

Kinetic and equilibrium modeling of biosorption of nickel (II) and cadmium (II) on brewery sludge

Rajeswari M. Kulkarni, K. Vidya Shetty and G. Srinikethan

ABSTRACT

In the current study, utilization of industrial waste brewery sludge for the biosorption of nickel (II) and cadmium (II) has been explored. The suitable conditions for the effective removal of Ni (II) and Cd (II) from aqueous solutions were examined. The kinetic evaluation showed that the biosorption process using the sludge followed pseudo-second order kinetics. In the presence of a metal co-ion, competitive and preferential biosorption was observed. The Langmuir model and Freundlich model were able to describe the sorption equilibrium for biosorption of Ni (II) and Cd (II) ions in single and dual metal systems. The effects of co-ion concentrations onto mono-component isotherm parameters (Langmuir and Freundlich) were studied and the inhibitory effect of co-ion concentration was observed. The effective reusability of biomass was assessed by three cycles of sorption-desorption. The sludge, owing to its high biosorption intensity and large availability from the local supply, is a better biosorbent for the treatment of Ni (II) and Cd (II) contaminated water.

Key words | brewery sludge, cadmium and nickel ions, kinetics, preferential biosorption

Rajeswari M. Kulkarni (corresponding author)
Department of Chemical Engineering,
Ramiah Institute of Technology,
Bangalore,
India
E-mail: rmkulkarni@msrit.edu

Rajeswari M. Kulkarni
K. Vidya Shetty
G. Srinikethan
Department of Chemical Engineering,
National Institute of Technology,
Surathkal, Karnataka,
India

INTRODUCTION

The growing population and industrial development pose a serious threat to water resources and ecosystems. One threat is the accretion of heavy metals, such as cadmium, mercury, nickel, lead, chromium, arsenic and their compounds. These are very toxic and some are subjected to bio-magnification (Orhan & Büyükgüngör 1993; Aksu & Dönmez 2006; Ahmaruzzaman 2011). Nickel and cadmium are of special interest since they are widely used together in many industries such as electroplating, smelting, alloy preparation, electronics, and battery manufacturing (Abu Al-Rub *et al.* 2003; Febrianto *et al.* 2009). The concentrations of these metals in the groundwater of certain areas of the state of Karnataka in India are high (KSPCB; Singh *et al.* 2010). According to the Central Pollution Control Board (India), the permissible discharge level of Ni (II) and Cd (II) with many of the industrial effluents into inland water is 3 mg/L and 2 mg/L respectively (CPCB).

The technology used in the removal of metal ions from wastewater in the process industries has evolved from conventional methods like chemical precipitation to adsorption processes using biosorbents. Recently, there has been a considerable amount of research regarding the use of low-cost industrial waste as biosorbents for detoxification of

water contaminated with metal ions (Table 1). Micro-organisms such as bacteria and yeast are used in breweries and food industries to aid fermentation. These industries are facing problems related to safe sludge disposal (Kuyucak 1990). In the current study, assessing the possible utilization of industrial waste brewery sludge, for the removal of Ni (II) and Cd (II) ions from aqueous solutions, has been explored. This study also addresses the effect of a co-ion presence during simultaneous biosorption of metal ions on the sludge.

METHODS

Preparation of biosorbent

Industrial waste sludge containing a yeast biomass of *Saccharomyces carlsbergensis* was obtained from United Breweries Limited, Nelamangala, India. The wet sludge was sun-dried for 72 h and later oven dried at 60 °C for 24 h. The dry sludge was powdered in a mortar and the yeast powder was sieved through 80–100 mesh to obtain an estimated average particle size of 150 µm.

