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INVESTIGATION ON THE POTENTIAL USAGE OF LIGNOCELLULOSIC WASTES FOR Cd(II) REMOVAL

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ABSTRACT. Various lignocellulosic waste materials were assessed for their potential usage as biosorbents for Cd(II) removal from wastewaters. Sunflower seed shells, carrot peel, bean pods, eggplant peel, and orange peel in dry form and different grain sizes were evaluated. Contact time, initial Cd(II) concentration, and biosorbent amount were also tested. Eggplant peel was the most efficient biosorbent with an experimental biosorption capacity of 9.33 mg/g, a monolayer capacity (Langmuir) of 18.05 mg/g, and maximum % yield removal of 97.33%. Experimental data best fitted the Langmuir isotherm model (exception, orange peel) and the pseudo-second-order kinetic model (all materials).

Keywords: *cadmium(II), biosorption, waste valorisation, circular economy, sunflower seed shell, carrot peel, bean pod, eggplant peel, orange peel*

INTRODUCTION

Pollutants, such as heavy metals, are serious threats to the environment. Most of the metals are non-biodegradable, highly toxic and carcinogenic in nature [1].

Cadmium metal ions are very dangerous pollutants due to their high solubility in water, which makes them mobile in soil with a serious tendency to bioaccumulate [2]. They occur naturally in soil of volcanic areas but are becoming abundant in many territories as a result of uncontrolled industrialization, unsustainable urbanization, and intensive agricultural practices [2-4].

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Excessive accumulation of cadmium, Cd(II), in vegetables poses a serious threat to human health; therefore, it is urgent to screen and cultivate vegetables with low, or, if it is possible, non-existent cadmium accumulation in the edible parts [4].

Cultivation of agricultural crops and harvesting, generate an abundant amount of waste (e.g., peels, shells, straw, etc.) that can be used for wastewater treatment. It is estimated that approximately 998 million tons of agricultural waste is produced annually [5].

Nowadays, the potential of food and agricultural waste to remove heavy metals from contaminated water and soil has been intensively studied [6-8].

Vegetable wastes are easily available and have no economic use. The applicability of vegetable waste as low-cost adsorbent leads to significant decrease of waste discharge in the environment [9].

Biosorbents are composed of mainly cellulose, hemicelluloses, lignin, extractives, and many other compounds such as lipid, starch, hydrocarbons, simple proteins, and ash [10]. The biosorption mechanism onto biomass can consist of several steps including chemisorption, complexation, physisorption, diffusion through pores, and ion exchange [8].

In the removal of metals from aqueous solution, different types of plant parts are used such as stems, stalks, leaves, husk, shells, roots, barks, and many others [4].

Adsorption/biosorption process is considered to be attractive in terms of its performance for heavy metals removal from dilute waste solutions. Heavy metals are removed on different rates depending on the adsorbent / biosorbent and the metal itself [7].

In this study, the biosorption potential for cadmium (II) of some lignocellulosic wastes materials resulted from domestic use of carrots (*Daucus carota*), sunflower (*Helianthus annuus*), beans *(Phaseolus vulgaris*), eggplants (*Solanum Melongena L*), and orange (*Citrus sinensis*) was explored.

Sunflower seed shells (SFss), carrot peel (Cp), bean pods (Bp), eggplant peel (EPp), and orange peel (Op) were investigated under various working parameters.

RESULTS AND DISCUSSION

The results obtained for the investigation of Cd(II) removal on lignocellulosic waste materials are presented as follows, in terms of biosorption capacity and % yield for all the parameters examined.

Grain size influence was studied for all materials using the following reaction conditions: C_i = 25 mg Cd(II)/L, 1 g biosorbent, 22±2°C, 5.48 pH, and 500 rpm for 180 min with <0.4, 0.4-0.6, and 0.6-1.25 mm fractions. Two main trends were observed: (a) for SFss and Op a decrease in % yield removal (Table 1) and biosorption capacity was observed, suggesting that internal diffusion might become rate-determining step; (b) for Cp, Bp (Figure 1), and EPp, % yield removal and biosorption capacity, (Table 1), increased indicating that the biosorption process takes place mainly on the outer surface of the grain (lower porosity or inaccessible pores).

