

Influence of Process Variables and Kinetic Modelling on Mercury Removal Using *Paecilomyces variotii* Biomass—Effect of Process Parameters and Kinetics

N. Rajamohan* and M. Rajasimman¹

Department of Chemical Engineering, Sohar University, Sohar, Sultanate of Oman

¹Department of Chemical Engineering, Annamalai University, India

✉ Rnatarajan@soharuni.edu.om

Received August 20, 2015; revised and accepted December 15, 2015

Abstract: In this present work, a novel fungal biosorbent was synthesized using *Paecilomyces variotii* species and employed for the removal of mercury under batch conditions. The effect of process parameters such as pH, sorbent dose, initial mercury concentration and agitation speed on metal removal efficiency was investigated. The metal uptake was found to increase in the pH range 2.0 – 5.0 and the maximum uptake obtained was 26.0 mg/g at an optimal pH of 5.0. The biosorbent achieved 86% metal removal efficiency when the mercury concentration was 100 mg/L. The effect of shaking speed was studied in the range of 100-400 rpm and the optimal speed was determined as 300 rpm. The sorption process was identified as exothermic in nature. Pseudo-first order and pseudo-second order model were tested with the kinetic data. The pseudo-second order model represented the kinetic experiments very well with higher values of R^2 (>0.95). The pseudo-second rate constant (k_2), was evaluated as $2.090 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ at an initial mercury concentrations of 100 mg/L. Thermodynamic studies revealed the activation energy for this process as 58.25 kJ/mol.

Key words: Metal, kinetics, uptake, fungi, rate constant.

Introduction

Industrial activities related to mining, electroplating, pesticide manufacturing, ore refining and tanning have led to significant release of heavy metals into the terrestrial and aquatic ecosystem. These metals affected the ecological balance by their entry into food chain and tendency to biomagnification and bioaccumulation. Heavy metals are comparatively more toxic and hazardous than the organic pollutants because of their non-biodegradable and recalcitrant nature (Boamah et al., 2015). Mercury is one of the hazardous heavy metals utilized in artisanal mining, voltaic cell manufacturing and medical analytical devices production. Mercury is present in both ionic and non-ionic forms. Methyl

mercury is one of the most hazardous forms through which mercury gains entry (Plaza et al., 2011). The United States Environmental Protection Agency (USEPA) has categorized mercury as a priority pollutant and has set up the maximum contamination levels of mercury in surface or ground water as 0.00003 mg/L (Nguyen et al., 2013). Mercury contamination in fish has led to a tragic event in Japan and mercury poisoning was reported to cause severe damages to nervous, respiratory and renal systems (Plaza et al., 2011). In addition, mercury can cause rheumatoid arthritis when the permissible level is exceeded (Barakat et al., 2011).

Removal of mercury has become a stringent norm with the regulatory bodies of the various industrialized nations. The techniques available for the treatment

*Corresponding Author

of mercury contaminated water include physical and chemical methods like precipitation, coagulation, filtration, oxidation, electrochemical separation, reverse osmosis and ion exchange. High cost and low efficiency have proved to be the demerits with these methods (Park et al., 2010; Wan Ngah and Hanafiah, 2008; Bhattacharya et al., 2008). Biological methods such as water purification systems, sewage treatment, wet land system and reed bed approaches have been tried (Fomina and Gadd, 2014). Adsorption has been employed using conventional adsorbents like activated carbon, which suffers from high regeneration cost in spite of good efficiency (Fu and Wang, 2011). Several plant-based adsorbents produced using *Lemna perpusilla* Torr (Tang et al., 2013), *wheat bran* (Rajesh Kannan et al., 2012) and *Eucalyptus camaldulensis* tree barks (Rajamohan et al., 2014b) and *Ricinus communis* L. powder (Al Rmalli et al., 2008) have been investigated for the removal of pollutants. However, these plant-based sorbents in their natural form suffer from low adsorption capacity and contribute to increase in COD value due to the release of organic content in the plant material. Processed or modified adsorbents were introduced to overcome these difficulties (Wan Ngah and Hanafiah, 2008).

Biosorption refers to a technique in which the property of a certain biomolecule (or type of biomass) to bind and concentrate ions or molecules selectively, is exploited (Park et al., 2010). Biosorption has been defined as a passive and metabolically-independent process (Fomina and Gadd, 2014; Ahluwalia and Goyal, 2007). It can be performed either by dead mass or live cells. Biosorption using dead biomass offers several advantages like low cost, eco-friendly, less complex and more selectivity (Khakpour et al., 2014; Michalak et al., 2013; Gupta et al., 2009). Several microbial species like yeast and fungi have shown promising results for the removal of contaminants from waste waters due to their unique cell wall components. Removal of selenium using dried biomass of baker's yeast, *Saccharomyces cerevisiae*, has been investigated in a two-stage process and an efficiency of 96.1% was reported (Khakpour et al., 2014). Mercury removal using modified *Phoenix dactylifera* biomass was investigated and an efficiency of 92% was reported (Rajamohan et al., 2014). Mercury uptake capacity of 37.2 mg/g was reported in the study using biosorbent produced from *Ricinus communis* L (Al Rmalli et al., 2008).

