BIOSORPTION OF COPPER (II), ZINC (II) AND NICKEL (II) FROM AQUEOUS MEDIUM USING AZADIRACHTA INDICA (NEEM) LEAF POWDER

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Abstract

Electroplating and metal working industries discharges effluent that contains toxic heavy metals such as copper (Cu(II)), nickel (Ni(II)) and zinc (Zn(II)) ions. Biosorption has been recognized as ahhigh efficiency and low-cost alternative method that can be used to treat the industrial effluent for heavy metal removal. In this study, mature leaves of neem (Azadirachta indica) was used as the potential biosorbent to study its adsorption behavior of Cu(II), Ni(II) and Zn(II) ions from aqueous medium solution in single and multicomponent system. The biosorption experiment was carried out in a batch process at constant room temperature and initial heavy metal concentration. Optimal biosorbent dosage, pH and contact time for the biosorption process of the three metals were investigated. At optimal pH of 6 and biosorbent dosage of 0.2g, the maximum metal uptake for Cu(II), Ni(II) and Zn(II) were 34mg/g, 26mg/g and 37mg/g respectively. For single metal solutions, biosorption equilibrium data for Cu(II) and Zn(II) fit the Freundlich model, while Ni(II) fitted the Langmuir isotherm. In the multicomponent system, the Langmuir isotherm fitted well for the equilibrium data of mixed solution of Cu(II), Ni(II) and Zn(II).

Keywords : Biosorption, neem leaves powder, heavy metal removal, batch process, single system, multicomponent system.

I. Introduction

Industrial processes such as metal cleaning, fertilizer industry, textile industry and mining industry release many types of toxic heavy metal such as copper, nickel, lead and chromium (Sulaiman & Garba, 2014). The presence of heavy metals in industrial wastewater effluent has been a major concern due to its possible negative effects to the environment and mankind if not disposed properly. Electroplating industry discharges
wastewater that contains hazardous and toxic materials including heavy metals. It is reported that the electroplating industries release a large amount of Cu(II), Zn(II) and Ni (II) in its effluent. At times the effluent is illegally disposed into main water stream without proper treatment(Sousa et al.,2009). These heavy metals are non-biodegradable and accumulate in the environment. Accumulated heavy metals can eventually affect human health when exposed via food and water sources, and threaten the wildlife and environment (Kulkarni, Shetty, & Srinikethan, 2014).

In order to overcome this problem, various methods and techniques have been proposed and used in treating the effluent to be free of heavy metal and safe to be discharged to the environment. Some of the methods are chemical precipitation, ion exchange, electrochemical treatment, membrane technologies and adsorption on activated carbon. But these techniques have their own limitations such as lack of efficiency, higher energy requirement and extremely expensive especially when treating a low concentration of heavy metal present in large amount of waste water (Wang & Chen, 2006) Removal of heavy metal by adsorption using activated carbon is an easy operation with higher efficiency which is widely acceptable and well-established in industry. However, it may need additional chemicals to enhance the effectiveness. Due to the disadvantages of the conventional technologies used, a more convenient technique which is lower in cost and higher in efficiency is approached. In the past few decades, biosorption by means of metabolism-independent reaction that involve the adsorption of heavy metals using microbial biomass as adsorbent has been developed as a potential technique for removal and recovery of heavy metal from waste effluent. The adsorbent used can be both living and dead organisms, such as algae, seaweed, powdered leaves, coconut shell, lignin, saw dust and ash (Lima et al., 2007). Biosorption using natural resources exhibit more efficient adsorption process, low operation cost, less sludge formation, no additional chemical required, regeneration of biosorbent and metal recovery (Arshad, Zafar, Younis, & Nadeem, 2008).

