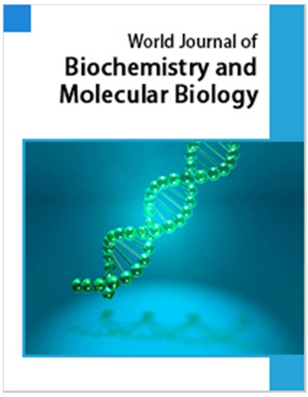
World Journal of Biochemistry and Molecular Biology
2017; 2(6): 46-51
http://www.aascit.org/journal/wjbmb

American Association for Science and Technology



Removal of Fe (III), Cu (II), and Co (II) from Aqueous Solutions by Orange Peels Powder: Equilibrium Study

Khaled Muftah Elsherif[1, *], Abdunaser Mabrok Ewlad-Ahmed[2], Abdullah Treban[2]

[1]Chemistry Department, Faculty of Science, University of Benghazi, Benghazi, Libya
[2]Chemistry Department, Faculty of Arts and Science Msallata, Al-Mergheb University, Al-Khoms, Libya

Email address

elsherif27@yahoo.com (K. M. Elsherif)
[*]Corresponding author

Citation

Khaled Muftah Elsherif, Abdunaser Mabrok Ewlad-Ahmed, Abdullah Treban. Removal of Fe (III), Cu (II), and Co (II) from Aqueous Solutions by Orange Peels Powder: Equilibrium Study. *World Journal of Biochemistry and Molecular Biology.* Vol. 2, No. 6, 2017, pp. 46-51.

Keywords

Biosorbent,
Heavy Metals,
Orange Peels,
Fe,
Cu,
Co

Received: September 12, 2017
Accepted: November 16, 2017
Published: December 18, 2017

Abstract

We have studied the efficiency of a low-cost biosorbent for the removal of some heavy metal ions. In this work, orange peels (OP) powder for the removal of Fe(III), Cu(II), and Co(II) ions from aqueous solutions has been investigated. Several parameters which affect the adsorption process have been evaluated. These parameters included; pH, contact time, biosorbent dose, and initial metal ion concentration. Batch adsorption studies were carried out to evaluate theses effects. The best biosorption conditions were found as follows: pH at (4-5), biomass dosage of 0.1 g, and contact time at 30 mins. Freundlich and Langmuir isotherm models were used to fit the adsorption data. The adsorption capacity of OP for metal ions were also evaluated using Langmuir isotherm model. The maximum adsorption capacities (Q_m) estimated from the Langmuir isotherm model for Fe(III), Cu(II), and Co(II) were 12.26, 129.9 and 11.48 mg/g respectively. The Freundlich constant (n) and separation factor (R_L) values suggest that the metal ions were favorably adsorbed onto biosorbent.

1. Introduction

Wastewater from industrial activities is the major source of aquatic pollution. Heavy metals contamination is the major concern of the aquatic pollutants due to their toxicity and threat to human life and the environment. Aqueous industrial wastes; which are either discharged directly or transported into the environment, from several activities, such as metal plating, mining, tanning, etc. cause contamination by heavy metals [1-4].

Therefore, removal of heavy metals from wastewater are too important to save public health and environment [5]. There are several methods for treating wastewater which contains heavy metal have been developed and evaluated. These methods include liquid extraction or electro-dialysis [6], oxidation/reduction, ion exchange [7], filtration, membranes and evaporation [8-11], and precipitation [12, 13]. Most of them are extremely expensive or inefficient for metal removal from diluted solutions containing from 1 to 100 mg/L of heavy metals [14]. For low concentration of heavy metal ions (< 100 mg. L^{-1}), adsorption methods are much preferable techniques. Activated carbon as an adsorbent has been widely used for treating industrial wastewater. At present, the widespread industrial use of low-cost biosorbents for wastewater treatment is strongly recommended, due to their local availability, technical feasibility, engineering applicability and cost effectiveness [15, 16]. Many biomaterials have been studied as biosorbents for removal of heavy metals such as clay, leaves, peels, husks, stems and roots [17].