The choice of the fungal species was justified by the fact that the fungal cell wall is composed of structural components like chitins, glucans, polysaccharides, lipids, pigments etc. and thereby ensures the ability of

diversified functional groups to bind metal ions (Fomina and Gadd, 2014). In this background, this research study was aimed at producing a novel fungi-based biosorbent using *Paecilomyces variotii* species. The effect of operating parameters like initial pH, biomass dosage, contact time, initial mercury concentration and agitation speed on the mercury removal efficiency and uptake was studied. Kinetic modelling was done to determine the sorbate removal mechanism using pseudo-first order and pseudo-second order models to determine the sorbate removal mechanism.

Materials and Methods

Metal Solution

Mercury solution was prepared by diluting aliquots of the stock solution which contains 1000 mg/L of Hg (NO₃)₂.1/2 H₂O in double distilled water. All other reagents were of analytical reagent grade and were obtained from Sigma Aldrich chemicals.

Fungal Growth and Processing

The fungal species, *Paecilomyces variotii* (MTCC 6581) used in this study was supplied by Microbial Type culture collection, India as freeze-dried cultures. The strain was cultured in minimal medium with the following composition (in g L⁻¹): NH₄NO₃, 3.0; MgSO₄.7H₂O, 0.2; NaCl, 0.2; KH₂PO₄, 1.0; Na₂HPO₄, 4.0; and CaCl₂, 0.05. The pH was adjusted to 7.0 and the procedure given was followed (Sachan et al., 2006). The medium was sterilized by autoclaving at a pressure of 1.5 atm and 121 °C for 20 min. The fungal species was grown for seven days and then deposited for the separation of liquid phase from solid phase. The fungal biomass was deactivated by autoclaving at 121°C and 1 atm for 20 minutes and freeze dried for 24h. The biomass was ground and sieved through a 100 mesh sieve. The pretreatment of the fungal cells were carried out using the non-living autoclaved biomass in ethanol solution for 20 minutes at room temperature. The ethanol treated biomass was centrifuged at 3600 rpm for 10 minutes and the supernatant solution was discarded. The processed biomass was rinsed with water to remove excess ethanol and adsorbed medium components (Khakpour et al., 2014). Further to washing, the sample was centrifuged and dried as done earlier. The dried sample was ground and sieved as mentioned above. These abovementioned steps in processing ensured the homogeneity of the biomass produced. This processed biomass was named as *Paecilomyces variotii* biomass (PVB) stored in a desiccator for further use.

Biosorption Experiments

The biosorption experiments were conducted in batch mode in order to optimize the process variables namely initial pH, biomass dosage, contact time, initial concentration and agitation speed. Batch experiments were conducted in 250 mL Erlenmeyer flasks by using a sample of 100 mL of the metal solution and agitated in an orbital shaker at different experimental conditions at a 300 rpm speed, 25°C temperature for an equilibrium time of 180 min. In the first set of experiments, the effect of pH on the metal uptake was studied within the range of 2.0-9.0 using 100 mg/L mercury concentration sample at fixed operating speed and temperature. The pH adjustment of the samples was done by adding either 0.1N HCl or NaOH as the buffering agent. In the second set of experiments, the effect of biomass dosages was studied in the range from 0.5 to 4.0 g/L at optimal pH and an initial metal concentration of 100 mg/L. The influence of initial metal concentration was studied in the range of 50-200 mg/L.

Similarly, the effect of agitation speed was studied in the range of 0-400 rpm. The samples were withdrawn at specified intervals of time and filtered through 0.45 µm pore size membrane filters. The mercury concentration was estimated with the filtered samples and the filtrate was analysed for residual metal concentrations using atomic absorption spectrophotometer at an analytical wavelength, λ_{\max} of 253.7 nm (Rajamohan et al., 2014a). All experiments conducted were in triplicate and the average values were reported. The deviation was less than 5%. The kinetic experiments were conducted using mercury solutions of different concentrations namely 50, 100, 150 and 200 mg/L at three different temperatures (303, 308 and 313 K respectively). The metal uptake was estimated by using the following equation (1):

$$q = (C_o - C_e)V/W \quad (1)$$

where q is the metal uptake (amount of metal adsorbed by adsorbent at any time t), (mg g^{-1}); C_o and C_e are the initial and final mercury concentrations (mg L^{-1}), respectively; V is the volume of sample solution (L) and W is the adsorbent dosage (g).

