 1-5, 2015
7- Y. Wang, Y. Mu, Q. Zhao, H. Yu” Isotherms, kinetics and thermodynamics of dye biosorption by anaerobic sludge” Separation and Purification Technology, V(50) , 1–7, 2006
8- W. Azharl, S. Iram “Kinetics, Equilibrium And Thermodynamics Studies On Biosorption Of Heavy Metals By Fungal Biomass” International Journal of Engineering Sciences & Emerging Technologies, V(7), No(3), 693-700, 2014.
9- N. Das, R. Vimala, P. Karthika “ Biosorption of heavy metals- An overview” Indian Journal of Biotechnology, V(7), 159-169, 2007.
10- Y. Ho, G. McKay ” Sorption of dyes and copper ions onto biosorbents”, Process Biochem. V(38),1047–1061, 2003.
11- V. Gupta, A. Mittal, L. Krishnan, V. Gajbe, “Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash”, Sep. Purif. Technol. V(40), 87–96, 2004.
12- N. Abdel-Ghani, M. Hefny, A. El-Chaghaby, “Removal of metal ions from synthetic wastewater by adsorption onto eucalyptus camaldulensis tree leaves” J Chil Chem Soc, V (53), 585–1589, 2008.
13- V. Mishra, C. Balomajumder, V. Agarwal ” Biosorption of Zn(II) onto the surface of non-living biomasses: comparative study of adsorbent particle size and removal capacity of three different biomasses”. Water Air Soil Pollut , V(211), 489–500, 2010
14- T. Davis, B. Volesky, A. Mucci “A review of the biochemistry of heavy metal biosorption by brown algae” Water Research, V (37), 4311 – 4330, 2003.
15- A. Sulaymon, S. Ebrahim, M. Ridha, “Equilibrium, kinetic, and thermodynamic biosorption of Pb(II), Cr(III), and Cd(II) ions by dead anaerobic biomass from synthetic wastewater, Environmental Science and

Pollution Research .Vol.20, No.1, pp 175-87. 2013.

16- A. Ofomaja, E. Unuabonah, N. Oladoja ”Competitive modeling for the biosorptive removal of copper and lead ions from aqueous solution by Mansonia wood sawdust” Bioresour Technol, V(101), 3844-3852, 2010

17- A. Sulaymon, S. Ebrahim, M. Ridha “Competitive biosorption of Pb(II), Cr(III), and Cd(II) from synthetic wastewater onto heterogeneous anaerobic biomass in single, binary, and ternary batch systems” Desalination and Water Treatment, doi:10. V(52), 5629–5638, 2014

18- APHA “Standard methods for the examination of water & wastewater” 19th Edition. American Public Health Association, Washington, DC, 1995.

19- A. Farhan, N. Salem, L. Ahmad, A. Awwad ”Kinetic, equilibrium and thermodynamic studies of the biosorption of heavy metals byCeratonia siliqua bark”. Am J Chem, V(2),335–342, 2012