The aim of the this work is to study the adsorption and removal of iron (III), copper (II), and cobalt (II) from aqueous solutions using orange peels powder as bioadsorbent. Adsorption equilibrium isotherms are carried out in batch process. The effect of different experimental conditions such as contact time, adsorbent mass, initial concentration and pH on the percent removal and adsorption capacity is studied. Equilibrium isotherm data are analyzed and modeled using different models.

2. Materials and Methods

2.1 Preparation of Orange Peels Powder

The orange peels were washed and dried in an oven at 70˚C for 24 hrs. The dried materials were ground using a laboratory mill and sieved through 500 µm size fraction using an American Society for Testing and Materials (ASTM) standard sieve

2.2 Preparation of Metal Solutions

All chemicals used were of analytical reagent (AR) grade. Metal stock solutions (Fe (III), Cu (II), and Co (II)) of 1000 mg/L were prepared by dissolving an appropriate amount of $Fe(NO_3)_3$, $Cu(NO_3)_2$, and $Co(NO_3)_2$ salts in deionized water. The stock solutions were diluted to the required concentrations using deionized water. The solution pH was adjusted using 0.1 mol/L HCl or 0.1 mol/L NaOH.

2.3 Analysis

The concentrations of metal ions in the solutions before and after equilibrium were determined by Molecular Absorption Spectrophotometer 6305 from JENWAY. The pH of the solution was measured with pH Meter 3505 from JENWAY. The determination of iron (III) and cobalt (II) as thiocyanate complex, and copper (II) as ammonia complex were carried out according to the published work [18, 19]. The range of calibration curve concentrations of metal ions prepared from stock solution varies between 1-5 ppm, 100-600 ppm, 5-40 ppm for Fe, Cu, and Co respectively. The absorption spectra and calibration curves for three complexes are shown in Figure 1.