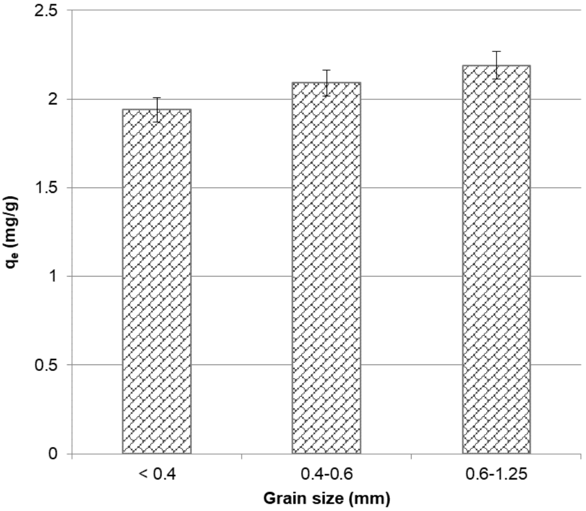

Figure 1. Grain size influence over biosorption capacity for Cd(II) removal on bean pods; C_i = 25 mg/L, 1 g, 22±2°C, 5.48 pH, 500 rpm.

Biosorbent quantity influence was studied for all materials using the following reaction conditions: C_i = 25 mg Cd(II)/L, 0.4-0.6 mm, 22±2°C, 5.48 pH, and 500 rpm for 180 min with 0.5, 1, and 2 g of lignocellulosic material. As the biosorbent quantity increases, the % yield removal increases, while biosortion capacity (mg per mass unit) decreases, Table 1, since for the same initial concentration, a higher surface/quantity is available, which leads to a smaller Cd(II) amount being removed per mass unit. Figure 2 shows as an example, the extent of biosorbed Cd(II) amount decrease for SFss.

Cd(II) concentration influence was studied for all materials using the following reaction conditions: 1 g, 0.4-0.6 mm, 22±2°C, 5.48 pH, and 500 rpm for 180 min with concentrations in 25-115 mg/L range. Time evolution was also followed for all the concentrations used. An increase in Cd(II) concentration led to a decrease in removal % yield and an increase in the biosorption capacity (Table 1). This results suggest that the optimum initial concentration must be correlated with desired % yield removal based on the specific conditions (industrial, municipal, leachate). Figure 3 shows the evolution of biosorption capacity for EPp as was one of the two (along with Bp) for which an increase was observed over the whole range of concentrations. For SFss and Cp the biosorption capacity decreased for the maximum concentration studied (115 mg/L), Table 1.

Table 1. Cd(II) removal % yields (top) and biosorption capacities, in mg/g, (bottom) for the considered lignocellulosic wastes under various working conditions.

	Grain size (mm)			**Amount (g)**			**Cd(II) concentration (mg/L)**				
	<0.4	**0.4-0.6**	**0.6-1.25**	**0.5**	**1**	**2**	**25**	**50**	**75**	**95**	**115**
SFss	95.71	92.58	90.61	84.12	92.58	96.41	92.58	87.95	88.76	65.13	40.70
	2.48	2.40	2.35	4.36	2.40	1.25	2.40	4.58	6.79	6.20	4.77
Cp	88.64	89.90	90.32	88.53	89.80	90.85	89.80	87.46	86.48	77.10	55.80
	2.30	2.33	2.34	4.58	2.33	1.18	2.33	4.55	6.72	7.34	6.54
Bp	74.97	80.53	84.47	93.40	80.53	83.31	80.53	82.59	81.08	83.73	69.54
	1.94	2.09	1.08	4.84	2.09	1.08	2.09	4.30	6.30	7.97	8.15
EPp	96.87	95.71	97.10	94.09	95.71	97.33	95.71	95.39	93.18	96.85	76.71
	2.51	2.48	2.52	4.87	2.48	1.26	2.48	4.96	7.35	9.22	9.33
Op	94.70	92.61	89.11	88.99	92.61	90.88	92.61	-	81.85	-	-
	2.38	2.37	2.26	4.51	2.37	1.12	2.37	-	4.06	-	-

Table 2. Langmuir and Freundlich coefficients for Cd(II) biosorption onto lignocellulosic wastes; C_i = 25-115 mg/L, 1 g, 0.4-0.6 mm, 22±2°C, 5.48 pH, 500 rpm.