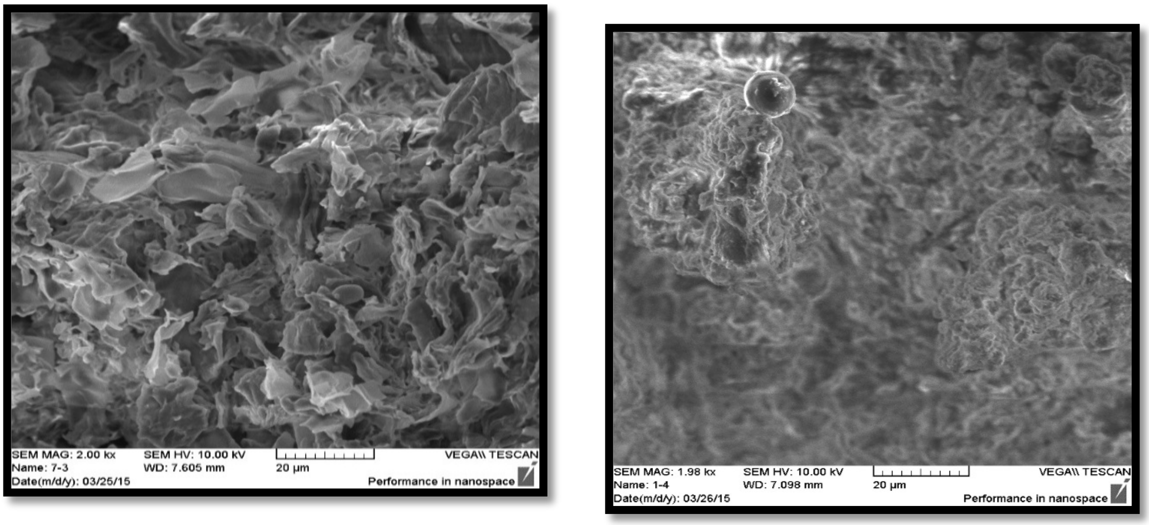
.

20- N. Salem, A. Awwad, A. Al-Dujaili “Biosorption of Pb(II), Zn(II), and Cd(II) from aqueous solution by (Eriobotrya japonica) loquat bark” Int J Environ Prot V(2), 1–7, 2012

21- A. Witek-Krowak, R. Szafran, S. Modelski, “Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent” Desalination V(265),126–134, 2011

22- M. Khani, A. Keshtkar, B. Meysami, M. Zarea, R. Jalali "Biosorption of uranium from aqueous solutions bynonliving biomass of marinealgae Cystoseirandica", Electronic Journal of Biotechnology, V(9),No. (2), 100-106, 2006

23- N. Babarinde, J. Babalola, J. Adegoke, O, Maranzu, T. Ogunbanwo, E. Ogunjinrin” Kinetic, isothermal and thermodynamic studies of the biosorption of Ni (II) and Cr (III) from aqueous solutions using banana (Musa acuminata)”, International of Physical Sciences, V(7), No.(9), 1376 – 1385, 2012.



a) b)

Figure 1: a) SEM image for raw IB b) SEM image for IB loaded with heavy metal ions, 20 μm performance in nanospace

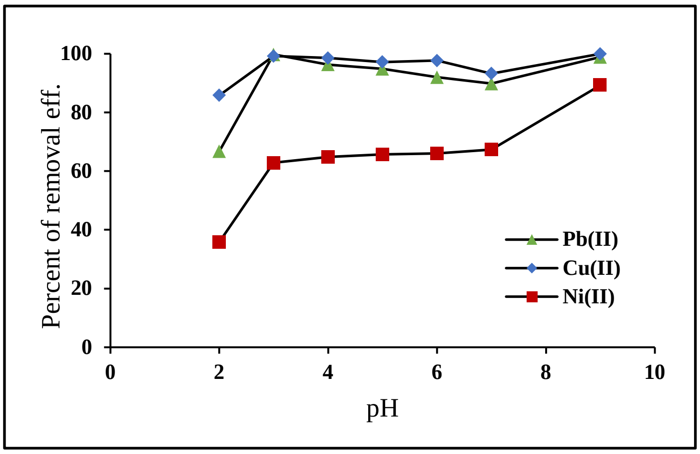


Figure 2: Effect of solution pH on removal efficiency, $C_{o\ (Pb(II),\ Ni(II),\ or\ Cu(II))}$=50 mg/l, (Single system), IB=1g, time=3h, temp. =25oC, agitation speed=200 rpm, V=100 ml