Table 1 | Biosorption capacity of different low cost and industrial waste biosorbents for Ni (II) and Cd (II) removal

Metal	Biomass type	Metal uptake (mg/g)	Reference
Ni (II)	Fly ash	0.03	Rao <i>et al.</i> (2002)
	Baker's yeast	11.40	Padmavathy <i>et al.</i> (2003)
	Bagasse fly ash	1.12	Gupta <i>et al.</i> (2003)
	Tea factory waste	15.26	Malkoc & Nuhoglu (2005)
	Activated sludge	4.06	Ajaykumar <i>et al.</i> (2009)
	Brewer's yeast	5.34	Cui <i>et al.</i> (2010)
	Sugarcane bagasse	2.00	Alomá <i>et al.</i> (2012)
	<i>Sacchromyces cerevisiae</i>	1.57	Galedar & Younesi (2013)
	Nanocellulose fibers of rice straw	8.55	Kardam <i>et al.</i> (2014)
	<i>Elaeagnus Angustifolia</i>	2.42	Amiri <i>et al.</i> (2014)
	Brewery sludge	7.87	Present study
Cd (II)	<i>Aspergillus niger</i>	4.0	Kapoor & Viraraghavan (1998)
	Bagasse fly ash	1.24	Gupta <i>et al.</i> (2003)
	Activated sludge	18.08	Ajaykumar <i>et al.</i> (2009)
	Brewer's yeast	10.17	Cui <i>et al.</i> (2010)
	<i>Aspergillus aculeatus</i>	14.24	Panday & Banerjee (2012)
	Baker's yeast	2.36	Wang (2012)
	<i>Sacchromyces cerevisiae</i>	3.74	Galedar & Younesi (2013)
	Nanocellulose fibers of rice straw	9.7	Kardam <i>et al.</i> (2014)
	<i>Elaeagnus Angustifolia</i>	1.97	Amiri <i>et al.</i> (2014)
	Brewery sludge	13.96	Present study

Preparation of metal ion solution and metal ion analysis

Metal ion solutions of Ni (II) and Cd (II) of desired concentrations were prepared by suitably diluting the stock solutions. Stock solutions of 100 mg/L of Ni (II) and 100 mg/L of Cd (II) were prepared in 1,000 mL standard volumetric flasks by dissolving 0.4479 g of nickel sulphate [NiSO₄.6H₂O] and 0.2744 g of cadmium nitrate [Cd (NO₃)₂.4H₂O] in distilled water. For mixed metal studies, desired combinations of Ni (II) and Cd (II) were prepared by mixing suitable volumes of stock solutions of both metals. The initial pH of the metal solution was adjusted by using dilute sodium hydroxide or sulphuric acid solution.

The initial metal ion concentration and the residual concentration of Ni (II) and Cd (II) in the biosorption medium after biosorption was determined by atomic absorption spectrometer (GBC 932 plus) at a wavelength of 351.5 nm for Ni (II) and 326.1 nm for Cd (II). Before the analysis of residual metal ion concentrations, the samples were centrifuged, filtered using Whatman Grade 42 filter paper and the filtrate was analyzed using an atomic absorption spectrometer.

Batch biosorption experiments

The biosorption process was studied through batch experiments, to examine the influence of different factors

such as initial pH (2.0–9.0), contact time (10–180 min), sludge dosage (2–40 g/L), initial metal ion concentration (10–50 mg/L), temperature (30–50 °C) and co-ion concentrations on biosorption of Ni (II) and Cd (II) on the sludge. The batch experiments were performed in 250 mL Erlenmeyer flasks with a working volume of 50 mL in an incubator orbital shaker at 150 rpm. All the experiments were conducted in duplicate and the mean values were shown in the results. Error bars are provided in all the related figures.

RESULTS AND DISCUSSION

Effect of initial pH

As shown in Figure 1, barely any biosorption was seen at a pH of 2.0 as there was a high concentration of protons, which compete with metal ions for the binding sites of the sludge. The percentage of biosorption for Ni (II) increased from 1% to 35% when the pH of the solution was increased from 2.0 to 5.0. Similarly, in the case of the Cd (II) ion, the percentage of biosorption was found to have increased from 49% to 73%, at pH of 2.0 to 6.0. At higher pH, the metal ions became more competitive with hydrogen ions, resulting in an increased biosorption (Bermúdez *et al.* 2011; Amiri *et al.*