	Langmuir coefficients			**Freundlich coefficients**		
	K_L (L/mg)	**q_{max} (mg/g)**	**R^2**	**n**	**K_f ($mg^{(1-1/n)}$ $L^{1/n}$/g)**	**R^2**
SFss	2.05×10^{-2}	5.75	0.9052	6.58	1.69	0.5438
Cp	4.97×10^{-2}	7.46	0.9690	3.39	1.51	0.8018
Bp	3.17×10^{-2}	7.04	0.9494	1.41	1.11	0.8169
EPp	2.00×10^{-2}	18.05	0.8941	2.69	0.25	0.5850
Op	5.38×10^{-2}	6.21	0.6403	3.56	1.45	0.9178

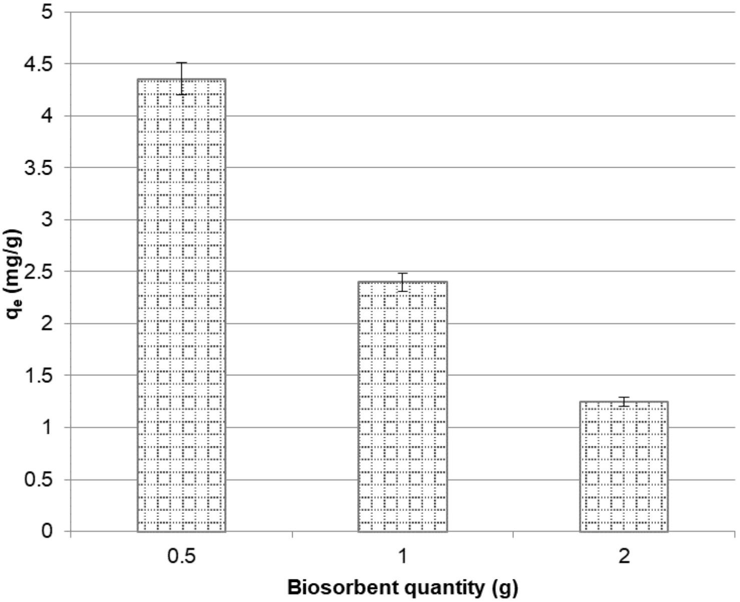

Figure 2. Biosorbent quantity influence over biosorption capacity for Cd(II) removal on sunflower seed shell; C_i = 25 mg/L, 0.4-0.6 mm, 22±2°C, 5.48 pH, 500 rpm.

The evolution of concentration in time shows, for all lignocellulosic materials, (Cp presented as an example in Figure 4), a significant drop in concentration in the first 10 minutes, with equilibrium reached after about 120 min for lower range of concentrations (25-75 mg/L) and 180 minutes for 95 and 115 mg/L.

Figure 5 presents the biosorption capacity for all lignocellulosic materials considered in this study for the same working conditions at 25 mg Cd(II)/L. The following sequence was identified, EPp > SFss > Op > Cp > Bp, with eggplant peel as the most efficient biosorbent among those analysed by us.

In literature, there are comparable data for Cd(II) biosorption onto lignocellulosic rezidues, for example 8.58 mg Cd/g for rice husk [8], 3.24 mg Cd/g for *Canola* biomass [11], 0.96 mg Cd/g and 0.98 mg Cd/g for sugarcane bagasse [12] and maize corncob [12], respectively.

Equilibrium experiments were performed in the concentration range of 25-115 mg Cd(II)/L, using 1 g biosorbent of 0.4-0.6 mm particle size, at 22±2°C, 5.48 pH, and 500 rpm. Langmuir and Freundlich isotherm models were used to establish how the biosorption process occurs. Results are presented in Table 2.