The percentage mercury removal efficiency is defined by

$$\begin{aligned} \text{\% mercury removal efficiency (\%RE)} \\ = \frac{(C_o - C_e)}{C_o} \times 100 \end{aligned} \quad (2)$$

Kinetic Modelling

Pseudo-first order and pseudo-second order models were fitted to the experimental data to study the effect of concentration and temperature on the rate of sorption by the selected biosorbent. Pseudo-first order equation (Ho and Mckay, 1999) can be written in the linear form as shown in Eq. 3.

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (3)$$

where q_e is the amount of metal adsorbed by adsorbent at equilibrium (mg/g), q = adsorbed at any time and k_1 is the pseudo-first order rate constant (min^{-1}).

Pseudo-second order equation (Ho and Mckay, 1999) can be written in the linear form as shown in Eq. 4.

$$\frac{t}{q} = \frac{1}{h_2} + \frac{t}{q_e} \quad (4)$$

where, $h_2 (= k_2 q_e^2)$, the initial sorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and the pseudo-second order constant k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) can be determined experimentally from the slope and intercept of plot $\frac{t}{q}$ versus t . Arrhenius plot was used to determine the activation energy of this sorption process.

Results and Discussion

Effect of pH

The fraction of free ions in the solution is strongly related to the solution pH and concentration of elements in the medium (Franco et al., 2013). Among all the process variables, pH is considered to be more significant as it decides the metal speciation, degree of ionization and surface charge density of the biosorbent (Park et al., 2010). In this set of experiments, the pH values were varied in the range of 2.0 to 9.0 and the effect on mercury uptake was plotted in Figure 1. Metal uptake increased from 6 to 26 mg/g when the

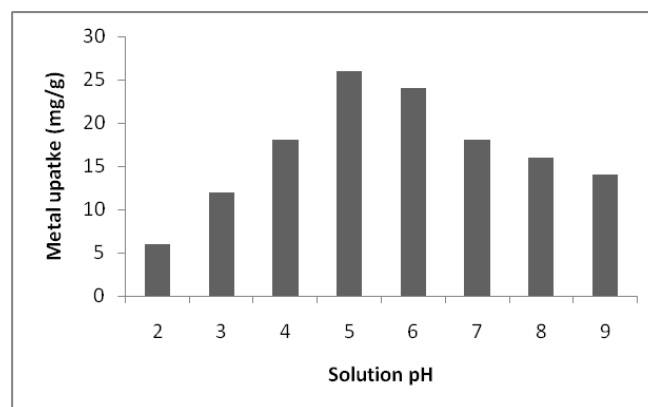


Figure 1: Effect of pH on mercury removal by PVB ($t = 24$ h, $C_o = 100$ mg/L, $M = 3.0$ g/L).

pH increased from 2.0 to 5.0. But, an inverse effect was observed when the pH exceeded 5.0 and the uptake decreased in the entire pH range of 6.0-9.0. Presence of competition by hydrogen ions at lower pH values was found to reduce the uptakes. Many studies have reported a competitive behaviour between positive metal ions and hydrogen ions for the same surface active sites (Rajamohan et al., 2014a, b; Franco et al., 2013). At low pH values, 2.0-4.0, electrostatic repulsion was reported to prevent the sorption of Hg^{2+} and $\text{Hg}(\text{OH})^+$ ions (Ghodbane and Hamdoui, 2008). The precipitation of metal hydroxide was reported to occur when pH was increased above 5.0 (Rajamohan et al., 2014a). The observations made in this set of experiments revealed that the increase in uptake with increase in pH from 2.0 to 5.0 could be related to ionization of the surface functional groups of the fungal biosorbent (Khakpour et al., 2014). The optimal pH was confirmed as 5.0 and used for all the other parametric experiments. Similar

observations on pH effect and an optimal pH of 5.0 was reported in biosorption of mercury onto yeast cells (Yavuz et al., 2006).

