

Bio-extraction of Copper and Manganese Ions from Acid Mine Drainage

R. Marandi¹, F. Doulati Ardejani², H. Soleimanifar²

¹Department of Environmental Eng. - North Tehran Branch- Islamic, Tehran, Iran

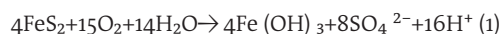
²Mining, Petroleum and Geophysics Dept., Shahrood University of Technology, Shahrood, Iran

Abstract The concentrations of Cu and Mn are high in the Acid Mine Drainage of Sarcheshmeh Copper Mine. In this study, the bioextraction of Cu and Mn by biosorption process from acid mine drainage was investigated by using a native fungus *Phanerochaete cryosporium*. The optimum biosorption parameters were determined in a batch system. The optimum pH range was 5–6. It was found that the biosorption process increased with temperature and amount of biosorbent. The results show that the second-order kinetics model was fitted well by the experimental data. The biosorption experiments were further carried out with a continuous system to compare the biosorption capacities obtained by this method and the batch system.

Key Words Acid Mine Drainage, Biosorption, Bioextraction, *Phanerochaete cryosporium*, batch, continues.

Introduction

Acid Mine Drainage (AMD) is the most important problem to the environmental facing the mining industry. Acid mine water can be generated within the mine or it can be leached from the waste heaps. This acid solution can dissolve heavy metals ions found in waste rock and tailings such as Pb, Zn, Cu, Mn, As, Se, Hg and Cd and increase their concentration in solution. Acid mine drainage and metal leaching are a particular concern because they can continue indefinitely, causing environmental damage long after mine operation ended and it costs a lot to mitigate the damage caused by AMD. The overall reaction, catalyzed by microbes, can be shown as:



The dissolved Fe^{2+} , SO_4^{2-} and H^+ represent an increase in the total dissolved solids and acidity of the water and unless neutralized, induce a decrease in pH. In many environmental settings, the consequence of AMD can be moderate to severe [1].

There are many alternative methods to treat or remediate AMD. The most common method is the chemical precipitation that is based on the actively adding alkalinity and neutralizing materials and settling the resulting precipitates. Another technology that is more passive in nature is the use of anoxic limestone drains [2]. The methods of the aerobic wetlands are generally constructed to treat the mine waters that are net alkaline [3]. In contrast to aerobic wetlands, the key reactions that occur in compost bioreactors used to mitigate AMD are anaerobic [4]. Passive bioremediation systems that utilize a combination of aerobic and anaerobic wetlands have been used for full-scale treatment of AMD. These methods are not economical in and also leave much chalk sludge [5].

Another method is based on the biological treatment. Many microbial species such as bacteria, fungi and yeast are known to be capable of adsorbing heavy metals on their surface and/or accumulating the metals within their structure. It is possible that micro-organisms can be used in the removal of toxic metal ions from the AMD and even in the recovery of them by using the adsorption properties of the micro-organisms [6].

This research, is a study on "Sarcheshmeh Copper Mine" (Located in South of Iran) for AMD Biotreatment by bio-extraction of copper and magnesium ions. The concentrations of Copper and Manganese were higher than other metals in AMD. So we focused on bio-extraction of these two elements using a native fungus that isolated from the soil of the mine called *Phanerochaete cryosporium*.

Methods

AMD Preparation

AMD from Sarcheshmeh Copper Mine was sampled five discrete times, placed in 20-liter standard containers and transferred to the laboratory. Table 1 reports initial chemistry of AMD before experiments.

Table 1 AMD chemical analysis results.

