DOI: 10.46793/SBT28.323SN

KINETIC AND EQUILIBRIUM STUDIES OF BIOSORPTION OF Cd(II) IONS USING SILICA-ALGINATE-YEAST COMPOSITE

Slobodanka Stanojević-Nikolić[1,2], Milan P. Nikolić[1], Marina Šćiban[2], Vladimir V. Srdić[2], Vladimir B. Pavlović[3]

Abstract: Viable *Saccharomyces cerevisiae* cells were immobilized by silica-alginate matrix and obtained spherical composite particles and used for biosorption of Cd(II) ions. The obtained composite displayed high cadmium removal efficiency of 99.2, 95.7, 88.3 and 78% in the successive four adsorption steps. The adsorption capacity after four step of Cd(II) removal was ~14,2 mg of Cd(II) per g of biosorbent. Pseudo-second-order kinetic agree well with the experimental values suggesting both adsorption and ionic exchange are simultaneously performed on the surface of used biosorbent.

Keywords: biosorption, heavy, *Saccharomyces cerevisiae,* metals, biocomposite

Introduction

Global industralization and urbanization are responsible for increasing amounts of toxic pollutants in the effluents and soil. Environmentally relevant most hazardous substances which contaminate environment, expecially water, are heavy metals, due to their persistent, non-biodegradable, and toxic nature (Hazrat et al., 2019). Cadmium is highly toxic, non-essential heavy metal which may couse serious health problems to all living organisms (Genchi et al., 2020). Due to its ability to be accumulated in living organisms, it has harmful impact on lungs, kidneys, liver, reproductive organs etc. Both short-term or long-term exposure to cadmium can cause serious health problems such as renal and hepatic dysfunction, pulmonary edema, testicular damage. Thus, it is very important to prevent cadmium from getting into the environment from industrial effluents. It is well known that both geogenic and anthropogenic

[1]University of Kragujevac, Faculty of Agronomy, Cara Dušana 34, Čačak, Serbia (slobodankasnikolic@gmail.com)
[2]University of Novi Sad, Faculty of Technology Novi Sad, Blvd. Cara Lazara 1, 21000 Novi Sad, Serbia
[3]University of Belgrade, Faculty of Agriculture, Nemanjina 6, 11080 Belgrade, Serbia.

sources can elevate Cd concentrations in soils and groundwater. Significant sources of natural Cd emissions are hydrothermal vents, weathering of rocks and airborne soil particles from deserts, sea spray, forest fires, biogenic material and volcanoes. Sources of anthropogenic Cd emissions are non-ferrous metal production, fossil fuel combustion, phosphate fertilizer manufacturing, iron, steel, and cement production and road dust. Municipal and sewage sludge incineration can also release cadmium into air, water, and soil (Kubier et al., 2019). Furthermore, Cd can be found in products such as pigments, coatings, platings, stabilizers for polyvinyl chloride (PVC) and alloys. Phosphate fertilizers contain between 36 and 77 mg Cd per kg P_2O_5, making them one of the most important sources of Cd contamination in soils (Kubier et al., 2019).

The application of biosorption for removal of heavy metals from wastewater has been concidered as an effective procedure for water treatment (He and Chen, 2014). Major advantages of biosorption over conventional treatment methods (precipitation, adsorption, reduction, coagulation, and membrane filtration) is low cost, eco-friendliness, high binding ability, high efficiency of removal metal ions in low concentration, low biological sludge, etc (Aryal 2019). Low cost and eco-friendly biosorption of heavy metal ions using nonpathogenic microbial biomass is generally regarded as safe and it is receiving more attention in recent years (Mishra et al., 2020).

The immobilization of microbial cells on numerous matrices via entrapment was found to enhance bioremediation of heavy metals (Keskin et al., 2018) and dyes (San et al., 2014) from wastewater. Immobilized microbial cells have following advantages over the free cells in metals biosorption process: easy manipulation, higher stability of composites, easy separation after biosorption procedures, potential use in real continuous systems (Giese 2020).

In order to make advanced biosorbents for removal of cadmium ions from aqueous solutions, we have developed processing method for immobilization of non-pathogenic and safe *Saccharomyces cerevisiae* cells in silica-alginate composite material. Kinetic and equilibrium studies of biosorption of Cd^{2+} ions using silica-alginate-yeast composite have been investigated.