Effect of Biosorbent Dosage

Biosorption process efficiency is strongly dependent on the surface area availability. Surface area can be varied by changing the biosorbent dosage. Figure 2 represents the influence of biosorbent dose on the mercury removal efficiency and uptake in the range of 0.5 to 4.0 g/L. The initial metal concentration was fixed at 100 mg/L and the experiments were carried out at optimal pH. The metal removal efficiency increased with increase in biosorbent dose and the increase showed two different patterns. An exponential increase in efficiency from 35% to 86% was observed in the dosage range of 0.5 to 2.5 g/L followed by a plateau region with decreased slope. This increase in removal percentages with biosorbent dosage was related to increase in surface area available. With increase in sorbent dose/metal ion ratio, the surface sites available increased for the same

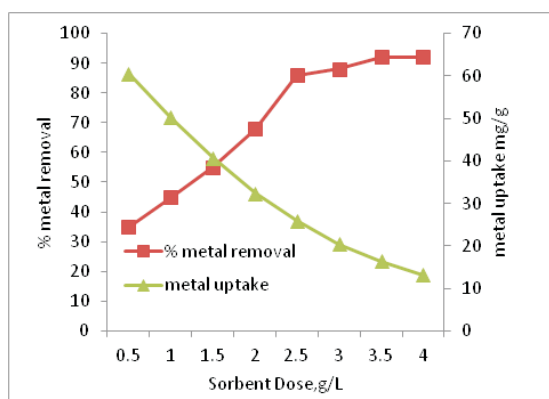


Figure 2: Effect of adsorbent dose on % mercury removal and uptake by PVB ($t = 180$ min, $C_0 = 100$ mg/L, $T = 35$ °C).

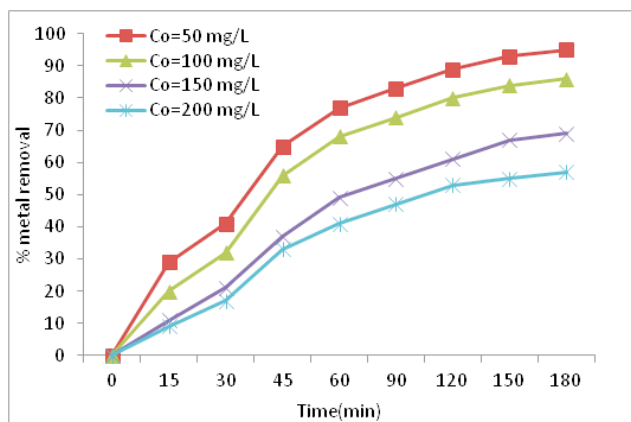


Figure 3: Effect of initial mercury concentration on % mercury removal by PVB ($t = 180$ min, $C_0 = 100$ mg/L, $T = 35$ °C).

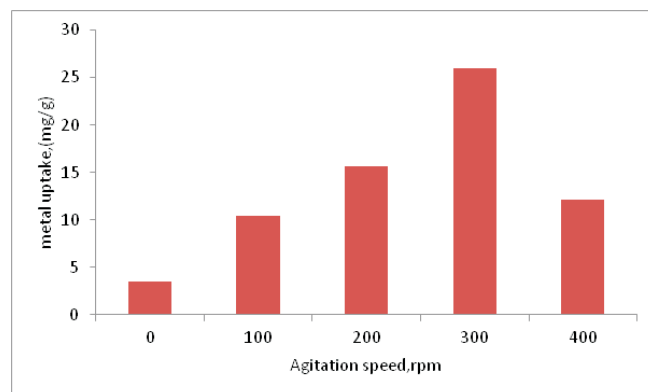


Figure 4: Effect of shaking speed on metal uptake by PVB ($t = 180$ min, $C_0 = 100$ mg/L, $T = 35$ °C).

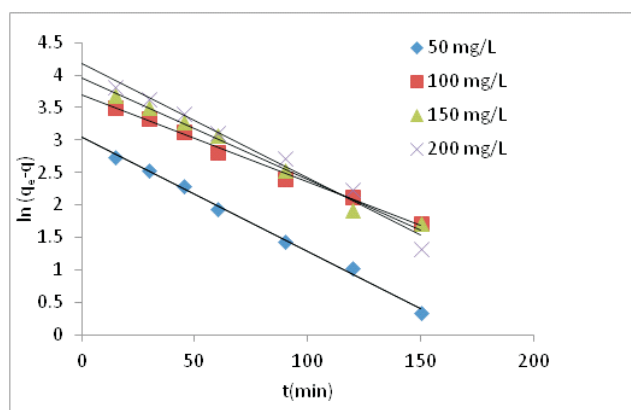


Figure 5: Pseudo-first order kinetic model plot for the sorption of mercury at 303 K.