This study will focus on biosorption using \textit{Azadirachta indica} (Neem) leaves as the biosorbent to remove heavy metals from industrial wastewater. \textit{Azadirachta indica} or Neem tree is belonging to \textit{Meliaceae} mahogany family. The plant grows in tropical and sub-tropical regions and is native to India, Bangladesh, Thailand, Nepal and Pakistan (Khadivinia et al., 2014). Neem tree is well-known for insecticidal, fungicidal and antibacterial properties. All the parts of the trees are usually used for medication purposes such as dental care, antiseptics and treatment for malaria. Fresh Neem leaves contain 59.4% moisture, 22.9% carbohydrates, 7.1% proteins, 6.2% fiber, 3.4% minerals, 1% fats and host of other chemical (Sharma & Bhattacharyya, 2005). The surface of the Neem leaves has negative charge due to the presence of polar groups such as –NH2, -COOH, and -OH. The surface structure of the leaf remains stable during long-time agitation treatment, making it a good adsorbent (Febriana, Lesmana, Soetaredjo, Sunarso, & Ismadji,2010). The objectives of this study are to investigate the effectiveness of neem
leaves powder in biosorption of Cu(II), Zn (II) and Ni (II) from the aqueous medium in single and multicomponent system using the adsorption isotherms.

II. Experimental Procedure

a) Biosorbent Preparation

The biosorbent was prepared from mature and fresh leaves of neem tree. The collected neem leaves were cleaned and washed thoroughly to remove impurities to obtain a clean stock of biomass. A clean stock of biomass is desired to ensure any undesired effect on biosorption performance can be avoided. After a few times of washing process, the leaves were dried under sunlight for 6 hours, and then the drying process was continued using oven for 24 hours at 60°C to obtain crisp structures. Temperature of 60°C is chosen in order to maintain the active functional group on the surface of the neem leaves' surface. The, the crisp dried leaves were grinded to obtain a neem leaves powder (NLP). The powder was sieved for particle size range of 90 to 100 μm and kept in container for experiment use.

b) Preparation of chemical solution

The stock solution of Cu(II), Zn(II) and Ni(II)) ions were prepared by diluting copper(II) chloride hexahydrate salts, zinc(II) nitrate hexahydrate salt and nickel(II) nitrate hexahydrate salt with deionised water to obtain 1L stock solution to obtain concentration of 100mg/L for each ions. For the multicomponent sample, equal ratio of volume from each stock solution was mix and stirred. Standard solutions of 5mg/L, 10mg/L, 30mg/L, 50mg/L and 70mg/L for each solutions were prepared for spectroscopic calibration of Inductively Coupled Plasma Spectrometer (Optima 7000 DV ICP-EOS by Perkin Elmer).

c) Adsorption experiment

The adsorption of Cu(II), Zn(II) and Ni(II) on NLP were analyzed in batch mode experiment. Biosorbent dosage of 0.2g, 0.4g, 0.6g, 0.8g and 1.0g were added into six different conical flasks containing 100mL of Cu(II) ion aqueous solution. The flasks were agitated at room temperature using shaker at constant speed of 125rpm. At every 15 minutes interval for the first one hour, 1mL of aqueous solution was withdrawn from the conical flask and diluted with 9mL of deionised water. The process was repeated for the subsequent 2 hours with 30 minutes interval. The diluted sample solutions were then analyzed using ICP to determine the remaining concentration of metal ions after the adsorption process. The experiment was repeated using Zn(II) and Ni(II) ion solutions. Once the optimal biosorbent dosage was obtained, the optimal pH was identified using the same experimental procedure. The amount of metal uptake by the NLP was evaluated using equation (1).

\[
q_t = \frac{C_0 - C_t V}{m}
\]

Where,
**d) Adsorption isotherm**

The isotherm of biosorption process defines the functional relationship between the adsorbate and the biosorbent at constant temperature. Adsorption isotherm is used to evaluate the efficiency of the interactions between metal ion and biomass (Amirnia, Ray, & Margaritis, 2015). In this study, the adsorption isotherm is used to study the effectiveness of NLP biosorption in single system and multicomponent system. Langmuir adsorption isotherm is used to predict the monolayer adsorption of material onto the adsorbent surface. The equation is shown as in equation (2).

\[
\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m}
\]

(2)

Where,
- \(C_e\) = equilibrium concentration of adsorbate (mg/L)
- \(q_e\) = equilibrium adsorption capacity of adsorbent (mg/g)
- \(q_m\) = maximum adsorption capacity (mg/g)
- \(K_L\) = Langmuir sorption equilibrium constant (L/mg)