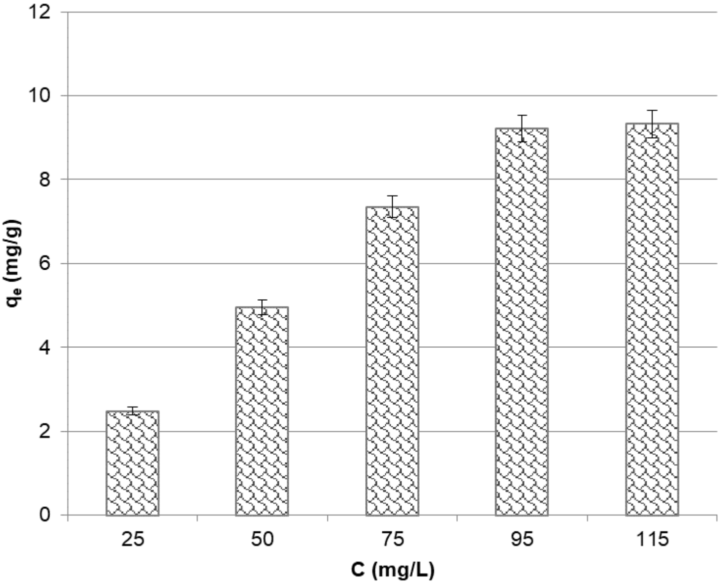

Figure 3. Initial concentration influence over biosorption capacity for Cd(II) removal on eggplant peel; 1 g, 0.4-0.6 mm, 22±2°C, 5.48 pH, 500 rpm.

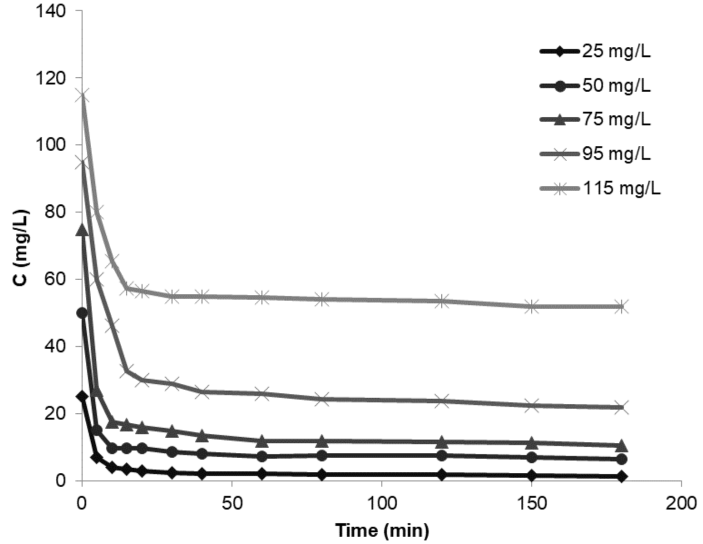

Figure 4. Cd(II) concentration time evolution for biosorption on carrot peel; 1 g, 0.4-0.6 mm, 22±2°C, 5.48 pH, 500 rpm.

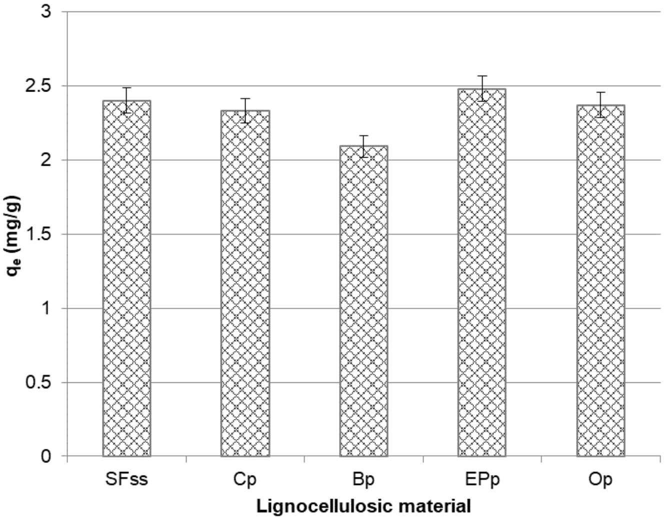

Figure 5. Comparative biosorption capacities for Cd(II) removal on lignocellulosic wastes; C_i = 25 mg/L, 1 g, 0.4-0.6 mm, 22±2°C, 5.48 pH, 500 rpm.

A closer look at the correlation coefficients indicates that with exception of orange peel (most likely due to its distinct cells, which will lead to specific surface properties upon drying), all the other lignocellulosic materials experimental data best fit on the Langmuir model, suggesting a monolayer adsorption, similar with other literature data [13,14]. The highest calculated value for the maximum adsorption capacity belongs to the eggplant peel in good correlation with the experimental data. Studies on similar systems In literature, show that the maximum adsorption capacity was 88.33 mg Pb(II)/g for treated eggplant peel [14,15], 140 mg Pb(II)/g for eggplant peels activated charcoal [16], and a small Cd(II) removal efficiency for eggplant powder, in particular conditions (Y,% =14±4%) [17].