number of metal ions. Contrarily, increase in sorbent dose resulted in decreased metal uptake values. The metal uptake decreased from 60.5 to 13.2 mg/g when the resin dose increased from 0.5 to 4.0 g/L. Due to unsaturation of sorption sites occurring at higher sorbent dosages, metal uptakes decreased (Rajamohan et al., 2014a). In addition, overlapping of sorption sites was reported to occur at higher dosages which decreased the surface area (Nguyen et al., 2013). The equation ($R^2 = 0.9992$) relating the metal uptake and biosorbent dose was represented by Eq (5):

$$\text{Metal uptake} = 77.489e^{-0.221\text{sorbent dose}} \quad (5)$$

Effect of Initial Metal Concentration

The metal concentration is a varying parameter in the industrial effluents due to the variations in process conditions. The effect of initial mercury concentration on the metal removal efficiency by PVB was studied in the range of 50-200 mg/L to identify the metal absorbing potential of the fungal biosorbent and is presented in Figure 3. The metal removal efficiency attained with 50 mg/L mercury concentration was 95% and decreased with increase in metal concentration. When the mercury concentration was increased to 200 mg/L, the removal efficiency for Hg^{2+} decreased from 92% to 56% when the initial mercury concentration was increased from 0 to 200 mg/L. The ratio between surface active sites and metal ions was low at high metal concentrations. High resistance to diffusion exists at higher metal concentrations due to the surface coverage of the sorption sites by the mercury ions (Rajamohan et al., 2014). Studies on removal of selenium using yeast biomass (Khakpour et al., 2014), mercury(II) from aqueous media using Eucalyptus bark (Ghodbane and Hamdaoui, 2008) and modified activated sludge-based biosorbent (Natarajan and Manivasagan, 2015) reported similar observations. The rate of metal sorption was found to be very high during the first 60 minutes of the contact time which equilibrated at 180 min. This phenomenon was attributed to the availability of more vacant surface sites and increased driving force due to concentration difference during the starting phase of sorption process.

Effect of Agitation Speed

Figure 4 represents the effect of agitation speed on the mercury uptake at a fixed initial concentration of 100 mg/L. The metal uptake achieved at 0 rpm (static

conditions) was 3.48 mg/g which proved the necessity of shaking conditions. The uptake increased from 10.44 to 26.0 mg/g when the speed increased from 100 to 300 rpm. The influence of changing agitation speed on the mercury uptake was studied in the range of 0-400 rpm and is shown in Figure 4. The metal uptake observed under static condition was 4.0 mg/g and increased from 12 to 29.33 mg/g for a corresponding increase in speed of 100-300 rpm. The speed of agitation was reported to decrease the boundary layer thickness and enhanced the external film transfer coefficient (Ghodbane and Hadaoui, 2008). At the maximum speed of 400 rpm, the uptake capacity decreased which may be due to the shearing of sorbate from the surface of the sorbent. Similar effects of speed of agitation has been reported in other biosorption studies (Rajamohan et al., 2014; Natarajan and Manivasagan, 2015).

Kinetic Studies

Kinetic studies are aimed to identify the reaction mechanism and to determine the rate-determining step. The kinetic data was collected by conducting experiments at different mercury concentrations namely 50, 100, 150 and 200 mg/L at three different temperatures. The linearized form of the pseudo-first order model (Eq. 3) was plotted between $\ln(q_e - q)$ versus t . Figures 5-7 represent the model at 303, 308 and 313 K respectively. The model constants, q_e and k_1 were calculated from the slopes and intercepts of the best fit lines. Pseudo-second order model was plotted in Figures 8-10 and the kinetic constants of the pseudo-second order model, q_e and k_2 were estimated from the slope and intercept of the lines. The values of correlation coefficient, R^2 , (>0.97) were high for the pseudo-second order model in comparison to pseudo-first order model. The kinetic constants evaluated at different conditions are presented in Table 1.

Pseudo-second order model assumes the occurrence of two reactions. The first reaction is assumed to be fast and reaches equilibrium quickly. Whereas, the second reaction is a slower one continuing for longer duration. This model predicts the adsorption pattern over the whole duration and assumes chemisorption as the rate controlling step (Ho and McKay, 1999). The sorption mechanism was proved as chemisorption in nature by the suitability of pseudo-second order model with comparatively higher values of R^2 (>0.95). The values of the pseudo-second order rate constant, k_2 , decreased with increase in concentration of mercury. The values

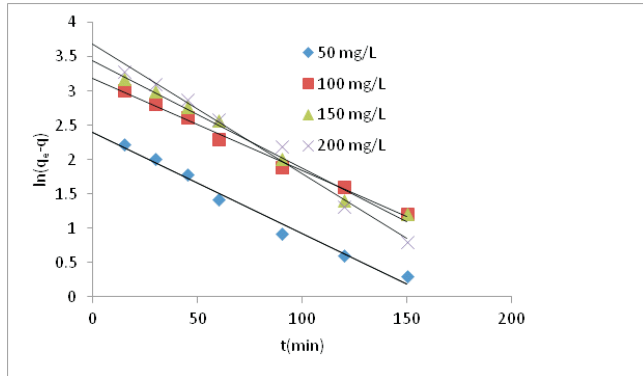


Figure 6: Pseudo-first order kinetic model plot for the sorption of mercury at 308 K.