Multilayer adsorption of ions to the binding site of the biosorbent is described by Freundlich adsorption isotherm. The equation is expressed as in equation(3).

\[
\log q_e = \log K_F + n_F \log C_e
\]

(3)

Where,
- \(C_e\) = equilibrium concentration of adsorbate (mg/L)
- \(q_e\) = equilibrium adsorption capacity of adsorbent (mg/g)
- \(n_F\) = dimensionless Freundlich adsorption affinity
- \(K_F\) = Freundlich sorption equilibrium constant (L/mg)

**III. Results and Discussion**

a) Effect of Contact time

The effect of contact time on heavy metals uptake by NLP was investigated at 5 different dosage of NLP and the results are shown in Fig. 1. The adsorption experiment was conducted within 3 hours at constant room temperature and initial metal concentration.
From Fig. 1, the trend of metal uptake rate by NLP for each heavy metal shows the same pattern. The metal uptake rates were increasing rapidly up to 15 minutes, and then attain equilibrium until 180 minutes. Rapid biosorption of heavy metals at first 15 minutes was due to high availability of active sites present on the NLP. After that, the number of active sites available became less and eventually all were fully occupied. Hence, no more heavy metals were adsorbed. At this point equilibrium was achieved.

Fig. 1 Effect of contact time on biosorption capacity for different metal ions (a) Cu (II), (b) Zn (II) and (c) Ni (II) with different NLP loadings
The influence of NLP dosage on biosorption process of heavy metals was investigated at room temperature; 15 minutes contact time and initial concentration of 100mg/L for 5 different biosorbent dosages which were 0.2g, 0.4g, 0.6g, 0.8g and 1.0g. Referring to Fig. 2, as the NLP dosage increases, the metal uptake rate decreased for all the three ions. The decrease for Cu(II), Zn(II) and Ni(II) were from 36mg/g to 8mg/g, 32mg/g to 4.5mg/g and 38mg/g to 5.5mg/g respectively, when the NLP dosage increased from 0.2g to 1.0g. Hence, 0.2g is concluded as the optimal NLP dosage since it gave the highest adsorption capacity for all the three ions. The reduction of adsorption capacity at higher NLP dosage could be due to the interaction of the biosorbent particles. At higher dosage, NLP tend to aggregate, thus reducing the total biosorbent surface area. (Khataee, Vafaei, & Jannatkhah, 2013).

Fig. 2 Equilibrium biosorption capacity of metal ion at different loadings of NLP

(c) Effect of pH

pH plays an important role in improving the biosorption process efficiency. pH influences the adsorbate solubility and ionizing capacity of the functional group in the biomass (Khataee et al., 2013). The experiment to investigate the optimal pH was carried out by varying pH values between 4 and 7 at room temperature and optimal NLP dosage of 0.2g. Fig. 3 clearly shows that the optimum pH for Zn(II) and Cu(II) is 6 with maximum equilibrium adsorption capacity of 41mg/g and 39mg/g respectively. The maximum Ni(II) uptake is observed pH 7 with adsorption capacity of 37mg/g. Lower adsorption capacity is observed at lower pH due to accumulation of H+ ions that will compete with the metal ions during adsorption process which will disturb the metal uptake by the biomass. Increasing pH value will reduce the competition between the heavy metal ions and the H+, hence improving biosorption capacity. At pH higher than the optimal pH, accumulation of OH- will decrease the biosorption of metal ions at adsorbent-adsorbate interface, thus reducing the adsorption capacity of metal ions.
IV. Adsorption Isotherm