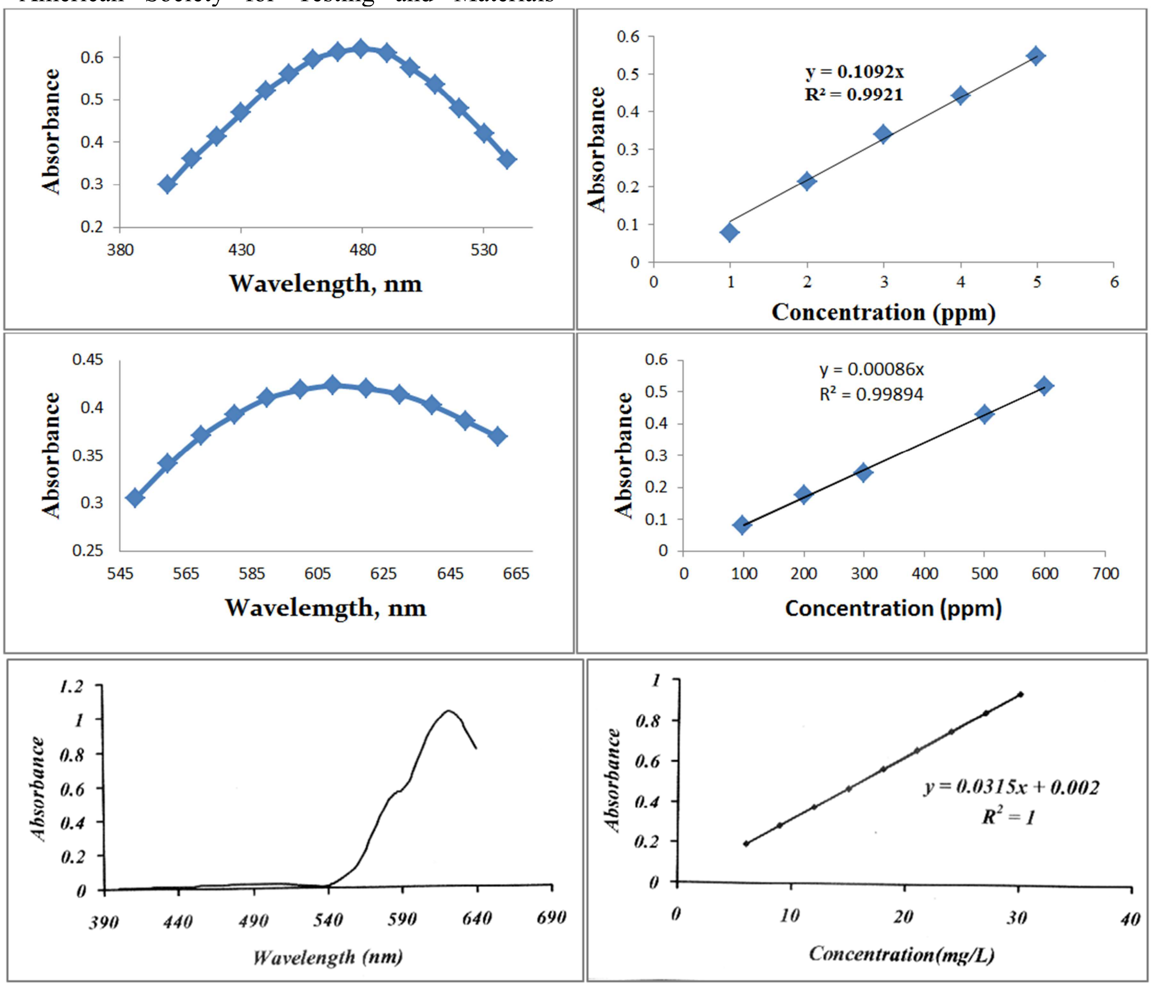


Figure 1. *Absorption spectra and calibration curves for: (a) $Fe(SCN)^{+3}$ (b) $Cu(NH_3)_4^{+2}$ (c) $Co(SCN)^{+2}$.*

2.4 Batch Biosorption Experiments

The adsorption experiments were carried out in a series of 150 mL Erlenmeyer flasks containing 50 ml of metal ions solution, 0.500 g orange peels powder and if necessary, an appropriate volume of HCl or NaOH solutions was used to adjust the pH of the solution. The solutions were shaken (150 rpm) at 25°C. Then solutions were filtered by Whatman filter paper. The removal percentage (% R) was calculated according to the following equation:

$$(\%R) = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

Where: C_o and C_e are initial and final concentrations in mg. L^{-1}, respectively. The amount of biosorption was calculated based on the difference between the initial (C_o, mg. L^{-1}) and final concentration (C_e, mg. L^{-1}) in every flask, as follows:

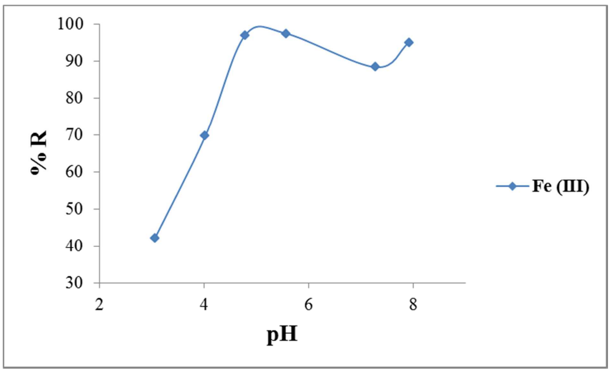
$$(Q_e) = \frac{C_o - C_e}{M} \times V \quad (2)$$

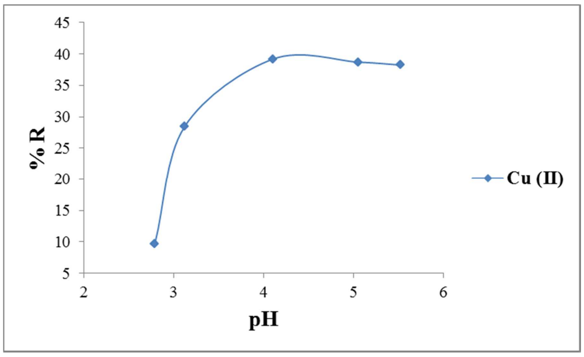
where Q_e is the metal uptake capacity (mg. g^{-1}), V the volume of the metal solution in the flask (L) and M is the dry mass of biosorbent (g)