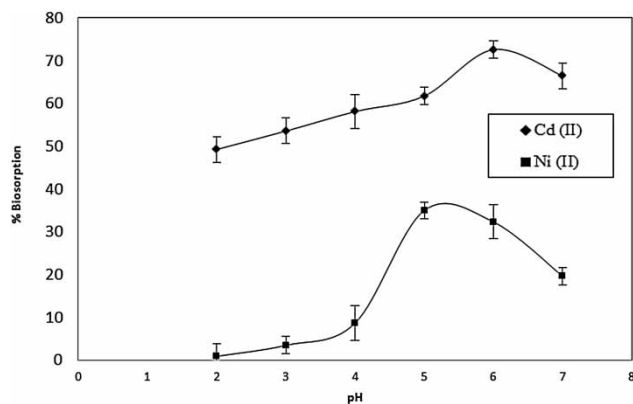


Figure 1 | Percentage metal biosorption vs pH during biosorption of Ni (II) and Cd (II) on the sludge in a single metal ion system at a temperature of 30 ± 2 °C, 24 h contact time, 50 mg/L initial metal ion concentration, 4 g/L biosorbent dosage, average particle size 150 μ m.

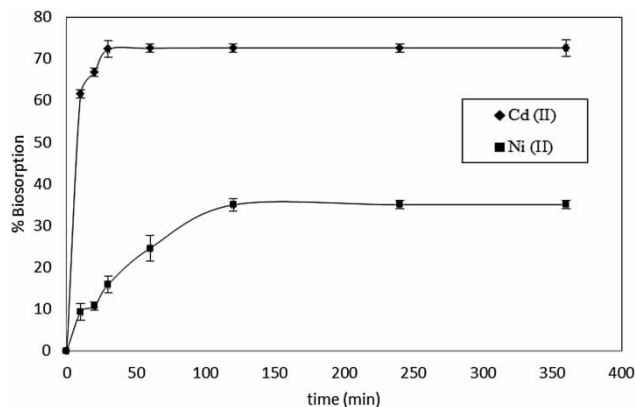


Figure 2 | Effect of contact time on % biosorption of Ni (II) and Cd (II) on the sludge in a single metal ion system at a temperature of 30 ± 2 °C, 50 mg/L initial metal ion concentration, 4 g/L biosorbent dosage, average particle size 150 μ m, pH 5.0 for Ni (II) and pH 6.0 for Cd (II).

2014). The negative charge of the functional groups on the sludge promoted biosorption with metal cations. In an alkaline condition, formation of metal hydroxide complex inhibits the contact of metal ions to the biomass. The maximum biosorption of Ni (II) and Cd (II) on the yeast biomass was observed at a pH of 5.0 for Ni (II) and at pH 6.0 for Cd (II).

Effect of contact time and biosorption kinetics

As shown in Figure 2, the maximum removal rate for Ni (II) was 35% and 73% for Cd (II) at 120 min when equilibrium was achieved. The applicability of the pseudo- first order (Equation (1)) and pseudo- second order kinetic models (Equation (2)) were tested using the data shown in Figure 2.

$$\log(q_e - q) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (1)$$

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

where, q and q_e are metal uptake (mg/g) at time t and at equilibrium time, k_1 is the pseudo- first order rate constant (min^{-1}), t is the contact time (min), and k_2 is the pseudo- second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$).

The calculated model parameters are presented in Table 2. Ni (II) and Cd (II) biosorption onto the sludge follows a pseudo- second order kinetic model ($R^2 \approx 0.99$) but not a pseudo- first order model. This indicates that the surface reaction through sharing or exchange of ions is the rate controlling step for biosorption of Ni (II) and Cd (II) ions by the sludge (Ho & McKay 1999; Alomá et al. 2012).

Effect of sludge dosage

The increase in the sludge dosage increases the number of binding sites for biosorption. It is seen from Figure 3 that as the sludge dosage increased from 2 g/L to 40 g/L, the percentage biosorption was found to increase from 26% to 39% for Ni (II) and 66% to 79% for Cd (II). The dosage effect (2–40 g/L) is similar for both Ni (II) and Cd (II) biosorption, with a total increase in the removal rate of around 13%. The increase in the sludge dosage can be attributed to an increase in the active biosorbent sites (Akar et al. 2009; Kulkarni et al. 2018).