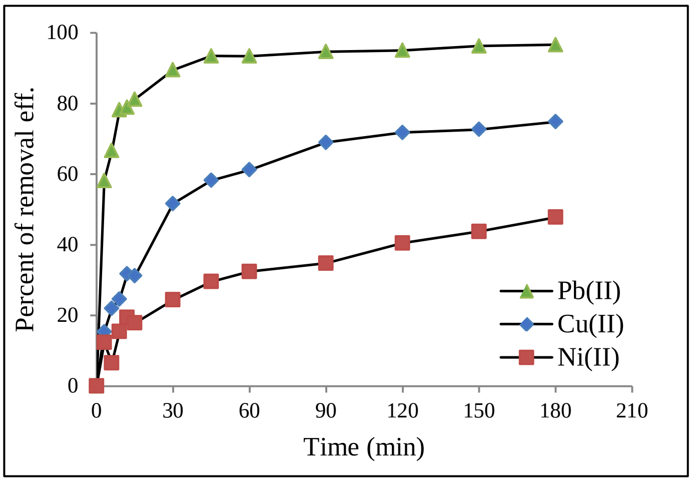


Figure 3: Effect of contact time on removal efficiency, $Co_{\ (Pb(II),\ Ni(II),\ Cu(II))}$=50 mg/l, (Single system), IB=1g, pH= 5, temp. =25 °C, agitation speed=200 rpm, V=100 ml**.**

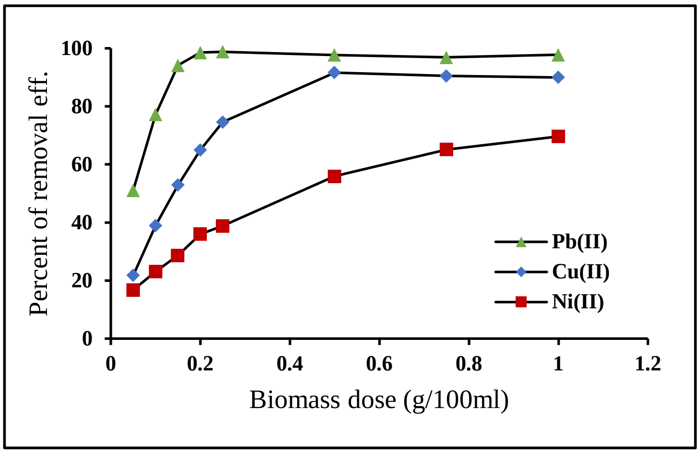


Figure 4: Effect of IB doses on removal efficiency, $Co_{\ (Pb(II),\ Ni(II),\ Cu(II))}$= 50 mg/l,(Single system), pH= 5, Time=3h, Temp. =25 °C, agitation speed= 200rpm, V= 100 ml

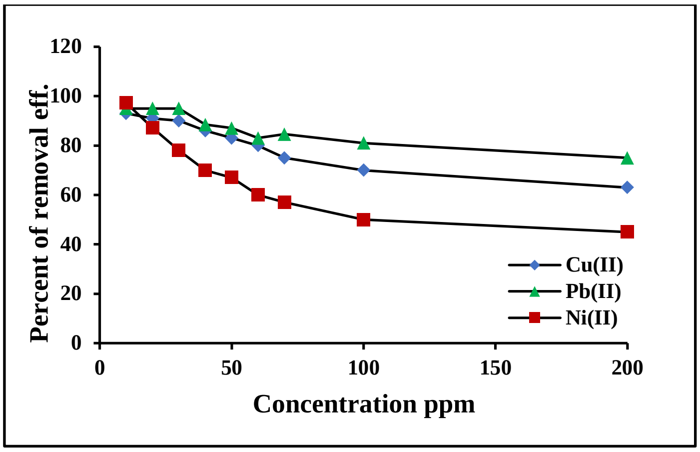


Figure 5: Effect of concentration on removal efficiency, (Single system), IB=1g, pH=5, time=3hrs, temp. =25 °C, agitation speed=200rpm, V=100 ml.