Materials and methods

0.5 g of the yeast cell biomass was mixed with 2 ml of silicate solution (having a Na_2O/SiO_2 molar ratio of 0.4 and SiO_2 concentration 362 g/L) and 8 ml of 5% w/v alginate solution. The mixture of sodium silicate, alginate and microbial cell was slowly added (Figure 1b) into previously prepared 0.1 M calcium chloride solution (Figure 1). The silica-alginate- *S. cerevisiae* (SA-Sc) composite particles were washed and dried at room temperature.

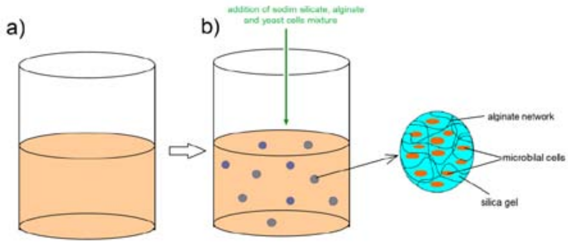

Figure 1. Preparation of SA-Sc composite particles (Stanojević-Nikolić et al., 2022)

The kinetics of adsorption of cadmium ions from aqueous solution by alginate-silica-microbial cell composite were investigated by dispersing of 0.2 g of this composite material in 10 mL of 1 mmol/L aqueous cadmium(II) sulphate solution at a constant temperature (25°C) and pH=6. After appropriate contact time between 5 to 120 minutes, the small aliquots of sample supernatant were diluted in 1% (w/w) nitric acid.

The cadmium concentration, both in the initial and final solution, was determined by flame atomic absorption spectrometry using Perkin Elmer AAnalyst 200 system after calibration with stock solutions in the range of concentration of 0.5-4 mg/L. The equilibrium amount (adsorption capacity) (q_e) of cadmium ions adsorbed on sorbent phase (mg Cd^{2+}/g dry sorbent) was calculated in the following way:

$$q_e = \frac{(C_0 - C_e)}{m} \cdot V \tag{1}$$

where C_0 (mg/L) is the initial concentration of Cd^{2+}, C_t (mg/L) is the concentration of Cd^{2+} at time t, V (L) is the total volume of solution and m (g) is the mass of bisorbent. All experiments were performed in triplicates and the mean values were used in the data analysis.

In order to investigate the mechanism of biosorption, characteristic constants of adsorption rate were determined at individual concentrations for silica-alginate-yeast composite and at different time by using a pseudo-first-order equation (Eq. (2)) of Lagergren based on solid capacity, and pseudo-second-order equation (Eq. (3)) based on solid phase adsorption:

$$ln(q_e - q_t) = -k_t + lnq_e \tag{2}$$

$$\frac{t}{q_t} = \left(\frac{1}{q_e}\right) t + \frac{1}{k_2 q_e^2} \quad (3)$$

where q_t and q_e (mg/g) are the amounts of the metal ions biosorbed at time t (min) and equilibrium (mg/g), respectively and k_1 is the rate constant (min^{-1}) of the pseudo-first model equation, k_2 (g/mg min) is the rate constant of the second order equation. The biosorption rate constants (k_1) can be determined experimentally by plotting of $\ln(q_e - q_t)$ versus t. On the other hand, the biosorption rate constants (k_2) can be determined experimentally by plotting t/q_t versus t.

The size and morphology of the particles were examined using a scanning electron microscope (SEM, JSM-6390 LV JEOL, operating at 30 kV) coupled with energy dispersive spectrometer (EDS) (Oxford Instruments X-MaxN). Prior to SEM imaging, the samples were sputtered with gold.

Results and discussion

Figure 2 shows SEM micrographs of silica-alginate-*S. cerevisiae* (SA-Sc) composite particles. Average particle size is about 3 mm (Fig. 2a). The microbial cells are clearly visible on the surface of particles (Fig. 2b). EDS insertion on Fig. 2b shows the presence of high levels of cadmium on gthe surface of biosorbent.