Table 2 | Pseudo first order and pseudo second order kinetic parameters for Ni (II) and Cd (II) biosorption on the sludge with goodness of fit of model

Metal ion	Experimental q_e (mg/g)	First order kinetics			Second order kinetics		
		Predicted q_e (mg/g)	k_1 (min^{-1})	R^2	Predicted q_e (mg/g)	k_2 (g/mg.min)	R^2
Ni (II)	4.37	2.28	0.026	0.8493	4.95	0.005	0.991
Cd (II)	9.07	0.31	0.029	0.7155	9.10	0.111	0.999

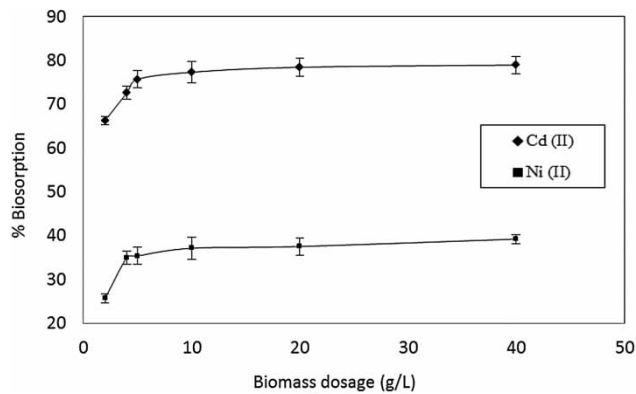


Figure 3 | Effect of biosorbent dosage on % biosorption of Ni (II) and Cd (II) on the sludge in a single metal ion system at a temperature of 30 ± 2 °C, 120 min contact time, 50 mg/L initial metal ion concentration, average particle size 150 µm, pH 5.0 for Ni (II) and pH 6.0 for Cd (II).

Effect of initial Ni (II) and Cd (II) metal ion concentration and temperature

The percentage biosorption decreased from 49% to 35% at 30 °C, 41% to 31% at 40 °C and 33% to 23% at 50 °C, with an increase in Ni (II) ion concentration from 10 mg/L to 50 mg/L (Figure 4). Similarly, the percentage biosorption decreased from 86% to 73% at 30 °C, 81% to 65% at 40 °C and 74% to 54% at 50 °C with an increase in Cd (II) ion concentration from 10 mg/L to 50 mg/L (Figure 5). The decrease in biosorption is due to the increased number of metal ions competing for the available active sites on the sludge (Guyo *et al.* 2016). It is evident from Figures 4 and 5 that the biosorption of Ni (II) and Cd (II) ions onto the sludge is controlled by an exothermic process. The maximum uptake occurred at 30 °C in the selected temperature range of 30 °C to 50 °C.

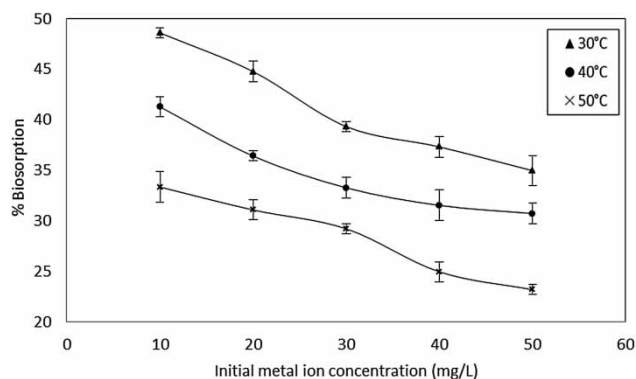


Figure 4 | Effect of initial Ni (II) ion concentration and temperature on % biosorption of Ni (II) on the sludge in a single metal ion system at pH 5.0, 120 min contact time, 4 g/L biosorbent dosage, average particle size 150 µm.