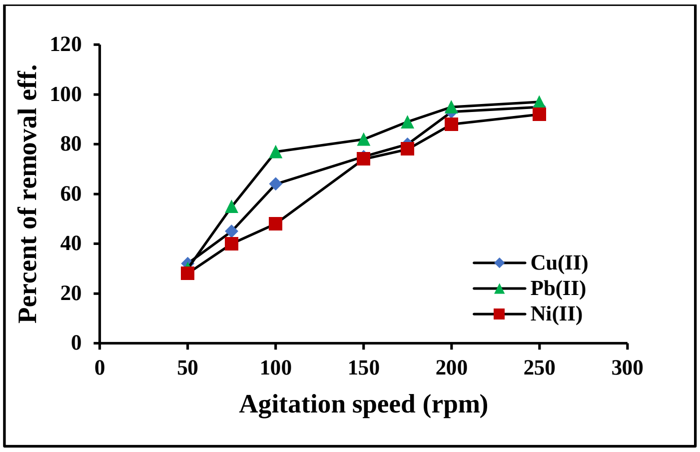


Figure 6: Effect of agitation speed on removal efficiency, Co (Pb(II), Ni(II), Cu(II))= 50 mg/l (Single system), IB=1g, pH=5, time=3h, temp. =25 °C, V=100 ml.

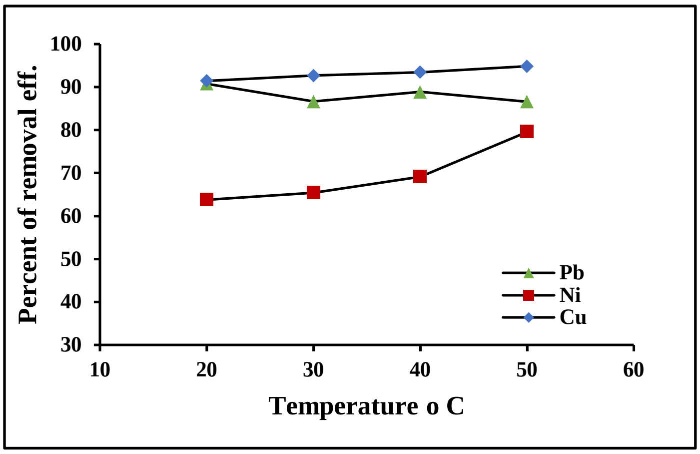


Figure 7: Effects of Temperature on removal efficiency, Co $_{(Pb(II),\ Ni(II),\ Cu(II))}$=50 mg/l,

(Single system), IB=1g, pH=5, Time=3h, agitation speed=200rpm.

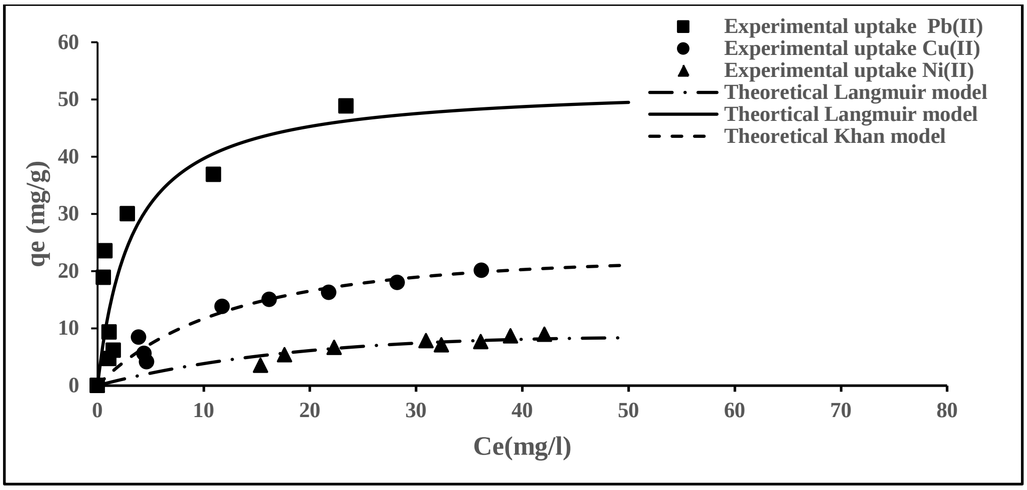


Figure 8: Equilibrium isotherm models, Co $_{(Pb(II), Ni(II), Cu(II))}$=50 mg/l, (Single system), IB=0.05 to 1 g, pH=5, Time=3h, agitation speed=200rpm, V=100 ml.