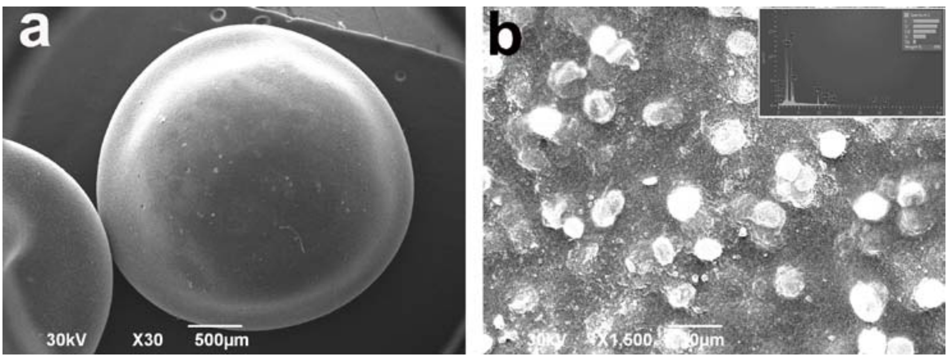

Figure 2. SEM micrograph of SA-Sc composite

The effect of reaction time on cadmium binding capacity of SA-Sc composite particles is shown in the Figure 3. The saturation capacities in four cycles was reached after approximately 20, 50, 70 and 90 minutes and have values of 3.9, 3.8, 3.6 and 2.9 mg/g, respectively.

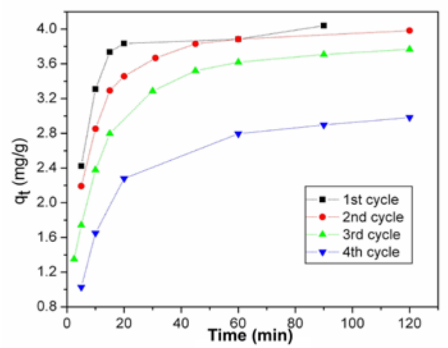

Figure 3. Effect of reaction time on cadmium binding capacity of SA-Sc composite in four adsorption cycles

The removal efficiency of Cd(II) ions in successive four steps using silica-alginate-yeast composites is shown on Table 1. It shows high removal efficiencies which gradually decreased from 99.22% for the first cycle to 78% for the fourth cycle.

Table 1. Removal efficiency of cadmium ions in four adsorption cycles

The cycle number	1st cycle	2nd cycle	3rd cycle	4th cycle
Removal efficiency (%)	99.22	95.77	88.28	78.00

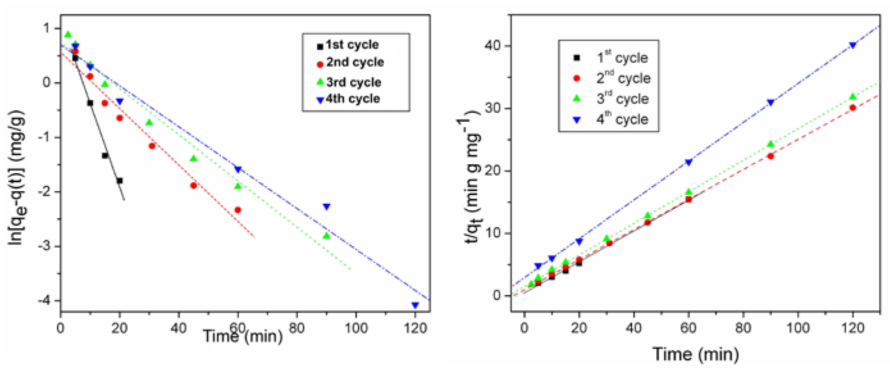

Figure 4. Application of two models to the adsorption kinetics of Cd(II) ions onto SA-Sc composite: pseudo-first order model (left); pseudo-second-order model (right)

The graphics application of the pseudo-first-order and pseudo-second-order kinetics on the obtained experimental results is shown on Figure 4. The corresponding pseudo-first-order and pseudo-second-order rate constants are calculated from graphics shown in Figure 4 and listed in Table 2. Table 2 shows that these constants decreased as the cycle number increased. The calculated values of q_e for pseudo-second-order kinetic agree well with the experimental values, with values of R^2 > 0.999 indicating that this model could be applied over the entire adsorption process. Pseudo second-order kinetic suggests that both adsorption and ionic exchange are simultaneously performed on the surface of used biosorbent, and the rate determining step was chemical bonding at the active cites of biosorbent (Coleman et al., 1956).