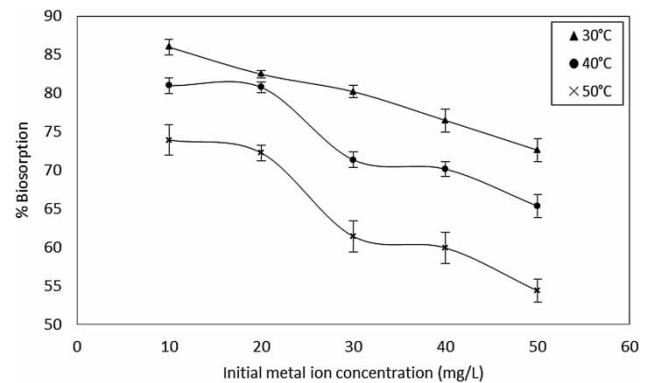


Figure 5 | Effect of initial Cd (II) ion concentration and temperature on % biosorption of Cd (II) on the sludge in a single metal ion system at pH 6.0, 120 min contact time, 4 g/L biosorbent dosage, average particle size 150 µm.

Isotherms for single metal biosorption

The Langmuir and Freundlich models were used to describe the equilibrium biosorption data (Table 3). The linearized form of the Langmuir isotherm (Equations (3) and (4)) and the Freundlich isotherm (Equation (5)) are

$$\frac{1}{q_e} = \frac{1}{q_{\max} b C_e} + \frac{1}{q_{\max}} \quad (3)$$

$$R_L = \frac{1}{1 + b C_0} \quad (4)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K \quad (5)$$

where q_{\max} is the maximum monolayer biosorption capacity of the biosorbent (mg/g), b is biosorption affinity in L/mg, K and n are equilibrium constants indicative of biosorption capacity ($\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$) and biosorption affinity respectively, R_L is the Hall separation factor, C_0 is the initial metal ion concentration in mg/L.

The values of the coefficient of determination being near to one (>0.97) suggest that both models provide a good fit to the equilibrium biosorption data at all the studied temperatures. Table 1 provides a summary of the sludge biosorption capacity compared with the different low cost and industrial waste biosorbents for Ni (II) and Cd (II) removal. It is clearly evident from the comparison that the maximum biosorption capacity of the sludge is fairly high compared to some of the reported biosorbents.

Effect of co-ions in biosorption of nickel (II) and cadmium (II)

Biosorption of Ni (II) and Cd (II) ions from the binary solutions of metal ions on the sludge was examined and

Table 3 | Langmuir and Freundlich isotherm parameters for Ni (II) and Cd (II) biosorption on brewery sludge

Metal ion	Temperature (°C)	Langmuir isotherm				Freundlich isotherm		
		q_{\max} (mg/g)	b (L/mg)	R_L	R^2	K	n	R^2
Ni (II)	30	7.874	35.45×10^{-3}	0.36	0.9986	0.40	1.45	0.9956
	40	7.092	28.67×10^{-3}	0.41	0.9961	0.28	1.36	0.9995
	50	6.514	22.17×10^{-3}	0.47	0.9977	0.22	1.40	0.9827
Cd (II)	30	13.966	12.53×10^{-2}	0.13	0.9989	1.80	1.56	0.9924
	40	12.886	10.04×10^{-2}	0.16	0.9839	1.51	1.64	0.9659
	50	10.193	8.64×10^{-2}	0.18	0.9885	1.15	1.71	0.9686

contrasted with that of single metal ion biosorption (Tables S1 and S2 found in the online supplement, as are other tables and figures numbered with the prefix S). The metal uptake was found to decrease with an increase in co-ion concentration, indicating competitive biosorption and interference of co-ions during biosorption. Competition between metal ions for vacant sites resulted in the decrease in metal uptake by the sludge.