3. Results and Discussion

3.1. Effect of pH

The effect of pH on the adsorption of Fe(III), Cu(II) and Co(II) ions onto orange peels powder was studied because it has been identified as one of the most important parameter that effects metal adsorption. The studied were as follows: 2.0–8.0 for Fe and Co, and 2-6 for Cu, as shown in Figure 2. In acidic media (pH < 3), the metal adsorption was low, which is due to the competition ability of hydrogen ions ($[H^+]$ is high) with metal ions to active sites on the biosorbent surface. The maximum adsorption (higher percent removal % R) was observed at pH between (5.0-6.0) for Fe and (4.0-5.0) for Cu and Co. Therefore, all remaining biosorption experiments were carried out at these pH values. Lower pH values (highly acidic solutions –pH < 2.0) have not been studied because the overall active sites on the biosorbent surface became positive and completely bonded with protons, which results in lower uptake of metal. Decreasing in percent removal at higher pH (pH > 6) is related the formation of metal hydroxyl.





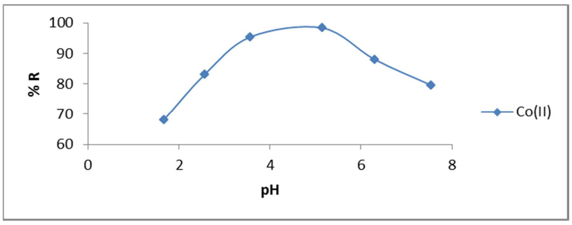
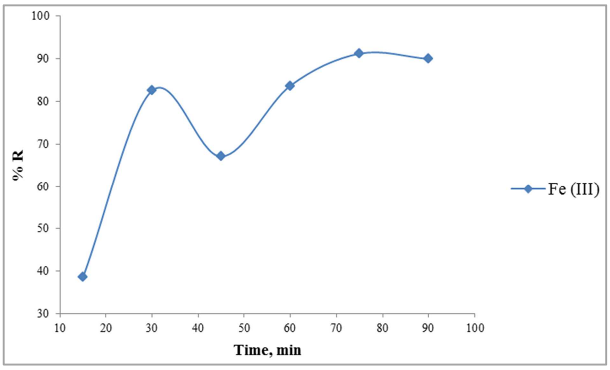
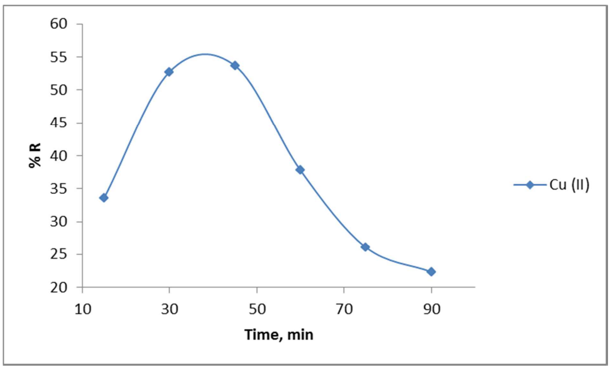


Figure 2. Effect of pH on percent removal of metal ions.

3.2. Effect of Contact Time

The time required for the system to reach the equilibrium is an important parameter for designing batch adsorption experiments. Therefore, the effect of contact time on the adsorption of Fe(III), Co(II) and Cu(II) onto orange peels powder has been evaluated. The percent removal of Fe(III), Co(II) and Cu(II) increased gradually until the contact time reached 30 min (for Fe and Co) and 40 min (for Cu), as shown in Figure 3. Further increase in contact time did not increase the adsorption. Therefore, the best contact time was selected as 30 min (for Fe and Co) and 40 min (for Cu) for further experiments.





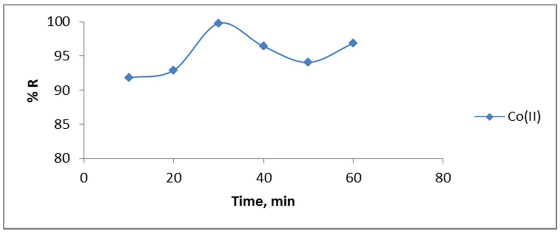


Figure 3. *Effect of contact time on percent removal of metal ions.*

3.3. Effect of Initial Metal Ion Concentration

Fe(III), Co(II), and Cu(II) ions adsorption onto orange peels powder has been investigated in batch experiments using different initial metal ion concentrations. The relation between metal uptake (mg. g^{-1}) and initial metal ion concentration is shown in Figure 4. As shown in Figure 4, metal ion adsorption is possible at lower concentrations, but as the concentration is increased, the driving force also increased [21], which favored the adsorption at higher concentrations. The equilibrium uptake of the adsorbent was observed increasing with an increasing the initial concentration of metal ions and then reach a maxima at a concentration of 100 ppm and 600 ppm in the case of Co and Cu, respectively.