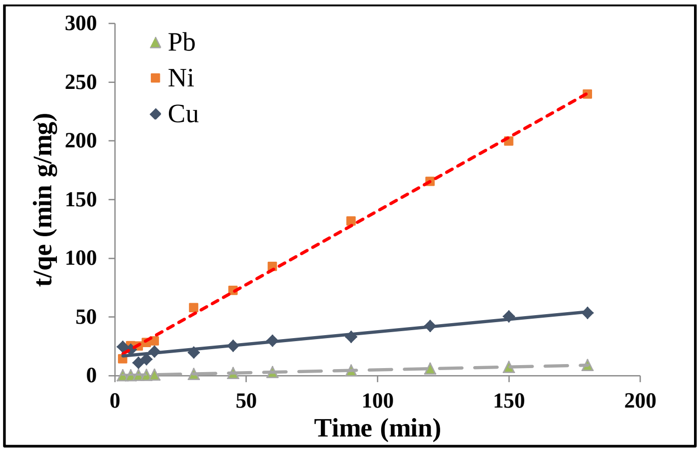


Figure 9: Pseudo-second order kinetic model for biosorption of Pb(II), Cu(II), and Ni(II) onto IB

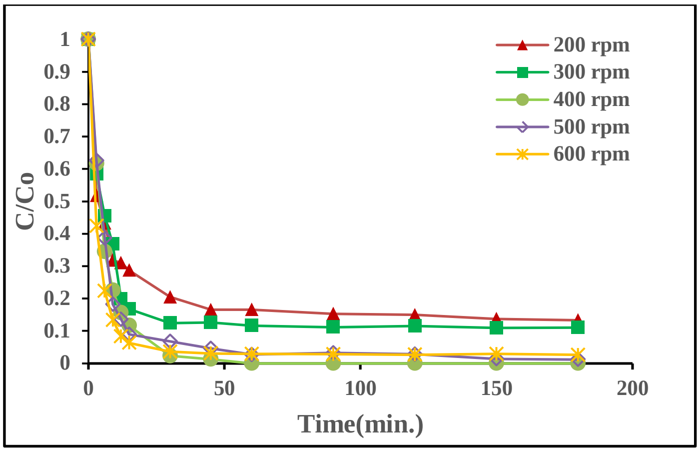


Figure 10: Effect of agitation speed, $C_{o\ Pb(II)}$=50 mg/l, (Single system), pH=5, Time=3h, Temp. =25 ^{0}C, IB=2.08 g, V= 1000 ml.

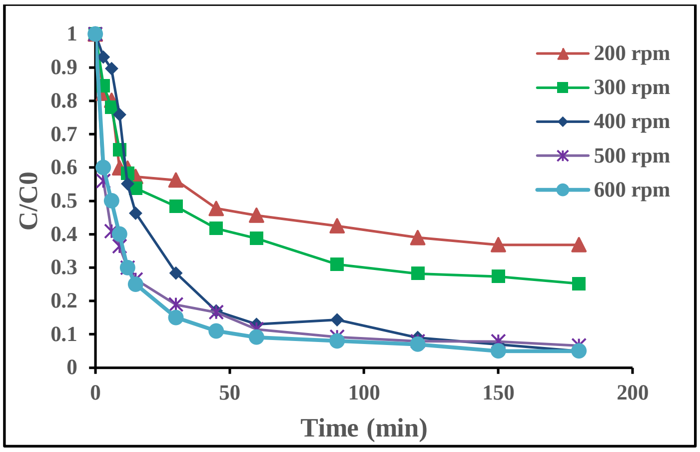


Figure 11: Effect of agitation speed, $C_{o\ Cu(II)}$=50 mg/l,(Single system), pH=5, Time=3h, Temp. =25°C, IB= 11.8 g, V=1000 ml.