Parameters	AMD
Fe^{2+} (ppm)	0.097
(ppm)Ni	0.003
(ppm)Pb	0.65
(ppm) Ag	0.057
Cu (ppm)	8.265
Mn (ppm)	10.401
pH	5.4
BOD ₅ (mg/l)	225
COD (mg/l)	350
D.O.(mg/l)	1.54
Turbidity(NTU)	167.9

Biomass production

The fungus *Phanerochaete cryosporium* was isolated from sample soil of the mine field near the River and then propagated in potato dextrose agar. The culture was maintained on slants and was incubated for 5–7 days at 33±2 °C [7]. Living biomass was boiled in 0.5N NaOH solution for 15 min and then washed with generous amounts of deionized water till the pH after washing received to the near-neutral range (7.0±7.2) [8]. After washing, the biomass was dried at 60 °C for 24h and powdered. The powdered biomass residue obtained (particle size less than 75 mm) was used for bio-extraction process.

Batch biosorption experiments

Batch forms of kinetic and isotherm sorption experiments were conducted separately to evaluate the effects of pH, time, temperature and biomass concentration on removal of copper and manganese ions.

A known quantity of dried biomass was added to AMD samples in 250 ml Erlenmeyer flasks before pH adjustment. The pH of each solution was adjusted to the required value (3, 4, 5, 6, 7 and 8) by using sodium phosphate (0.1 mol/l) for pH 3, ammonium acetate (0.1 mol/l) for pH 4–7 and ammonium chloride (0.1 mol/l) for pH 8. Shaking was active (150 to 250 rpm) for all the experiments, at indoor temperature for 2 hrs (equilibrium time). Different grams of the biomass are added to each one, then the time variation effect in the range of t=5–180 min is studied. The amount of adsorbed metal ions per unit biosorbent (mg of Cu and Mn g⁻¹ of dry biosorbent) was obtained by using the following expression:

$$q = \frac{(C_0 - C_e)V}{M} \tag{2}$$

Where:

- q = amount of metal adsorbed on the biomass (mg/g);
- C₀ = initial metal ion concentration in solution (mg/L);
- C_e = equilibrium metal ion concentration in solution (mg/L);
- V = volume of the medium (l);
- M = amount of the biomass used in the reaction mixture (g).

The percent biosorption of Cu and Mn was calculated as follows:

$$\text{Biosorption\%} = \frac{(C_i - C_f)}{C_i} \times 100 \tag{3}$$

Where C_i and C_f are the initial and final Cu and Mn concentration, respectively.

Absorption isotherm

Adsorption isotherm demonstrates the relationship between equilibrium concentrations of adsorbate in the solid phase *q*, and in the liquid phase *C* at constant temperature. Among the many different isotherm models suggested for the adsorption of solutes in a liquid solution onto a solid surface, the Langmuir adsorption model is one of the more common. A linear expression for the Langmuir isotherm can be expressed as follows [9]:

$$\frac{1}{q} = \left(\frac{1}{bq_{\max}} \right) \left(\frac{1}{C_e} \right) + \left(\frac{1}{q_{\max}} \right) \tag{4}$$

Where:

- q_{max} = maximum metal uptake corresponding to the saturation capacity (amount of metal ions per unit weight of biosorbent to form a complete monolayer on the surface) (mg/g);
- b = energy of adsorption (the ratio of adsorption / desorption rates) (l/mg);
- q = amount of metal adsorbed on the biomass (mg/g);
- C_e = equilibrium (residual) metal concentration in solution (mg/L).

The constants q_{max} and *b* are the characteristics of the Langmuir isotherm and can be determined from Equation (4). A plot of 1/q versus 1/C_e gives a straight line with a slope of (1/bq_{max}) and an intercept of (1/q_{max}).

The empirical Freundlich adsorption isotherm is obtained on the assumption that the sorption takes place on a heterogeneous adsorbent surface, where the sorption energy distribution decreases exponentially.

The model can be linearized by taking logarithms as:

$$\ln q = \ln K_f + \left(\frac{1}{n} \right) \ln C_e \tag{5}$$

from which the Freundlich constants can be determined.