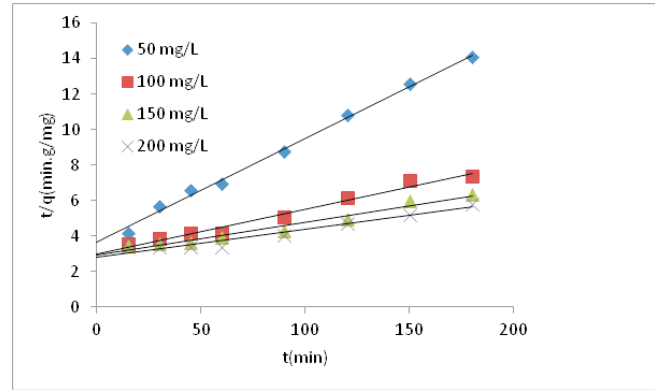


Figure 9: Pseudo-second order kinetic model plot for the sorption of mercury at 308 K.

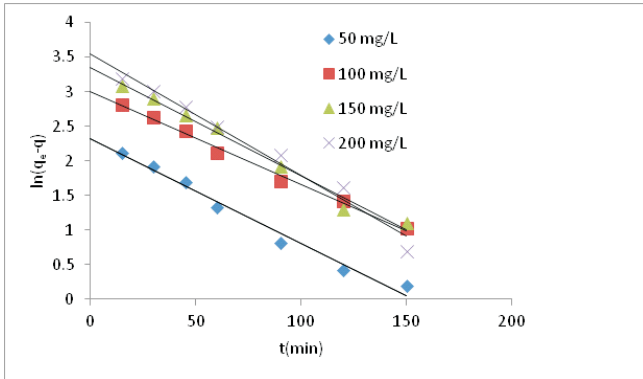


Figure 7: Pseudo-first order kinetic model plot for the sorption of mercury at 313 K.

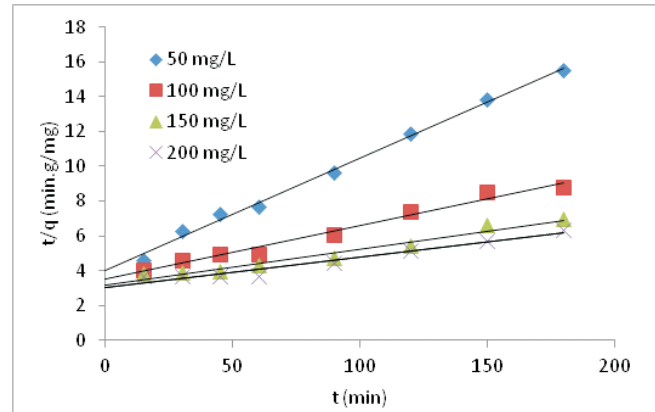


Figure 10: Pseudo-second order kinetic model plot for the sorption of mercury at 313 K.

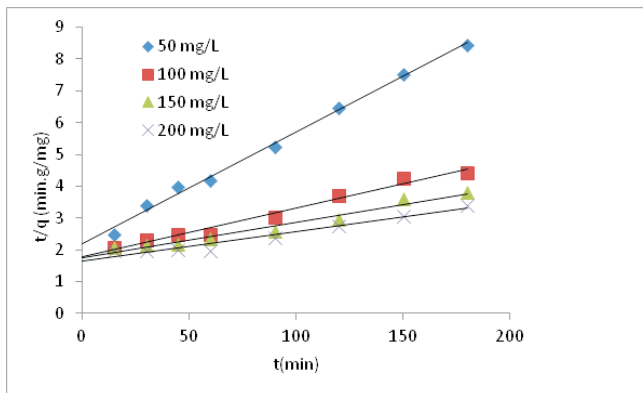


Figure 8: Pseudo-second order kinetic model plot for the sorption of mercury at 303 K.

of equilibrium uptake increased with concentration and decreased with increase in temperature. The values of q_e calculated using pseudo-second order model decreased from 65.789 to 32.368 mg/g for an initial mercury concentration of 100 mg/L when the temperature increased from 303 to 313 K. Studies on biosorption of selenium using yeast biomass reported similar relations