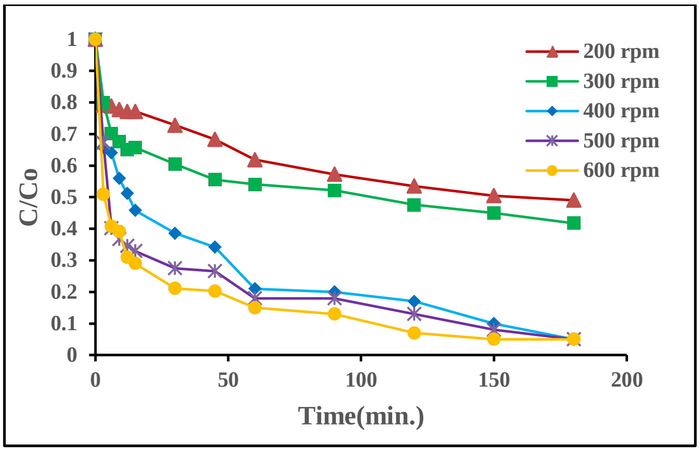


Figure 12: Effect of agitation speed, $C_{o\ Ni(II)}$=50 mg/l,(Single system), pH=5, Time=3h, Temp. =25°C, IB=37.4 g, V=1000 ml.

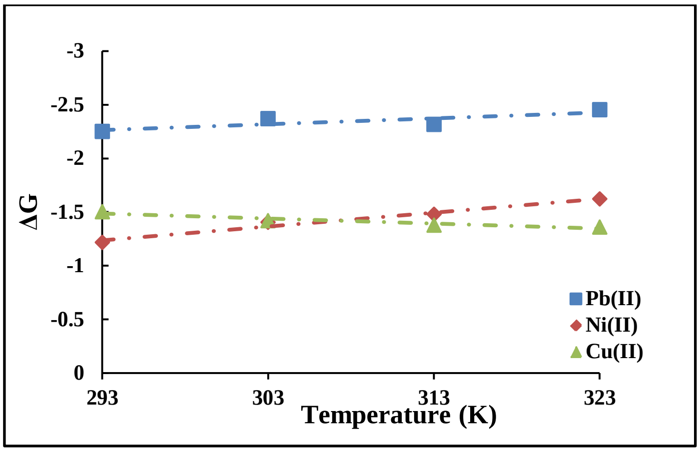


Figure 13: Thermodynamic constants of adsorption of Pb(II), Cu(II) and Ni(II) onto IB

Table 1: Physical and chemical characteristics of IB

Physical characteristic	
Particle diameter (mm)	0.433
Surface area (m^2/g)	1.575
Actual density (kg/m^3)	1746
Bulk density (kg/m^3)	555.8
Particle porosity (−)	0.6193
Chemical characteristic	
pH	7.2-7.5
Pb(II) content in raw biomass (mg/l)	Nil
Cu(II) content in raw biomass (mg/l)	1.063
Ni(II) content in raw biomass (mg/l)	Nil

Table 2: Main physicochemical properties of the metal ions tested

Properties	Pb(II)	Cu(II)	Ni(II)
Formula	Pb(II) from $Pb(NO_3)_2$	Cu(II) from $Cu(NO_3)_2$	Ni(II) from $Ni(NO_3)_2$
Appearance	White colorless crystals	blue crystals hygroscopic	emerald green hygroscopic
Molar mass (g/mol)	331.20	187.56	290.79
Standard atomic mass	207.2	63.54	58.69
Solubility in water (g/100 ml)	52	156	243
Charge	2^+	2^+	2^+
Density (g/cm^3)	4.53	3.05	2.05