The rate constants, calculated biosorption capacities, and correlation coefficients for pseudo-first- and pseudo-second-order kinetic models are presented in Table 3 for one of the concentrations used in the kinetic study (50 mg Cd(II)/L). Based on these values it can be concluded that the biosorption onto the lignocellulosic materials tested best fit on the pseudo-second-order kinetic model, sugesting that the biosorption step is rate-determining. Highest rate constant was calculated for EPp in good correlation with the experimental results. Figure 6 presents the pseudo-second-order plots for SFss and clearly indicates that the increase in concentration does not change system's behavior.

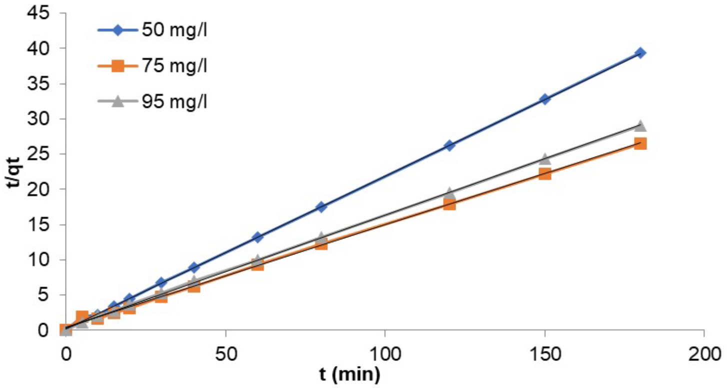

Figure 6. Pseudo-second-order plots for Cd(II) removal on sunflower seed shell; C_i = 50-95 mg/L, 1 g, 0.4-0.6 mm, 22±2°C, 5.48 pH, 500 rpm.

Table 3. Pseudo-first-order and pseudo-second-order rate constants, calculated and experimental q_e values for Cd(II) biosorption onto lignocellulosic wastes; C_i = 50 mg/L, 1 g, 0.4-0.6 mm, 22±2°C, 5.48 pH, 500 rpm.

	q_e (exp) (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1 (1/min)	q_e (calc) (mg/g)	R^2	k_2 (g/mg·min)	q_e (calc) (mg/g)	R^2
SFss	4.58	6.58×10^{-2}	0.97	0.6057	2.03×10^{-1}	4.63	0.9997
Cp	4.55	1.91×10^{-2}	0.53	0.5776	2.30×10^{-1}	4.54	0.9999
Bp	4.30	1.67×10^{-2}	0.95	0.6172	2.33×10^{-2}	4.29	0.9997
EPp	4.96	3.31×10^{-2}	1.36	0.8957	7.93×10^{-2}	5.03	0.9999
Op	3.22	3.00×10^{-2}	2.47	0.8682	3.11×10^{-2}	4.20	0.9920

CONCLUSIONS

The proposed study on the investigation of the posible usage of lignocellulosic wastes for Cd(II) removal from wastewater showed that all the considered materials have great biosorption properties even at high concentrations (75-95 mg/L). The highest biosorption capacity and the concentration they were obtained at are as follows: EPp (9.33 mg/g – 115 mg/L); SFss (6.79 – 75 mg/L); Op (4.06 – 75 mg/L); Cp (7.34 mg/g – 95 mg/L); Bp (7.97 mg/g – 95 mg/L). Therefore it can be concluded that this type of materials could be succesfully used for heavy metal ions removal from wastewater and also indicates that the presence of lignocellulosic materials (food waste) in solid waste landfills could potentially treat in-situ the generated leachate.

EXPERIMENTAL SECTION

Materials

The lignocellulosic wastes used in this work – sunflower seed shells (SFss), carrot peel (Cp), bean pods (Bp), eggplant peel (EPp), and orange peel (Op) – were subjected to various treatment steps before usage, as follows: washing in distilled water to remove impurities, drying at 105°C, grinding (mortar and pestle), and size separation using a set of sieves (0.4, 0.6, and 1.25 mm). The biosorbents prepared as described above were transferred to closed jars and kept for further usage. Figure 7 shows images of some of the biosorbents used in this study.

$Cd(NO_3)\cdot 4H_2O$ of analytical purity was used to prepare the stock solution and chromatographic purity Cd(II) solution in nitric acid was used to calibrate the atomic absorption spectrometer. Distilled water was used throughout this work.