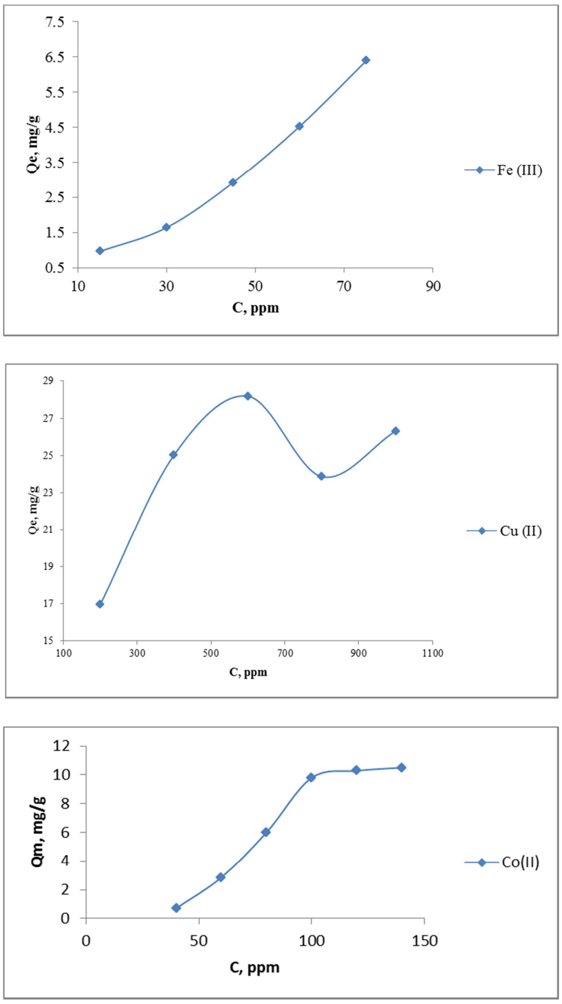


Figure 4. *Effect of initial concentration on metal uptake in mg/g.*

3.4. Effect of Adsorbent Dose

The adsorbent dosage is an important parameter to determine the capacity of a biosorbent for a given initial ion concentration. Adsorption of Fe(III), Cu(II), Co(II) onto orange peels powder was studied by adding different dosage of orange peels powder from 0.1 to 1.0 g in the treated aqueous solution. Figure 5 shows metal uptake (mg. g^{-1}) by orange peels powder as a function of biosorbent dose. The metal uptake sharply decreases with the biosorbent dose up to 1 g. This can be explained by the fact that the surface of the biosorption has more binding sites remain unsaturated and the number of these sites which are available for adsorption decreases by increasing the biosorbent dose.