Table 3: Equilibrium parameters for different isotherm models for biosorption of metal ions onto IB

Model	**parameters**	**Pb(II)**	**Cu(II)**	**Ni(II)**
Langmuir $q = \frac{bq_m C_e}{1 + bC_e}$	qm(mg/g)	52.763	27.785	36.973
	b(l/mg)	0.3029	0.0699	0.0172
	R_L	0.06	0.25	0.54
	R2	**0.9107**	**0.9682**	**0.8976**
Freundlich $q = KC_e^{1/n}$	K, (mg/g)(mg/l)(1/n)	14.283	3.291	1.069
	n,-	2.551	1.941	1.387
	R2	**0.8797**	**0.9711**	**0.8917**
Redlich–Peterson $q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{\beta_{RP}}}$	k_{RP}(mg/g)	65.284	10	68.960
	a_{RB}(l/mg)	458.1931	0.4	640.86
	ß,-	0.60811	0.01	0.279
	R2	**0.87974**	**0.835**	**0.8911**
Sips $q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}$	ks, (l/g)	13.106	3.917	8.533
	ß	0.325	28.631	46.920
	as,(l/mg)	0.093	0.309	0.8165
	R2	**0.8799**	**0.6077**	**0.6211**
Khan $q_e = \frac{q_{max} b_k C_e}{(1 + b_k C_e)^{a_k}}$	q_{max} (mg/g)	1.518	38.07	69.615
	b_k,(l/mg)	307.441	0.0484	0.007
	a_k	0.608	1.2045	3.568

	R2	**0.8796**	**0.9783**	**0.9070**
Radke–Prausnitz $q_e = \frac{K_{RP}C_e}{1+\left(\frac{K_{RP}}{F_{RP}}\right)C_e^{1-N_{R}}}$	kRP,(l/mg)	69.625	------$^{\alpha}$	33.763
	FRP	14.284	------$^{\alpha}$	1.0423
	NRP	0.391	-------$^{\alpha}$	0.7248
	R2	**0.879**	-------$^{\alpha}$	**0.891**
Toth $q_e = \frac{q_{max}b_T C_e}{\left[1+(b_T C_e)^{\frac{1}{n_T}}\right]^{n_T}}$	qm (mg/g)	3671.7684	23.972	------$^{\alpha}$
	bT	15.3969	0.070	------$^{\alpha}$
	nT	9.8594	0.766	--------$^{\alpha}$
	R2	**0.878**	**0.9785**	--------$^{\alpha}$

α : the isotherm model could not be applied for the experimental data

Table 4: Pseudo-first-order and Pseudo-second-order kinetic models for the biosorption of of Pb(II), Cu(II), and Ni(II) onto IB

Model	**Parameters**	**Pb(II)**	**Cu(II)**	**Ni(II)**
Pseudo-first-order (Equation 2.24)	q_e(mg/g)	-0.0749	-0.0638	-0.0526
	K_1(min^{-1})	1.2137	0.3955	2.3183
	Correlation coefficient	0.7802	0.7985	0.5424
Pseudo-second-order (Equation 2.28)	qe cal. (mg/g)	20.5338	4.6904	0.7977
	K_2(mg/g.min)	0.0191	0.00283	0.1052
	h_0	8.0532	0.0622	0.0669
	Correlation coefficient	0.9997	0.9639	0.9983

Table 5: Thermodynamic parameters

Metal ions	Temperature (K)	ΔG° (kJ.mol^{-1})	ΔH° (kJ.mo1^{-1})	ΔS° (J.mol^{-1}K^{-1})	R^2
Pb(II)	293 303 313 323	-4.58242 -5.17754 -5.40474 -5.5097	4.099259	0.03009	93.68
Cu(II)	293 303 313 323	-6.47878 -6.39198 -6.92187 -7.81466	7.073726	0.04538	89.94
Ni(II)	293 303 313 323	-1.3811 -1.6072 -1.8627 -1.97303	4.550359	0.02031	98.83