Experiments

Cd(II) biosorption process was conducted in batch conditions, in a thermostated batch reactor using a magnetic stirrer (500 rpm), for 180 min (preliminary tests showed that adsorption equilibrium will be reached during this time). Various parameters that could influence the biosorption process were considered. Thus, the experiments were carried out using 100 mL of Cd(II) solution of different initial concentrations (25-250 mg/L) prepared from the stock solution of 1 g/L, with various amounts of biosorbent (0.5-2 g), and several grain sizes (<0.4, 0.4-0.6, and 0.6-1.25 mm). Experiments were performed at the initial solution pH of 5.5-6.0.

Cd(II) concentration in solution was determined using a GBC SensAA Series atomic absorption spectrometer (175-900 nm), which was calibrated using Cd(II) high purity solution. All the experiments were realized in triplicate, the presented values are averaged values

Biosorption capacity, q_e (mg/g), and % yield for Cd(II) removal were calculated in order to establish the effectiveness of the tested samples.

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

$$\%Y = \frac{(C_0 - C_e)}{C_e} \times 100 \tag{2}$$

where: C_0, C_e are the initial and equilibrium Cd(II) concentration in solution, in mg/L, V is the sample volume, in L, and m is the adsorbent quantity, in g.

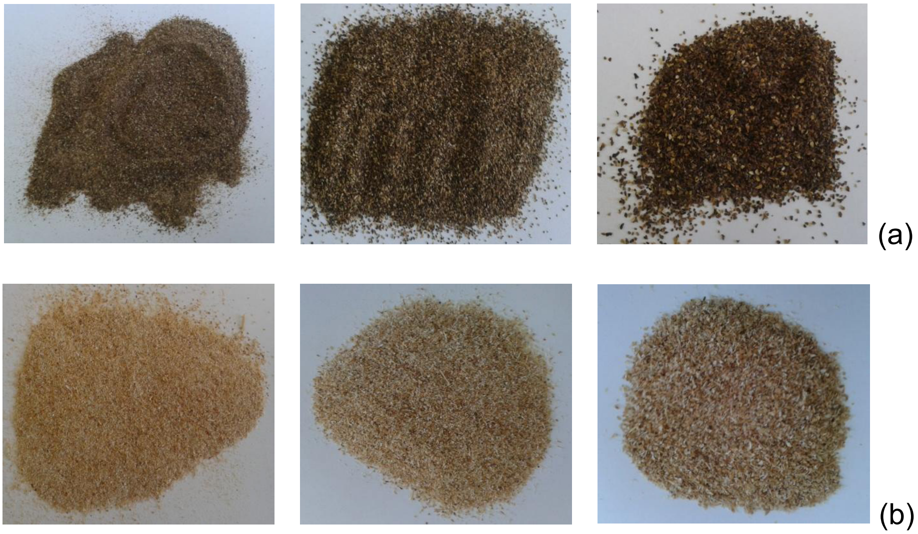

Figure 7. Eggplant peel (a) and bean pods (b) of the three grains size used.

Adsorption isotherms and kinetics

Langmuir and Freundlich isotherm models were used to perform the equilibrium analysis of the biosorption process of Cd(II) on the selected vegetables and citrus species samples.

Model's equations, in the linear form, are as follows:

- Langmuir model equation [18,19]:

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \cdot \frac{1}{C_e} + \frac{1}{q_m} \tag{3}$$

- Freundlich model equation [19, 20]:

$$\log q_e = \log K_F + \frac{1}{n} \cdot \log C_e \tag{4}$$

where: q_m is the monolayer capacity of the adsorbent in mg/g, K_L is the Langmuir adsorption constant in L/mg, K_F is the Freundlich isotherm constant in $mg^{(1-1/n)}L^{1/n}/g$, and n is a constant related to intensity of adsorption (Freundlich).

Pseudo-first- and pseudo-second-order kinetic models were used to explain the adsorption mechanism:

- pseudo-first-order equation (linear) [21, 22]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

- pseudo-second-order equation (linear) [23, 24]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where: k_1 is the pseudo-first-order rate constant in 1/min, k_2 is the pseudo-second-order rate constant in g/mg·min, q_t is the amount of Cd(II) adsorbed at time t in mg/g, and t is time in min.

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