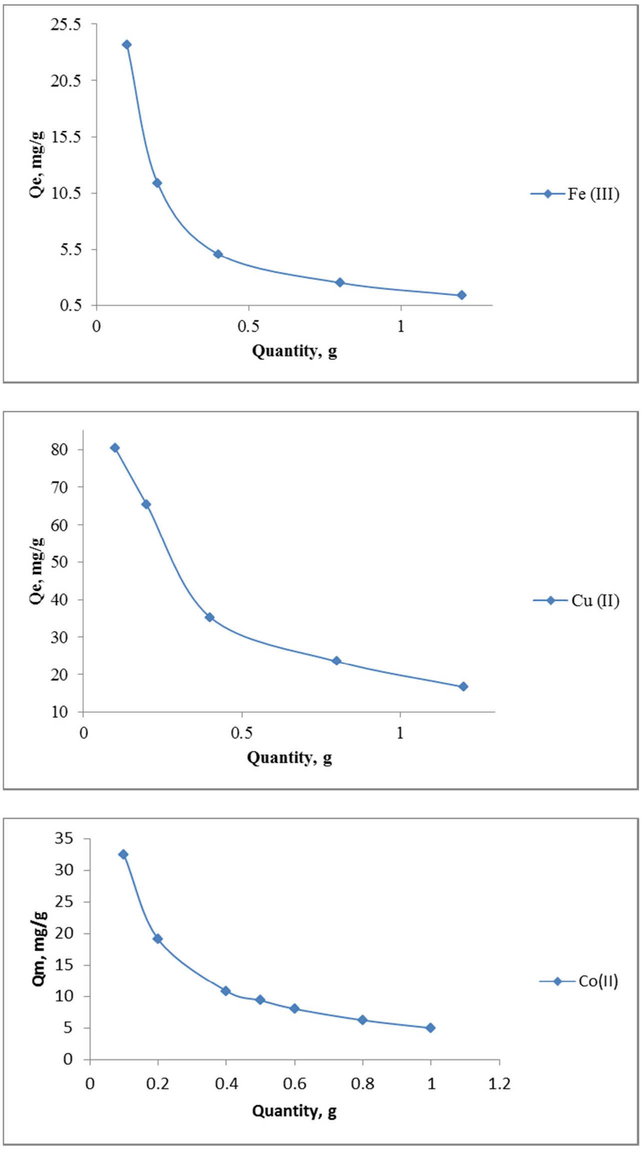


Figure 5. *Effect of adsorbent dose on percent removal of metal ion.*

3.5. Biosorption Isotherm

An adsorption isotherm describes the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Adsorption of Fe(III), Co(II), and

Cu(II) ions onto orange peels powder was modeled using two adsorption isotherms.

3.5.1. Langmuir Isotherm

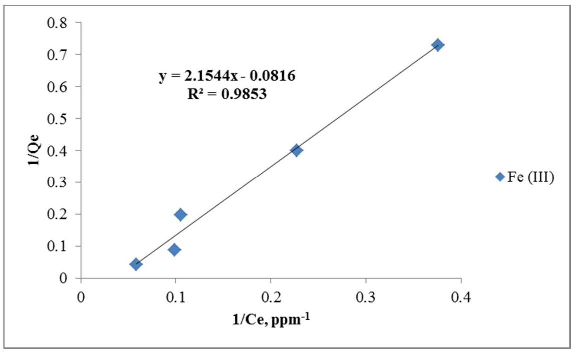
The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The linear form of the Langmuir isotherm model is described as [22]:

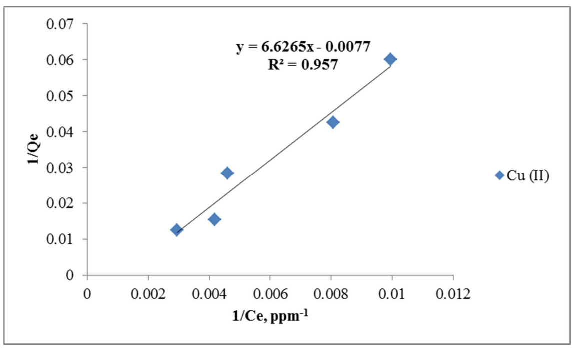
$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{bQ_mC_e} \quad (3)$$

where b is the Langmuir constant related to the energy of adsorption and Q_m is the maximum adsorption capacity (mg /g). Values of Langmuir parameters b and Q_m were calculated from the slope and intercept of the linear plot of $1/Q_e$ versus $1/C_e$ as shown in Figure 6. Values of Q_m, b and regression coefficient R^2 are listed in Table 1. These values for orange peels powder biosorbent indicated that Langmuir model describes the biosorption phenomena favorable. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, R_L expressed as in the following equation:

$$R_L = \frac{1}{1+bC_0} \quad (4)$$

The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The R_L was found to be 0.0 – 1.0 for concentration range used with metal ions, which indicates the favorable biosorption.