Table 6: Comparison of results obtained in this study with other studies for removal of heavy metals ions using different biomass

Metal ions		mg/g		
Pb(II)	Pseudomonas putida	56.2	Pardo et al. (2003)	Bacterial
Cu(II)	Pseudomonas putida	15.8	Pardo et al. (2003)	
Ni(II)	Bacillus thuringiensis	45.9	Ozturk (2007	
Pb(II)	Penicillium chrysogenum	116	Niu et al. (1993)	Filamentous
Cu(II)	Penicillium chrysogenum	92	Deng and Ting (2005a)	
Ni(II)	Penicillium chrysogenum	13	Tan and Cheng (2003)	
Pb(II)	Cladophora glomerata (G)	40	Romera et al., 2006	l g a

Cu(II)	Chlorella miniata (G)	35	Romera et al., 2006	
Ni(II)	Chlorella vulgaris	20	Romera et al., 2006	
Pb(II)	IB	**52**	This study	
Cu(II)		**38**		
Ni(II)		**27**		

التحقيق في الديناميكا الحرارية، الحركية والتوازن معلمات دفعة الامدصاص الحيوي لايونات الرصاص (II) والنحاس (II)، والنيكل (II) من الوسط المائي باستخدام مواد حيوية ممدصة منخفضة التكلفة

مهند جاسم محمد رضا
قسم الهندسة البيئية
جامعة بغداد

علي شهاب احمد
قسم التقانة الاحيائية
جامعة النهرين

نغم نافع رووف
قسم الهندسة البيئية
جامعة بغداد

الخلاصة

في هذه الدراسة لمواد حيوية ممدصة ميته حبيبية (قطر الحبيبة = 0.433 ملم) تم اخذها من احواض التجفيف لمحطة الرستمية لمعالجة المخلفات السائلة بغداد-العراق . استخدمة هذه المواد للتحقق من افضل الظروف لامدصاص ايونات الرصاص , النحاس و الكادميوم من الوسط المائي. تم دراسة تاثير كل من تركيز ايونات المعادن الثقيلة (50-200 ملغ/ لتر), زمن الاتزان (0-180 دقيقة), الاس الهيدروجيني (2-9) , سرعة الخلط (50-200 دورة/ دقيقة), قطر الدقائق (0.433 ملم) و تركيز المادة الممدصة (0.05-1 غ/ 100 ملم). تم استخدام ست موديلات رياضية لتمثيل اتزان الامتصاص الحيوي و ثوابت الموديلات الوضعية وذلك لايجاد اعظم قابلية سحب لايونات المعادن (Langmuir, Freundlich, Redlich–Peterson, Sips, Khan, and Toth) وقد بينت النتائج ان موديل Langmuir افضل موديل رياضي لتمثيل اغظم سحب لايونات كل من الرصاص و النيكل (52 و 36.97 ملغ/ غم) . بينما لايونات النحاس كان اعظم قابلية سحب 38.07 ملغ/غم باستخدام موديل خان.

الدراسة الحركية بينت افضل ظروف هي 400 دورة بالدقيقة لسرعة الخلط وكان اقل مقاومة لانتقال الملوثات الى المادة الممدصة تخضع لموديل الحركة من النوع الثاني ($R 2 = 0.99$), كافضل تطابق و كانت 42.84×10^{-5}, 2.85×10^{-5} , 1.57×10^{-5} m/s لكل من ايونات الرصاص النحاس والكادميوم

الدراسة الميكانيكية الحركية بينت ان التفاعل من النوع العفوية والطاردة للحرارة في الطبيعتها.