Biosorption isotherms – effect of co-ion on mono component isotherm parameters

Biosorption isotherms for the biosorption of Ni (II) and Cd (II) on the sludge were analyzed in both single and binary metal solutions to study the effect of co-ion concentrations on the mono-component isotherm parameters (Table 4). This helps in studying the alteration of equilibrium in the presence of co-ions. The values of the Langmuir and Freundlich constants, q_{\max} and K were found to decrease with an increase in co-ion concentrations. The b and n values obtained were found to be higher for Cd (II) than for Ni (II), indicating a higher affinity of the sludge toward Cd (II). The sequence of selectivity followed the order of

Table 4 | Biosorption isotherm constants for Ni (II) and Cd (II) biosorption on the sludge in the absence and in the presence of other metal co-ions

Metal ion	Co-ion mg/L	Langmuir constants			Freundlich constants		
		q_{\max} (mg/g)	b (L/mg)	R^2	K	n	R^2
Ni (II)	$C_{i\text{ Cd (II)}} = 0$	7.87	0.035	0.998	0.405	1.453	0.996
	10	7.25	0.028	0.994	0.281	1.363	0.992
	30	6.66	0.026	0.993	0.244	1.347	0.997
	50	6.48	0.020	0.999	0.194	1.341	0.996
Cd (II)	$C_{i\text{ Ni (II)}} = 0$	13.96	0.125	0.999	1.774	1.564	0.992
	10	13.16	0.092	0.994	1.360	1.533	0.985
	30	12.54	0.058	0.988	0.799	1.334	0.989
	50	11.34	0.056	0.978	0.696	1.328	0.988

decreasing electronegativity, increasing ionic radius and atomic weight and decreasing hardness (Aksu & Dönmez 2006; Kulkarni *et al.* 2014). Cd (II) will be preferentially biosorbed over Ni (II) due to greater affinity for the carboxylic groups existing on the sludge (Abu Al-Rub *et al.* 2003; Kleinübing *et al.* 2011). It was observed that the biosorption capacity of the sludge in the dual metal system was lower than the single metal ion system.

Characterization of biomass

The surface images of the sludge before and after Ni (II) and Cd (II) biosorption (Figure S1) were obtained using a scanning electron microscope (JEOL, Japan) with Energy Dispersive X-ray Spectroscopy (EDX). The biosorbent surface was observed to be rough before biosorption. Biosorption of metal ions has led to the formation of aggregates on the sludge surface, which may be due to complexation of metal ions with the cell surface. EDX analysis showed the presence of Ni (II) and the presence of Cd (II) on the biomass surface along with other components of the biomass sample (C,N,O,P,S) after Ni (II) and Cd (II) biosorption.

Infrared spectra of biosorbents loaded with and without metal ions were recorded using a Fourier transform-infrared (FTIR) spectrometer (Bruker alpha) in the range of 4,000–500 cm^{-1} , with a resolution of 4 cm^{-1} (Figure S2). After nickel biosorption, the band at 2,919.7 cm^{-1} shifts to 2,925.6 cm^{-1} , 1,641.5 cm^{-1} to 1,638.5 cm^{-1} , 1,532.6 cm^{-1} to 1,535.5 cm^{-1} and 1,037.3 cm^{-1} to 1,039.7 cm^{-1} . Similar observations were made with the FTIR spectra of the sludge after Cd (II) biosorption with a band shift from 2,919.7 cm^{-1} to 2,923.6 cm^{-1} , 1,641.5 cm^{-1} to 1,637 cm^{-1} , 1,532.6 cm^{-1} to 1,531.5 cm^{-1} and 1,037.3 cm^{-1} to 1,034.6 cm^{-1} , which indicates that the $-\text{CH}_2$, $-\text{OH}$, $-\text{C}=\text{O}$, $-\text{NH}_2$ and C-O anionic functional groups present on the sludge are involved in the biosorption.

Desorption, regeneration and reuse studies

The application of biosorbent towards detoxification of metal bearing effluents depends not only on its biosorption capacity, but also on how well the metal may be recovered from the biosorbent surface; the possibility of biomass regeneration and reuse. The metal loaded biomass, after biosorption was contacted with 50 mL of 0.1N HCl elutant to study desorption of metal ions (Table S3).