Kinetic modeling

Kinetic models are used to analysis the experimental data [11, 12, 13, 14, 15 and 16] to investigate the mechanism of the biosorption process. If the higher value is closed to unity, it means that model used for the kinetics of Cu and Mn biosorption is justified. In this research we choose two kinetic models.

The pseudo-first order kinetic model (Lagergren model) explains the biosorption rate based on the adsorption capacity. It can be shown shown as follows:

$$q_t = q_e [1 - \exp(-k_1 t)] \tag{6}$$

The pseudo-second order kinetic model (Ho *et al.* model) applied to biosorption as a adsorption kinetic, can be written as follow:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

If the second order kinetics is applicable, the plot of t/q_t versus t will be a linear relation. The values of k_2 and q_e will be determined from the intercept and the slope of the plot.

Column fixed bed absorption studies

A series of experiments were conducted with various natural and artificial wastewater and fungal biomass columns. The experiments involved four parts: biosorption of single-metal from AMD, studying the effect of presence of other metal ions on biosorption of one defined metal ion, studying the effect of flow rate on breakthrough curves and also the desorption of metal ions.

Experimental set-up

Continuous flow sorption experiments were conducted in a glass column (2.5 cm internal diameter and 50 cm height). All the experiments were conducted at room temperature. 4.5 g (dry weight) of immobilized fungal beads were packed into the column with a bed depth of 30 cm. AMD flow rate was adjusted to 6 mL/min. Samples were taken from the effluent at pre-determined time intervals and analyzed for the remaining concentration of metal ion in effluent. The experiments were continued until a constant effluent concentration of metal ion was obtained.

The Yoon–Nelson model

The Yoon–Nelson equation is expressed as [19]:

$$\frac{C_e}{C_0 - C_e} = \frac{\exp(k_{YN}t - \tau k_{YN})}{1 + \exp(k_{YN}t - \tau k_{YN})} \quad (8)$$

where k_{YN} is the rate constant (L/min) and τ is the time required for 50% adsorbate breakthrough (min).

The approach involves a plot of $\ln(C_e/(C_0 - C_e))$ versus sampling time (t) according. The parameters of k_{YN} and τ can be obtained using the non-linear regressive method.

Results and discussion

Effect of pH on biosorption

The maximum biosorption of Cu(II) and Mn(II) occurred at pH range between 5.0 and 6.0 (fig. 1). The adsorption of metal ions per unit weight of biosorbent increased gradually when pH increased from 3 to 6.

Batch kinetic experiments

Figure 2 showed that the results obtained with the

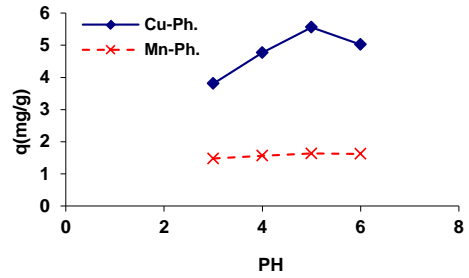


Figure 1 Effect of pH on Cu(II) and Mn(II) biosorption on *Phanerochaete cryso sporium*.

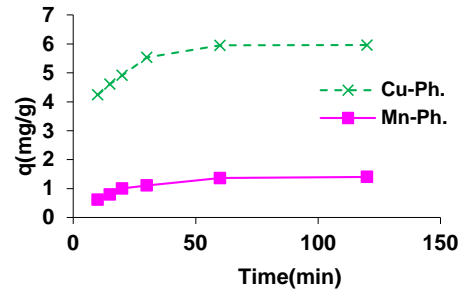


Figure 2 Effect of contact time on Cu(II) and Mn(II) biosorption on *Phanerochaete cryso sporium*.

milled biomass for biosorption of copper and manganese. Optimum contact time for copper sorption was 30 min while it was 60 min for manganese sorption. During these periods of time, 70% of copper was absorbed and 97% of total sorption of manganese during 120 min, occurred. So, this time was used for kinetic studies. Figure 2 indicates more clearly that sorption can be divided into two stages: one in which the sorption rate is very high (79% of biomass saturation capacity for sorption of copper was reached in a contact time of 15 minutes), followed by a second stage with a much lower sorption rate.