Table 1: Kinetic model constants for pseudo-first order model

T (K)	C_o (mg/L)	q_e (mg/g)	$k_1 \times 10^2$ (g mg ⁻¹ min ⁻¹)	R^2
303	50	11.325	1.760	0.992
	100	21.505	1.340	0.992
	150	28.011	1.570	0.997
	200	34.722	1.760	0.996
308	50	13.387	1.480	0.995
	100	22.831	1.340	0.993
	150	29.499	1.570	0.992
	200	36.630	1.880	0.993
313	50	15.083	1.510	0.988
	100	24.691	1.340	0.977
	150	30.960	1.570	0.991
	200	38.760	1.770	0.989

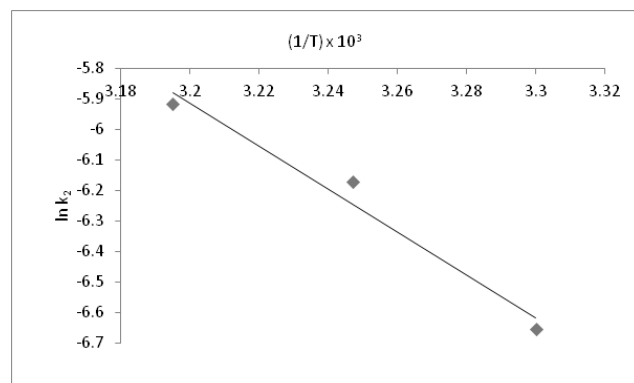
between metal concentration and pseudo-second order rate constant (Khakpour et al., 2014).

Table 2: Kinetic model constants for pseudo-second order model

T (K)	C_o (mg/L)	q_e (mg/g)	$k_2 \times 10^2$ (g mg ⁻¹ min ⁻¹)	R^2
303	50	28.409	5.680	0.995
	100	65.789	1.290	0.988
	150	89.286	0.720	0.997
	200	106.383	0.540	0.993
308	50	17.036	9.480	0.995
	100	39.841	2.090	0.982
	150	53.476	1.200	0.994
	200	62.893	0.910	0.971
313	50	15.480	10.430	0.995
	100	32.468	2.690	0.980
	150	48.544	1.330	0.974
	200	57.471	0.990	0.991

Thermodynamic Studies—Activation Energy Estimation

Arrhenius equation was used to correlate the rate constant of the best fit (pseudo-second order) model and temperature. The linearized form of Arrhenius equation was represented by Eq. (7) and plotted in Figure 11.

**Figure 11: Estimation of activation energy.**

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (7)$$

where E_a (kJ mol⁻¹) is the activation energy, A (g (mg·min)⁻¹) is the Arrhenius factor, R is the gas constant and T (K) is the solution temperature. The activation energy, estimated from the slope of the best fit line ($R^2 > 0.97$) in Figure 11, was found to be 58.25 kJ/mol.

Conclusions

Experimental data were collected on the batch biosorption studies on the removal of Hg(II) from its

aqueous solution using modified *Paecilomyces variotii* as an adsorbent. The optimal pH and biosorbent dosage were determined as 5.0 and 2.5 g/L respectively. The mercury removal efficiency increased with increase in sorbent dose due to increase in the available surface area. Higher mercury concentrations were found to inhibit the sorption process efficiency due to the limited availability of the surface active free sites. Kinetic modelling revealed the suitability of pseudo-second order model and chemisorption was proved to be the rate controlling step. The equilibrium uptakes calculated using pseudo-first order and pseudo-second order models were 22.831 and 39.841 mg/g for 100 mg/L mercury concentration at 308 K. The best fit model rate constant was used to determine the activation energy of the sorption process. The feasibility and sorption potential of a fungal biosorbent to remove mercury effectively was proved through this study.

References

- Ahluwalia, S.S. and D. Goyal (2007). Microbial and plant derived biomass for the removal of heavy metals from waste water. *Bioresource Technology*, **98**(12): 2243-2257.
- Al Rmaili, S.W., Dahmani, A.A., Abuein, M.M. and A.A. Gleza (2008). Biosorption of mercury from aqueous solutions by powdered leaves of castor tree (*Ricinus communis* L.). *Journal of Hazardous Materials*, **152**: 955-959.
- Barakat, M.A. (2011). New trends in removing heavy metals from industrial waste water. *Arabian Journal of Chemistry*, **4**: 361-367.
- Bhattacharya, A.K., Naiya, T.K., Mandal, S.N. and S.K. Das (2008). Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents. *Chemical Engineering Journal*, **137**(3): 529-541.
- Boamah, P.O., Huang, Y., Hua, M., Zhang, Q., Wu, J., Onumah, J., Sam Amoah, L.K. and P.O. Boamah (2015). Sorption of heavy metals onto carboxylate chitosan derivatives—A mini review. *Ecotoxicology and Environmental Safety*, **116**: 113-120.
- Fomina, M. and G.M. Gadd (2014). Biosorption: Current perspectives on concept, definition and application. *Bioresource Technology*, **160**: 3-14.
- Franco, P.E., Veit, M.T., Borba, C.E., Gonclaves, G.D.C., Kle, M.R.F., Bergamasco, R., Dasilva, E.A. and P.Y.R. Suzaki (2013). Nickel(II) and zinc(II) removal using amberlite IR-120: Ion exchange equilibrium and kinetics. *Chemical Engineering Journal*, **221**: 426-435.