The reusability of the sludge was evaluated in three consecutive cycles of biosorption-desorption using HCl elutant and regeneration using distilled water in a batch system. Acid treatment with 0.1 M HCl was found to be the most effective, where more than 90% of metal was desorbed from the spent sludge throughout the three cycles. Only 12.7% decrease in sorption of Ni (II) and 5.62% decrease in sorption of Cd (II) by the biomass were observed in three cycles, indicating effectiveness of the desorption – regeneration process (Table S4).

CONCLUSIONS

This study identified brewery sludge as a suitable biosorbent to be utilized for treating Ni (II) and Cd (II) ions from metal contaminated water. The optimal biosorption conditions for the selected metal removal were determined using the batch mode of studies. The biosorption mechanism followed the pseudo second order kinetic model. Preferential biosorption of Cd (II) over Ni (II) was observed in both cases of single and dual metal ion biosorption on to the sludge. The metal uptake was found to decrease with increase in co-ion concentration, indicating competitive biosorption and interference of co-ions during biosorption. Brewery sludge possesses advantages such as abundant availability, good biosorption capacity and intensity and ease of regeneration with possibilities of metal recovery. This makes biosorption by the sludge an attractive treatment option for Ni (II) and Cd (II)-bearing water.

ACKNOWLEDGEMENT

We are grateful to Ramaiah Institute of Technology, Bangalore and NITK, Surathkal, for their continuous support.

CONFLICT OF INTEREST

The authors have declared no conflict of interest.

REFERENCES

- Abu Al-Rub, F. A., Kandah, M. & Al-Dabaybeh, N. 2003 Competitive adsorption of nickel and cadmium on sheep manure wastes: experimental and prediction studies. *Separation Science and Technology* **38** (2), 483–497.
- Ahmaruzzaman, M. 2011 Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Advances in Colloid and Interface Science* **166** (1), 36–59.
- AjayKumar, A. V., Darwish, N. A. & Hilal, N. 2009 Study of various parameters in the biosorption of heavy metals on activated sludge. *World Appl Sci J 5 (Special Issue for Environment)* **5** (5), 32–40.
- Akar, T., Kaynak, Z., Ulusoy, S., Yuvaci, D., Ozsari, G. & Akar, S. T. 2009 Enhanced biosorption of nickel (II) ions by silica-gel-immobilized waste biomass: biosorption characteristics in batch and dynamic flow mode. *Journal of Hazardous Materials* **163** (2), 1134–1141.
- Aksu, Z. & Dönmez, G. 2006 Binary biosorption of cadmium (II) and nickel (II) onto dried *Chlorella vulgaris*: Co-ion effect on mono-component isotherm parameters. *Process Biochemistry* **41** (4), 860–868.
- Alomá, I., Martín-Lara, M. A., Rodríguez, I. L., Blázquez, G. & Calero, M. 2012 Removal of nickel (II) ions from aqueous solutions by biosorption on sugarcane bagasse. *Journal of the Taiwan Institute of Chemical Engineers* **43** (2), 275–281.
- Amiri, M. J., Fadaei, E., Baghvand, A. & Ezadkhasty, Z. 2014 Removal of heavy metals Cr (VI), Cd (II) and Ni (II) from aqueous solution by bioadsorption of *Elaeagnus Angustifolia*. *International Journal of Environmental Research* **8** (2), 411–420.
- Bermúdez, Y. G., Rico, I. L. R., Bermúdez, O. G. & Guibal, E. 2011 Nickel biosorption using *Gracilaria caudata* and *Sargassum muticum*. *Chemical Engineering Journal* **166** (1), 122–131.
- CPCB. Central Pollution Control Board. http://www.cpcb.nic.in/Industry_Specific_Standards.php
- Cui, L., Wu, G. & Jeong, T. S. 2010 Adsorption performance of nickel and cadmium ions onto brewer's yeast. *The Canadian Journal of Chemical Engineering* **88** (1), 109–115.
- Febrianto, J., Kosasih, A. N., Sunarso, J., Ju, Y. H., Indraswati, N. & Ismadji, S. 2009 Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. *Journal of Hazardous Materials* **162** (2), 616–645.
- Galedar, M. & Younesi, H. 2013 Biosorption of ternary cadmium, nickel and cobalt ions from aqueous solution onto *saccharomyces cerevisiae* cells: batch and column studies. *American Journal of Biochemistry and Biotechnology* **9** (1), 47–60.
- Gupta, V. K., Jain, C. K., Ali, I., Sharma, M. & Saini, V. K. 2003 Removal of cadmium and nickel from wastewater using