Pseudo-second order equation modeled biosorption process better. The results are shown in Table 2.

Effect of biosorbent concentration

Figure 3 showed that The maximum biosorption efficiency was obtained at 3 g/L of biosorbent for copper ion biosorption and further increases in biosorbent concentration decreased the maximum removal of metal ions. This can be explained by forming aggregates during biosorption which takes place at high biomass concentrations causing a decrease of the effective adsorption area. It has been suggested that several factors including pH, ionic strength, temperature, metal ion in

Metal ion	Pseudo-first order model constants		Pseudo-second-order model constants	
	k_1	R^2	k_2	R^2
Cu	0.105938	0.983	0.035262	0.999
Mn	0.057575	0.993	0.004384	0.997

Table 2 kinetic constants.

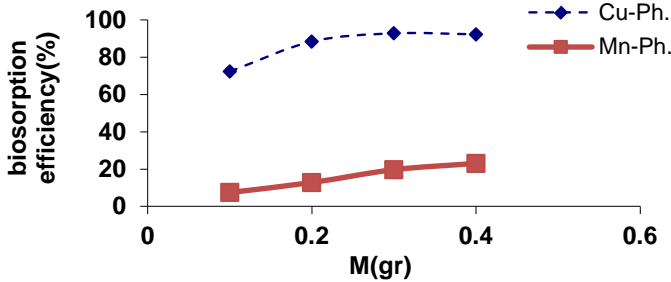


Figure 3 Effect biosorbent concentration on Cu(II) and Mn(II) biosorption on Ph. cryosporium.

solution and biomass concentration explain the decreased adsorption capacity at increasing biomass.

Biosorption isotherm

The empirical parameters of the two isotherms along with the correlation coefficients (R^2) are given in Table 3. Results show that the biosorption process follows well the Langmuir isotherm model.

Kinetics model of biosorption

A simple theoretical model developed by Yoon–Nelson was applied to investigate the breakthrough behavior of metal ions on fungal biomass. So the values of k_{YN} (a rate constant) and (the time required for 50% adsorbate breakthrough) could be obtained using non-linear regression analysis. Table 4 shows that biosorption rate was too much (4 times) faster for Mn and the column also was saturated sooner.

Conclusion

The present study evaluated the removal of copper and Manganese from Sarcheshmaeh Copper Mine AMD using Phanerochaete cryosporium-cells. The pretreatment of biomass by boiling in

0.5N NaOH solution for 15 min was performed. Live or dead fungal biomass can be used for the removal of toxic metal ions. The use of dead cells seems to be more advantageous than using live cells in metal ion removal. It was seen that initial pH, temperature and initial metal ion concentration highly affected the biosorption capacity of the sorbent. Phanerochaete cryosporium was sensitive to pH. A wastewater with a pH between 5.0 and 6.0 can be effectively treated for metal ion removal and the wastewater with pH lower than 5.0 would require pH adjustment. Biosorption capacity increased as metal ion concentration increased. Optimum contact time for biosorption of copper was 30 min while it obtained 60 min for manganese biosorption.

References

- [1] Ata, A. and Koldas, S., 2005, Acid Mine Drainage (AMD): Causes, treatment and case studies, Journal of Cleaner Production, 1–7.
- [2] Peppas, A., Komnitsas K. and Halkkia, , 2000, Use of organic covers for acid mine drainage control, Minerals Engineering, 13 (5), 563–574.
- [3] Costello, C., 2003, Acid Mine Drainage: Innovative Treatment Technologies, National Network of Environmental Management Studies Fellow.

Table 3 Linearised parameters of Langmuir and Freundlich isotherms for Cu(II) and Mn(II) adsorption on Phanerochaete cryosporium.