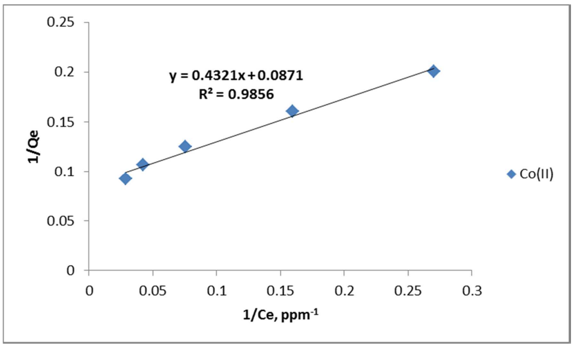


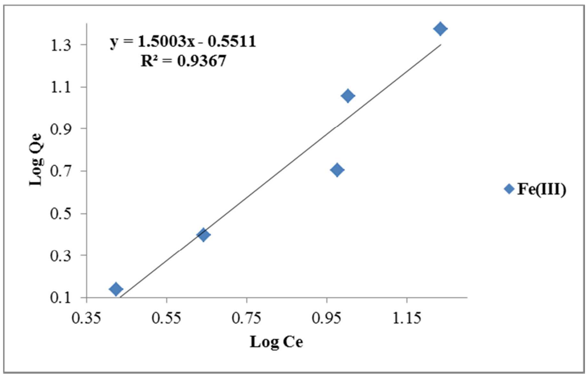
Figure 6. *Langmuir isotherm for Fe, Cu, and Co ions adsorption onto orange peels powder.*

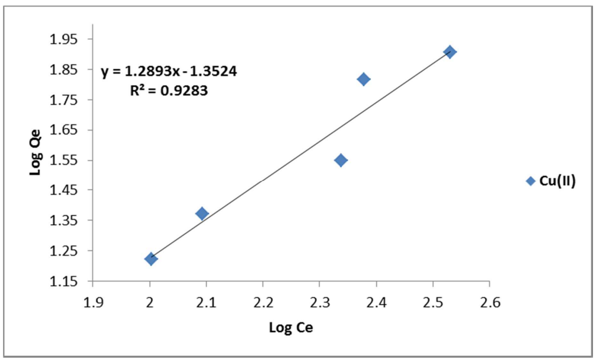
3.5.2. Freundlich Isotherm

The Freundlich isotherm model is the well-known earliest relationship describing the adsorption process. This model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules and the application of Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. This isotherm is an empirical equation and can be employed to describe heterogeneous systems and is expressed as follows in linear form [23]:

$$logQ_e = \frac{1}{n}logC_e + logK_f \quad (5)$$

where K_f is the Freundlich constant related to the bonding energy. 1/n is the heterogeneity factor and n (g/L) is a measure of the deviation from linearity of adsorption. Freundlich equilibrium constants were determined from the plot of $logQ_e$ versus $logC_e$, Figure 7, on the basis of the linear of Freundlich equation. The values of K_f, n, and R^2 are listed in Table 1.





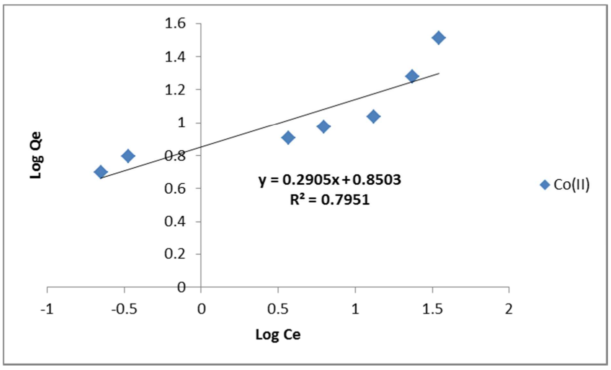


Figure 7. *Freundlich isotherm for Fe, Cu, and Co ions adsorption onto orange peels powder.*

Table 1. *Langmuir and Freundlich isotherm constants for biosorption of metal ions onto orange peels powder.*

Co (II)	Cu (II)	Fe (III)	Isotherm constants
Freundlich model			
3.442	0.776	0.667	n
7.084	22.511	3.557	K_f
0.7951	0.9283	0.9367	R^2
Langmuir model			
0.202	0.001	0.038	b (L mg^{-1})
11.481	129.870	12.255	Q_m (mg g^{-1})
0.9856	0.957	0.9853	R^2
0.047	0.676	0.357	R_L