- bagasse fly ash – a sugar industry waste. *Water Research* **37** (16), 4038–4044.
- Guyo, U., Sibanda, K., Sebata, E., Chigondo, F. & Moyo, M. 2016 Removal of nickel (II) from aqueous solution by *Vigna unguiculata* (Cowpea) pods biomass. *Water Science and Technology* **73** (10), 2301–2310.
- Ho, Y. S. & McKay, G. 1999 Pseudo second order model for sorption processes. *Process Biochemistry* **34**, 451–465.
- Kapoor, A. & Viraraghavan, T. 1995 Fungal biosorption – an alternative treatment option for heavy metal bearing wastewaters: a review. *Bioresource Technology* **53** (3), 195–206.
- Kapoor, A. & Viraraghavan, T. 1998 Biosorption of heavy metals on *Aspergillus niger*: effect of pretreatment. *Bioresource Technology* **63** (2), 109–113.
- Kardam, A., Raj, K. R., Srivastava, S. & Srivastava, M. M. 2014 Nanocellulose fibers for biosorption of cadmium, nickel, and lead ions from aqueous solution. *Clean Technologies and Environmental Policy* **16** (2), 385–393.
- Kleinübing, S. J., Da Silva, E. A., Da Silva, M. G. & Guibal, E. 2011 Equilibrium of Cu (II) and Ni (II) biosorption by marine alga *Sargassum filipendula* in a dynamic system: competitiveness and selectivity. *Bioresource Technology* **102** (7), 4610–4617.
- KSPCB. Karnataka State Pollution Control Board. http://kspcb.kar.nic.in/annual_reports.html
- 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.
- Kulkarni, M. R., Bhagyalakshmi, C., Anand, D. & Herle, R. N. 2018 Removal of remazol brilliant blue dye from aqueous solutions using water hyacinth root powder. *Desalination and Water Treatment* **122**, 331–338.
- Kuyucak, N. 1990 Feasibility of biosorbents application. In: *Biosorption of Heavy Metals* (B. Volesky ed.). CRC Press, Boca Raton, FL, pp. 371–378.
- Malkoc, E. & Nuhoglu, Y. 2005 Investigations of nickel (II) removal from aqueous solutions using tea factory waste. *Journal of Hazardous Materials* **127** (1), 120–128.
- Orhan, Y. & Büyükgüngör, H. 1993 The removal of heavy metals by using agricultural wastes. *Water Sci. Technology* **28** (2), 247–255.
- Padmavathy, V., Vasudevan, P. & Dhingra, S. C. 2003 Biosorption of nickel (II) ions on Baker's yeast. *Process Biochemistry* **38** (10), 1389–1395.
- Panday, A. & Banerjee, D. 2012 Biosorption of cadmium (II) using discarded biomass of *Aspergillus aculeatus* DBF9. *Terrestrial Aquatic Environ Toxicol* **6** (1), 8–13.
- Rao, M., Parwate, A. V. & Bhole, A. G. 2002 Removal of Cr⁶⁺ and Ni²⁺ from aqueous solution using bagasse and fly ash. *Waste Management* **22** (7), 821–830.
- Singh, M. J., Somashekar, R. K., Prakash, K. L. & Shivanna, K. 2010 Investigation of heavy metals in crystalline aquifer groundwater from different valleys of Bangalore, Karnataka. *Journal of Geography and Regional Planning* **3** (10), 262–270.
- Wang, Y. 2012 Optimization of Cadmium, Zinc and Copper biosorption in an aqueous solution by *Saccharomyces cerevisiae*. *International Journal of Chemistry* **01**, 1–13.

First received 13 July 2018; accepted in revised form 23 February 2019. Available online 7 March 2019