Cu(II)		Mn(II)	
Langmuir	Freundlich	Langmuir	Freundlich
$q_{max} = 8.183$	$K_f = 6.597$	$q_{max} = 1.823$	$K_f = 0.499$
$b = 1.808$	$n = 15.504$	$b = 0.305$	$n = 2.319$
$R^2 = 0.9952$	$R^2 = 0.7992$	$R^2 = 0.9912$	$R^2 = 0.9764$

Metal	K_{YN}	τ	R^2
Cu	0.001	1464	0.921
Mn	0.004	12.75	0.941

Table 4 Yoon-Nelson model’s parameters.

- [4] Randal, E. and Danielle, P., 2003. A critical stage in the formation of acid mine drainage colonization of pyrite by *Acidithiobacillus ferrooxidans* under pH-neutral conditions, *Geobiology*, 1, 81–90.
- [5] Barrie, D., Kevinand J. and Hallberg, B., 2005. Acid Mine Drainage remediation options: a review, *Science of the Total Environment*, 338, 3–14.
- [6] Luptakova, A. and Kusnierova, M., 2005. Bioremediation of acid mine drainage contaminated by SBR, *Hydrometallurgy*, 77, 97–102.
- [7] K. Parvathi, R. Nareshkumar, R. Nagendran, Biosorption of manganese by *Aspergillus niger* and *Saccharomyces cerevisiae*, *World J Microbiol Biotechnol* (2007) 23:671–676.
- [8] J.M. Smith, H.C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, fourth ed., McGraw-Hill, Singapore, 1987.
- [9] Langmuir, , 1918. The adsorption of gases on plane surfaces of glass, mica, and platinum. *J. Am. Chem. Soc.* 40, 1361–1368.
- [10] Freundlich, H., 1907. Über die adsorption in lösungen. *J. Phys. Chem.* 57, 385–470.
- [11] Khambhaty, Y., Mody, K., Basha, Sh., Jha, B., 2009. Kinetics, Equilibrium and thermodynamic studies on biosorption of hexavalent Chromium by dead fungal biomass of marine *Aspergillus.niger*. *Chemical Engineering journal* 145, 489–495.
- [12] Ho, Y.S., 2006. Second- order kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and non-linear methods. *Water Research* 40, 119–125.
- [13] Ho, Y.S., McKay, G., 2003. Sorption of dyes and copper ions onto biosorbents. *Process Biochemistry* 38, 1047–1061.
- [14] Weber, W.J., Morris, J.C., 1963. Kinetics of adsorption on carbon from solution. *Journal of Sanitary Engineering Div.:American Society Civil Engineering* 89, 31–60.
- [15] Low, M.J.D.,1970. Kinetics of chemisorption of gases on solids. *Chemical Rev.* 60, 267–312.
- [16] Lagergren, S., 1898. Zur theorie der sogenannten adsorption gelöster stoffe. *K. Sven. Vetenskapsakad Handl.* 24, 1–39.
- [17] Juan Wu, Han-Qing Yu., 2008. Biosorption of 2,4-dichlorophenol from aqueous solutions by immobilized *Phanerochaete chrysosporium* biomass in a fixed-bed column. *Chemical Engineering Journal* 138, 128–135.
- [18] C.E. Borba, R. Guirardello, E.A. Silva, M.T. Veit, C.R.G. Tavares., 2006. Removal of nickel(II) ions from aqueous solution by biosorption in a fixed bed column: Experimental and theoretical breakthrough curves. *Biochemical Engineering Journal* 30, 184–191.
- [19] Aksu, Z., Gonen, F., 2004. Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves. *Process Biochem.* 39, 599–613.
- [20] A. Kapoor, T. Viraraghavan, Heavy metal biosorption sites in *Aspergillus niger*, *Bioresour. Technol.* 61 (1997) 221–227.