Table 2. Kinetic parameters for removal of Cd(II) ions using SA-Sc composite

	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
	q_e (mg/g)	k_1 (mg/g·min)	R^2	q_e (mg/g)	$k_2\left(\frac{g}{min \cdot mg}\right)$	R^2
1st cycle	3,217	0,1543	0,982	4,047	0,1184	0,9982
2nd cycle	2,756	0,05176	0,968	4,15	0,0585	0,9982
3rd cycle	2,109	0,04243	0,9772	3,956	0,0426	0,99984
4th cycle	2,013	0,03757	0,978	3,219	0,0327	0,9997

Conclusion

In this work, in order to produce advanced biosorbents for cadmium removal from aqueous solutions, non-pathogenicand safe *Sacharomyces cerevisiae* cell biomass was immobilized in silica-alginate composite material. SEM micrographs showed spherical composite particle with average size of 3 mm. Energy dispersive spectroscopy showed cadmium ions adsorbed on internal and external surface of biosorbent. The obtained composite displayed high cadmium removal efficiency of 99.2, 95.7, 88.3 and 78% in the successive four adsorption steps. The adsorption capacity after four step of Cd(II) removal was ~14,2 mg of Cd(II) per g of biosorbent. Pseudo-second-order kinetic agree well with the experimental values suggesting both adsorption and ionic exchange are simultaneously performed on the surface of used biosorbent, and the rate determining step was chemical bonding at the active cites of biosorbent.

Acknowledgement

This work was financially supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, project ref. number 451-03-47/2023-01/ 200088.

References

Aryal M. (2019). Calcium alginate entrapped *Eupatoriumadenophorum* Sprengel stems powder for chromium (VI) biosorption in aqueous mediums. PLOS ONE. 14:e0213477

Coleman, N.T., McClung, A.C., Moore, D.P. (1956). Formation constants for Cu(II)-peat complexes, Science 123, 330-331.

Genchi G, Stefania Sinicropi M, Lauria G, Carocci A, Catalano A. (2020). The Effects of Cadmium Toxicity. Inter J Environ Res Public Health, 17, 3782-3805.

Giese EC. (2020). Mining applications of immobilized microbial cells in alginate matrix: an overview. Rev. Int. Contam. Ambie., 36, 775-787

Hazrat A, Khan E, Ilahi I. (2019). Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation. J. Chem., Article ID 6730305, 14 pages.

He J, Chen JP. (2014). A comprehensive review on biosorption of heavy metals by algal biomass: Materials, performances, chemistry, and modeling simulation tools. Bioresour. Technol., 160, 67–78.

Kubier A, Wilkin RT, Pichler T. (2019). Cadmium in soils and groundwater: A review. Appl. Geochem., 108, 104388.

Keskin NOS, Celebioglu A, Sarioglu OF, Uyar T, Tekinay T. (2018). Encapsulation of living bacteria in electrospun cyclodextrin ultrathin fibers for bioremediation of heavy metals and reactive dye from wastewater. Colloids Surf. B Biointerfaces. 161, 169–176.

Mishra A, Gupta B, Kuma N, Singh R, Varma A, Thakur IS. (2020). Synthesis of calcite-based bio-composite biochar for enhanced biosorption and detoxification of chromium Cr (VI) by Zhihengliuella sp. ISTPL4. Bioresour. Technol., 307, 123262.

San NO, Celebioglu A, Tümtaş Y, Uyar T, Tekinay T. (2014). Reusable bacteria immobilized electrospun nanofibrous webs for decolorization of methylene blue dye in wastewater treatment. RSC Adv., 4, 32249–32255.

Stanojević-Nikolić S, Pavlović KV, Nikolić MP, Srdić VV, Šćiban M. (2022). Removal of cadmium(II) ions using *Saccharomyces cerevisiae* and *Leuconostoc mesenteroides* immobilized in silica materials by two processing methods. Materials Research., 25, e20210568.