In the present study, the adsorption isotherm is used to study the effectiveness of NLP biosorption in single and multicomponent system. The Langmuir and Freundlich isotherm models were applied to the equilibrium data of Cu(II), Zn(II) and Ni(II). The results are shown in Fig. 4. Based on Fig. 4, the equilibrium data for Zn(II) and Cu(II) fit the Freundlich better than Langmuir with higher correlation correction which are $R^2 = 0.845$ and $R^2 = 0.782$ respectively. This shows that the adsorption involves multilayer adsorption where there is interaction between the adsorbed molecules and the adsorbent surface and the molecules in the solution. This also indicates that the surface of NLP consists of heterogeneous sorption active sites (Bharali & Bhattacharyya, 2015). Cu(II) has better biosorption mechanism compared to Zn(II) since the value of $n_F$ for Cu(II) is higher than Zn(II) which is 1.668. Meanwhile, the equilibrium data for Ni(II) fits Langmuir well with correlation correction of $R^2 = 0.664$. Langmuir isotherm implies monolayer adsorption by NLP and it shows that the surface of NLP is energetically homogenous (Mitrogiannis, Markou, Çelekli, & Bozkurt, 2015).

\[ y = 0.236x - 4.020 \]
\[ R^2 = 0.705 \]
Fig. 4 Single system (a) Langmuir plot for Zn(II); (b) Freundlich plot for Zn(II); (c) Langmuir plot for Cu(II); (d) Freundlich plot for Cu(II); (e) Langmuir plot for Ni(II); (f) Freundlich plot for Ni(II).

Fig. 5 shows the comparison of Langmuir isotherm and Freundlich isotherm for Zn(II) ions, Cu(II) ions and Ni(II) ions in a multicomponent system. The equilibrium data for all the three metals fit the Langmuir isotherm better than Freundlich isotherm with correlation coefficient of $R^2=0.969$, $R^2=0.968$ and $R^2=0.225$ for Cu(II), Zn(II) and Ni(II) ions respectively. This shows that only monolayer adsorption involved in multicomponent system. There is competition between the three components. From the Langmuir isotherm data, the maximum biosorption capacity, $max$ for Zn(II), Cu(II) and Ni(II) are 1.11mg/g, 0.43mg/g and 2.33mg/g. The order of the adsorption capacity is: Ni(II) > Zn(II) > Cu(II). The biosorption capacity for the three metals in multicomponent system is lower than in single system due to the competition between each metal ions (Akbari, Hallajisani, Keshtkar, Shahbeig, & Ali Ghorbanian, 2015; Kim, Song, Wei, & Yun, 2015).
V. Conclusion

The effect of contact time, biosorbent dosage and pH of solution on biosorption capacity of NLP has been investigated in this study. The adsorption equilibrium data is applied to the adsorption isotherms to study the biosorption behavior of Cu(II), Zn(II) and Ni(II). The optimal contact time and biosorbent dosage for all three cases are 15 minutes and 0.2g respectively. The optimal pH for Cu(II) and Zn(II) is 6, and for Ni(II) is 7. The maximum adsorption of Zn(II), Cu(II) and Ni(II) are 32mg/g, 36mg/g, and 38mg/g. The order of adsorption capacity is Ni(II) > Zn(II) > Cu(II). The study of adsorption behavior in single system shows that Cu(II) and Zn(II) fit the Freundlich isotherm model while Ni(II) fits the Langmuir isotherm model. As for multicomponent system, the equilibrium data for all three metal ions fit Langmuir isotherm better than Freundlich.

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Fig. 5 (a) Langmuir plot for Zn(II)(b) Freundlich plot for Zn(II); (c) Langmuir plot for Cu(II) (d) Freundlich plot for Cu(II); (e) Langmuir plot for Ni(II)(f) Freundlich plot for Ni(II) in multicomponent system

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References

I. Akbari, M., Hallajisani, A., Keshtkar, A. R., Shahbeig, H., & Ali Ghorbanian, S. (2015). Equilibrium and kinetic study and modeling of Cu(II) and Co(II) synergistic biosorption from Cu(II)-Co(II) single and binary mixtures on brown algae C. indica. *Journal of Environmental Chemical Engineering*, 3(1), 140–149. http://doi.org/10.1016/j.jece.2014.11.004

II. Amirnia, S., Ray, M. B., & Margaritis, A. (2015). Heavy metals removal from aqueous solutions using Saccharomyces cerevisiae in a novel continuous bioreactor–biosorption system. *Chemical Engineering Journal*, 264, 863–872. http://doi.org/10.1016/j.cej.2014.12.016

III. Arshad, M., Zafar, M. N., Younis, S., & Nadeem, R. (2008). The use of Neem biomass for the biosorption of zinc from aqueous solutions. *Journal of Hazardous Materials*, 157(2-3), 534–540. http://doi.org/10.1016/j.jhazmat.2008.01.017

IV. Bharali, R.K., & Bhattacharyya, K.G. (2015). Biosorption of fluoride on Neem (Azadirachta indica) leaf powder. *Journal of Environmental Chemical Engineering*, 3(2), 662–669.