4. Conclusion

Biosorption by orange peels powder is a safe, ecofriendly and effective method for the removal of Fe(III), Co(II), and Cu(II) ions from aqueous solutions. Biosorption process parameters like pH, initial metal ions concentration, biosorbent dose, and contact time were studied. The biosorption isotherms have been well be fitted by both the Langmuir and Freundlich models. It can be concluded that since the orange peels powder is an easily, locally available, low-cost adsorbent and has a considerable high biosorption capacity, it may be treated as an alternative adsorbent for treatment of aqueous solutions containing Fe(III), Co(II), and Cu(II) ions.

Acknowledgements

Authors are thankful for Chemistry Department, Faculty of Arts and Science Msallata, Elmergib University for providing the necessary facilities to carry out this work.

References

[1] E. P. Ortega, R. Leyva-Ramos, J. V. Flores-Cano, *Chem. Engin. J.,* 225 (2013) 535-546.

[2] F. Fu, Q. Wang. J., *Environ. Ger.,* 92 (2011) 407-418.

[3] H. Es-sahbany, M. Berradi, M. Belfakir, M. S. El Youbi, *Mor. J. Chem.,* 4 (2) (2016) 352-360.

[4] M. Berradi, A. El Harfi., *J. Wat. Sci. Envir. Techno.,* 1 (2) (2016) 76-80.

[5] J. Wang, C. Chen, *Biores. Techno.,* 160 (2014) 129-141.

[6] H. Bousfiha, E. Rifi, A. Essamri, Z. Hatim, *Comp. Rend. Chim.,* 8 (2005) 215-218.

[7] M. A. Khosa, S. S. Shah, X. Feng, *J. Chem. Engin.,* 244 (2014) 446-456.

[8] Maher, M. Sadeghi, A. Moheb, *Desalin,* 352 (2014) 166-173.

[9] K. M. Elsherif, A. El-Hashani, A. El-Dali and R. El-kailany, *Int. J. Res. Pharm. Chem.,* 4 (2) 2014 267-273.

[10] K. M. Elsherif, A. El-Hashani, A. El-Dali, M. Musa, *Int. J. Anal. Bioanal. Chem.,* 4 (2) 2014 58-62.

[11] K. M. Elsherif, A. El-Hashani, A. El-Dali, M. Saad, Int. *J. Chem. Pharm. Sci.,* 2 (6) 2014 890-897.

[12] S. Kubilay, R. Gürkan, A. Savran, and T. Sahan, *Adsorp,* 13 (2007) 41-51.

[13] D. Ozdes, C. Duran, and H. B Senturk, *J. Envir. Manage,* 92 (2011) 3082-3090.

[14] S. S. Gupta and K. G. Bhattacharyya, *J. Hazard. Mater,* 128 (2006) 247-257.

[15] S. Al-Asheh, F. Banat, R. Al-Omari, and Z. Duvnjak, *Chemosphere,* 41 (2000) 659.

[16] K. K. Panday, G. Prasad, and V. N. Singh, *Wat. Research,* 19 (7) (1985) 869-873.

[17] A. K. Chopra and Chakresh Pathak, *J. App. Natural Sci,* 2 (2) (2010) 318-329.

[18] Z. Marczenko, Spectrophotometric Determination of Elements, Ellis Harwood Ltd. Chichester Halsted Press, a Division of John Wiley and Sons. Inc., New York, London, Sydney, and Toronto, 1986.

[19] A. G. Iv and B. Tamhina, *Croatica Chem. Acta,* 76 (4) (2003) 323-328.

[20] E. M. Aboushloa and A. M. Etorki, *British J. Environ. Sci.,* 3 (6) 2015 54-64.

[21] K. Tiemann, J. Gardea, G. Gamez, K. Dokken, I. Cano, M. Renner, and L. Furenlid, *Environ. Sci. Technol.,* 34 (2000) 693–698.

[22] I. Langmuir, *J. Am. Chem. Soc.,* 40 (1918) 1361-1403.

[23] H. M. F Freundlich and W. Hellen, *J Amer. Chem Soc.,* 61 (1939) 2228-2230.