- Fu, F. and Q. Wang (2011). A review of Removal of heavy metal ions from wastewaters. *Journal of Environmental Management*, **92**(3): 407-418.
- Ghodbane, I. and O. Hamdaoui (2008). Removal of mercury(II) from aqueous media using Eucalyptus bark: Kinetic and equilibrium studies. *Journal of Hazardous Materials*, **160**(2-3): 301-309.
- Gupta, V.K., Carrott, P.J.M. and M.M.L. Ribeiro Carrott (2009). Low-cost adsorbents: growing approach to wastewater treatment—A review. *Critical Reviews on Environment Science and Technology*, **39**: 783-842.
- Ho, Y.S. and G. McKay (1999). Pseudo-second order model for sorption processes. *Process Biochemistry*, **34**: 451-465.
- Khakpour, H., Younesi, H. and M. Mohammad Hosseini (2014). Two-stage biosorption of selenium from aqueous solution using dried biomass of the baker's yeast *Saccharomyces cerevisiae*. *Journal of Environmental Chemical Engineering*, **2**(1): 532-542.
- Michalak, I., Chijnacka, K. and A. WitekKrowiak (2013). State-of-the-art biosorption process – A review. *Applied Biochemistry and Biotechnology*, **170**(6): 1389-1416.
- Natarajan, R. and R. Manivasagan (2015). Biosorptive Removal of Heavy Metal onto Raw Activated Sludge: Parametric, Equilibrium, and Kinetic Studies. *Journal of Environmental Engineering*, 10.1061/(ASCE)EE.1943-7870.0000961, C4015002.
- Nguyen, T.A.H., Ngo, H.H., Guo, W.S., Zhang, J., Liang, S., Yue, Q.Y., Li, Q. and T.V. Nguyen (2013). Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from waste water. *Bioresource Technology*, **148**: 574-585.
- Park, D., Yun, Y.S. and J.M. Park (2010). The Past, Present and Future Trends of Biosorption. *Biotechnology and Bioprocess Engineering*, **15**(1): 86-102.
- Plaza, J., Viera, M., Donati, E. and E. Guibal (2011). Biosorption of mercury by *Macrocystis pyrifera* and *Undaria pinnatifida*: Influence of zinc, cadmium and nickel. *Journal of Environmental Science*, **23**(11): 1778-1786.
- Rajamohan, N., Dilipkumar, M. and M. Rajasimman (2014a). Parametric and kinetic studies on biosorption of mercury using modified *Phoenix dactylifera* biomass. *Journal of the Taiwan Institute of Chemical Engineers*, **45**(5): 2622-2627.
- Rajamohan, N., Rajasimman, M., Rajeshkannan, R. and V. Saravanan (2014b). Equilibrium, kinetic and thermodynamic studies on the removal of Aluminum by modified Eucalyptus camaldulensis barks. *Alexandria Engineering Journal*, **53**(2): 409-415.
- Rajeshkannan, R., Rajasimman, M. and N. Rajamohan (2012). Removal of malachite green from aqueous solutions using wheat bran: Optimization, equilibrium and kinetic studies. *International Journal of Environmental Engineering*, **4**(1/2): 1-23.
- Sachan, S., Ghosh, S. and A. Mitra (2006). Biotransformation of p-coumaric acid by *Paecilomyces variotii*. *Letters in Applied Microbiology*, **42**(1): 35-41.
- Tang, Y., Chen, L., Wei, Yao, Q. and T. Li (2013). Removal of lead ions from aqueous solution by the dried aquatic plant, *Lemna perpusilla* Torr. *Journal of Hazardous Materials*, **244-245**: 603-612.
- Wan Ngah, W.S. and Hanafiah, M.A.K.M. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresource Technology*, **99**(10): 3935-3948.
- Yavuz, H., Denizli, A., Gungunes, H., Safarikova, M. and I. Safarik (2006). Biosorption of mercury on magnetically modified yeast cells. *Separation and Purification Technology*, **52**: 253-260.