V. Febriana, N., Lesmana, S. O., Soetaredjo, F. E., Sunarso, J., & Ismadji, S. (2010). Neemleaf utilization for copper ions removal from aqueous solution. *Journal of the Taiwan Institute of Chemical Engineers*, 41(1), 111–114. http://doi.org/10.1016/j.jtice.2009.04.003

VI. Khadivinia, E., Sharafi, H., Hadi, F., Zahiri, H. S., Modiri, S., Tohidi, A., … Noghabi, K. A. (2014). Cadmium biosorption by a glyphosate-degrading bacterium, a novel biosorbent isolated from pesticide-contaminated agricultural soils. *Journal of Industrial and Engineering Chemistry*, 20(6), 4304–4310. http://doi.org/10.1016/j.jiec.2014.01.037

VII. Khataee, a. R., Vafaei, F., & Jannatkhah, M. (2013). Biosorption of three textile dyes from contaminated water by filamentous green algal Spirogyra sp.: Kinetic, isotherm and thermodynamic studies. *International Biodeterioration and Biodegradation*, 83, 33–40. http://doi.org/10.1016/j.ibiod.2013.04.004

VIII. Kim, S., Song, M., Wei, W., & Yun, Y. (2015). Selective biosorption behavior of Escherichia coli biomass toward Pd (II) in Pt (IV) – Pd (II) binary solution. *Journal of Hazardous Materials*, 283, 657–662. http://doi.org/10.1016/j.jhazmat.2014.10.008
IX. Kulkarni, R. M., Shetty, K. V., & Srinikethan, G. (2014). Cadmium (II) and nickel (II) biosorption by Bacillus laterosporus (MTCC 1628). *Journal of the Taiwan Institute of Chemical Engineers*, 45(4), 1628–1635. http://doi.org/10.1016/j.jtice.2013.11.006

X. Lima, E. C., Royer, B., Vaghetti, J. C. P., Brasil, J. L., Simon, N. M., dos Santos, A. a., Silva, E. a D. (2007). Adsorption of Cu(II) on Araucaria angustifolia wastes: Determination of the optimal conditions by statistic design of experiments. *Journal of Hazardous Materials*, 140, 211–220. http://doi.org/10.1016/j.jhazmat.2006.06.073

XI. Mitrogiannis, D., Markou, G., Çelekli, A., & Bozkurt, H. (2015). Biosorption of methylene blue onto Arthospira platensis biomass: Kinetic, equilibrium and thermodynamic studies. *Journal of Environmental Chemical Engineering*, 3(2), 670–680. http://doi.org/10.1016/j.jece.2015.02.008

XII. Sharma, A., & Bhattacharyya, K. G. (2005). Utilization of a biosorbent based on Azadirachta indica (Neem) leaves for removal of water-soluble dyes. *Indian Journal of Chemical Technology*, 12(3), 285–295.

XIII. Sousa, F. W., James, M., Oliveira, I. R. N., Oliveira, G., Cavalcante, R. M., Fechine, P. B. A., Nascimento, R. F. (2009). Evaluation of a low-cost adsorbent for removal of toxic metal ions from wastewater of an electroplating factory. *Journal of Environmental Management*, 90(11), 3340–3344. http://doi.org/10.1016/j.jenvman.2009.05.016

XIV. Sulaiman, M. S., & Garba, M. D. (2014). Biosorption Of Cu (II) Ions from Aqueous Solution Using Azadirachta indica (Neem) Leaf Powder, 27(II), 1–12.

XV. Wang, J., & Chen, C. (2006). Biosorption of heavy metals by *Saccharomyces cerevisiae*: A review, 24, 427–451. http://doi.org/10.1016/j.biotechadv.2006.03.001