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Silica nanoparticles/ Pleurotus Ostreatus biomass nanocomposite for cadmium adsorption from aqueous solution[☆]

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Abstract:
This study presents a new nanocomposite obtained from the growth substrate of the macromycete *Pleurotus ostreatus* (POBM) and SiO_2 nanospheres synthesized by a modified Stöber method and its application as an effective adsorbent for the separation of Cd^{2+} from polluted aqueous media. Metal adsorption capacity was quantified by using adsorption isotherms and kinetic models.

Keywords: Cd^{2+}adsorption, SiO_2 nanosphere, *Pleurotus ostreatus*, nanocomposite

1. INTRODUCTION

Rapid industrialization has led to an increased use of heavy metal ions over the last few decades, resulting in a serious global environmental problem [1].

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Adsorption was recommended as a promising process for heavy metal decontamination [2]. The utilization of bio-sorbents as bacteria, fungi, algae, and yeast was reported [3] as they are inexpensive and environmentally benign adsorbents. In order to obtain new adsorbents with improved properties, coupling of these bio-sorbents with various inorganic adsorbents becomes a feasible alternative [4]. Nanocomposites based on silica has been efficiently used for heavy metal adsorption due to the superior stability, the versatile surface chemistry, large pores and high porosity of silica [5].

The present study aimed the synthesis and characterization of a new biosorbent by modifying the POBM (*Pleurotus ostreatus* spent growth substrate) using silica nanospheres in order to improve the adsorption properties, thermal stability, chemical and mechanical properties of the biomass-based sorbents, obtained in a previous study [6]. The efficiency of the materials was tested for the removal of Cd^{2+} ions from aqueous solutions.

2. MATERIALS AND METHODS

2.1. Materials

Tetraethylorthosilicate (TEOS) (98%) was used as the source of silica, NH_4OH solution (25%) as catalyst and an ethanol / water mixture as solvent. The biological material, the spent growth substrate of the macromycete *Pleurotus ostreatus* (POBM), was provided by the local producer Carnic SRL Târgoviște. In a 100 mL Erlenmeyer flask, 2 mL of ethanol, 2 mL of water, and 2 mL of TEOS were added. The mixture was stirred in an ultrasonic bath. 5 mL of 25% NH_4OH solution was added and stirring was continued until a white nanosuspension was obtained. After adding 2.5 g POBM, magnetic stirring was continued for 2 h and then in the ultrasonic bath for 10 h. The mass ratio between the two components was $1SiO_2/5$ POBM. The solid obtained was separated by centrifugation for 20 minutes at 4000 rpm, then washed with distilled water and dried in an oven at 100°C for 3 hours. This sample was labeled POBM_SiO_2_SD.

2.2. Metal sorption studies

In order to determine the maximum amount of metal retained by the tested materials, the batch sorption studies were performed in propylene vessels containing 0.1 g of biosorbent and 50 mL of 50 mg/L Cd^{2+} solution.

After being mixed with a mechanical stirrer for 2 hours, the solutions were filtered using syringe filters, and the metal concentration was determined by using a GBC Avanta flame atomic absorption spectrometer (FAAS) equipped with air-acetylene flame.

The Cd^{2+} adsorption capacity of biosorbents (q_e) and the removal efficiency (R%) were calculated using the following equations:

$$q_e = \frac{V(c_0 - c_e)}{m}$$

$$R\% = \frac{C_0 - C_e}{C_0} \times 100$$

where q_e is the amount of Cd^{2+}adsorbed by investigated biosorbent at equilibrium (mg/L), C_0 and C_e are the initial and equilibrium metal concentrations (mg/L), V is the volume of Cd^{2+} solution (L), and m is the mass of the biosorbent (g). The influence of the initial metal ion concentration was studied at concentrations ranging from 1-500 mg/L Cd^{2+} solution, solid/liquid ratio was 0.1 g/L, room temperature and contact time 2 h. The experimental data were fitted using Langmuir, Freundlich and Dubinin-Radushkevich isotherms. The kinetic studies were performed at room temperature by using 50 mL Cd^{2+} solution at a concentration of 50 mg/L and 0.1 g biosorbent. The sampling time intervals ranged from 5-120 minutes. In order to analyze the results, the experimental data were fitted with pseudo first-order, pseudo second-order and intraparticle diffusion kinetic models.

3. RESULTS AND DISCUSSION

A new composite, POBM_SiO_2_SD, was synthesized and was used as an effective adsorbent for the separation of Cd^{2+} from polluted aqueous media. The maximum sorption capacity, q_e, for the tested material was 25.28 mg/g at an initial Cd^{2+} concentration of 50 mg/L. The results can be compared with those obtained in other studies using similar materials, the new bio-sorbent having a maximum Cd^{2+} sorption capacity of 382 mg/g at 500 mg/L initial concentration of the cadmium in aqueous solution, as shown by the adsorption isotherms. It should be mention that at this Cd^{2+} concentration, the POBM biomass showed an adsorption of 20 mg/g, and the SiO_2 nanoparticles of 136 mg/g.

To illustrate the interactions between cadmium ions and the surface of the tested adsorbent material (POBM_SiO2_SD), three different adsorption models were used (Langmuir, Freundlich, and Dubinin-Radushkevich). The parameters of the three types of isotherms are shown in Table 1. The results show that the best correlation (R^2=0.999) was obtained when fitting the data using the Langmuir model. Also, the calculated value of q_m (381.76 mg/g) is close to the experimental value (394.1 mg/g). The favorability of the sorption process is confirmed by the value of the separation factor R_L.

Thus, we can conclude that the adsorption of Cd^{2+} occurs in a monolayer, with identical binding centers. The value of n, calculated by nonlinear fitting with the Freundlich model, indicates favorable adsorption (n>1). The Dubinin-Radushkevich model was the least suitable for the obtained experimental data (R^2=0.935). The value of the free adsorption energy calculated from the nonlinear analysis of this model indicates a physisorption process (E <8 KJ mol^{-1}).

Table 1. Parameters obtained by nonlinear fitting of experimental data using the Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models.

Model of isotherm	Nonlinear equation	Parameters	Values
Langmuir	$q_e = q_m K_L C_e/(1 + K_L)$	q_m(mg/g)	381,76
		K_L(L/mg)	0,042
		R_L	0,99
		R^2	0,999
		n	1,642

Freundlich	$q_e = K_F C^{1/n}$	K_f	27,156
		R^2	0,989
Dubinin-Radushkevich	$q_e = q_m e^{-k\varepsilon^2}$	q_s (mg/g)	263,98
		K_D	6,229
		E (KJ/mol)	0,283
		R^2	0,935

To investigate the rate-determining step, the experimental data were evaluated using pseudo first-order, pseudo second-order, and intraparticle diffusion models. Table 2. present the linear fitting analysis of the three kinetic models, as well as the values of the kinetic parameters obtained. According to the value of R^2 (0.999), the pseudo second -order model has the highest degree of correlation. Also, the calculated value of q_m (22.123 mg/g) was consistent with the experimentally obtained value of this parameter (q_m=21.90 mg/g) at an initial concentration of Cd^{2+} ions of 50 mg/L. The graphical representation of the intraparticle diffusion model does not pass through the origin and shows two linear regions, confirming that diffusion is not the only factor involved in the metal ion absorption process.

Table 2. Kinetic parameters obtained by linear fitting of experimental data for an initial Cd^{2+} concentration of 50 mg/L

Kinetic	Parameters	Values
Pseudo-first order	K_1 (min^{-1})	0.979
	q_e(mg/g)	0.963
	R^2	0.988
Pseudo-second order	K_2(g/mg min)	0.038
	q_e(mg/g)	22.123
	R^2	0.999
Intraparticle diffusion	Ki (mg g^{-1})	0.035
	I (mg g^{-1})	19.648
	R^2	0.931

4. CONCLUSION

This study presents a new composite, POBM_SiO_2_SD, obtained from the growth substrate of the macromycete *Pleurotus ostreatus* (POBM) and SiO_2 nanospheres synthesized by a modified Stöber method, and its application as an effective adsorbent for the separation of Cd^{2+} from polluted aqueous media. Equilibrium studies suggested that Cd^{2+} adsorption on the bio sorbent occurs according to the Langmuir isotherm model. Studies of adsorption kinetics validated pseudo second-order kinetic of the adsorption process. All these results, analyzed in comparison with similar materials for Cd^{2+} adsorption, indicate the potential use of this new bio adsorbent composite for the efficient removal of cadmium ions from polluted aqueous environments.

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