Biosorption of Cd(II) Ions from Aqueous Solution Onto Eggshell Waste

Kinetic and equilibrium isotherm studies

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Eggshell waste as adsorbent was successfully used for the removal of Cd(II) ions from model synthetic aqueous solutions. Batch biosorption studies were conducted in order to evaluate the effect of various parameters, such as: contact time and initial metal ion concentration. The changes in the morphological structure were evaluated by TEM and SEM analysis. The experimental isotherm data were analysed using Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin isotherm equations, using regression analysis linear and non-linear form. Langmuir model was found to be in better correlation with experimental data (R^2=0.99). Biosorption kinetics data were tested using pseudo-first-order, pseudo-second-order, intra-particle and liquid film diffusion models. Kinetics studies showed that the biosorption followed a pseudo-second-order reaction. Removal efficiencies up to 92 % and a maximum adsorption capacity of 8.2 mg/g Cd(II) were obtained experimentally and 7.14 mg/g Cd(II) were obtained from Langmuir isotherm model. The percentage of metal sorption (C_i=11 mg/L, E,(%)=92.42), EDS analyses, and bioconcentration factor were also calculated. The investigation findings suggested that the physical adsorption is controlling the adsorption rate. Results of this study indicate that eggshell waste can be effectively used for the removal of Cd(II) ions from aquatic environments. The process is feasible, reliable and eco-friendly.

Keywords: eggshell, Cd(II) ions, removal, water treatment

Waters from many areas in the world are polluted with toxic metals present in the industrial effluents, radionuclides/hydrocarbons from oil refineries and pesticides from agricultural industries. Unlike the organic wastes, metals are non-biodegradable, and heavy metals such as arsenic, selenium, zinc, manganese, lead, mercury and cadmium, need to be removed from the environment [1]. Heavy metals are elements having atomic weights between 63.5 and 200.6 and a specific gravity greater than 5.0 [2]. Whenever natural eco-systems are exposed to toxic metals, accumulation of metal ions in the human body will occur through either direct intake or the food chain [3]. Heavy metals are among the most toxic pollutants for natural water bodies due to their long persistence in the environment [4].

Cadmium metal is used in the steel and plastics industry, while cadmium compounds are widely used in batteries. This heavy metal is often released to the environment through the wastewater causing diffuse and local pollution.

Food is the main source of daily exposure to cadmium, none the less, it is considered very toxic to the aquatic life and to humans as well. Cd (II) can cause bone demineralisation either through direct bone damage or indirectly as a result of renal dysfunction [5,6]. Overdose of cadmium causes proteins spilling in the urine and disruption of potassium metabolism [7]. Chronic exposure to cadmium can affect the nervous system, liver, kidney, cardiovascular system, and may ultimately lead to death [8, 9]. According to the Romanian legislation, the maximum concentration limit for Cd(II) discharge into surface waters is 0.2 mg/L and $5 \cdot 10^{-3}$ mg/L in potable waters [10,11].

There are several methods for removing heavy metal ions, such as ion-exchange, chemical precipitation, membrane filtration, reverse osmosis, electrochemical treatment technologies and adsorption. Adsorption is now recognized as an effective and economic method for treating wastewater contaminated with heavy metals. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process [12].

Biosorption has been confirmed to be a flexible alternative method with a very promising future, best described as cost effective, cheap, naturally available in form of different adsorbents, and easy to handle [13-15]. Typical biosorbents can be derived from three sources as follows: (1) non-living biomass, such as bark [16], potato peel [17], tree sawdust [18], grape stalks [19], carrot residues [20], grapefruit peel [21], coffee husks [22], walnut shells [23]; (2) mushrooms [24], algae [25] biomass; (3) microbial biomass [26] *e.g.* bacteria, fungi [27] and yeast [28,29].

In this paper, hen-eggshell is used as low-cost, non-conventional biosorbent to remove Cd(II) ions from wastewaters. About 250.000 tons of eggshell waste are produced annually worldwide by the food processing industry only [30].

Hen eggshell typically consists of ceramic materials constituted by three-layered structure: cuticle on the outer surface, spongy medium layer and an inner layer (lamellar). The chemical composition (by weight) consists of calcium

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carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%), and organic matter (4%) [31].

Since eggshell is composed mainly of calcium carbonate, sorption onto eggshell should occur primarily via an exchange reaction, and it should be possible to use it as a biological sorbent for heavy metal ions [32].

In order to investigate the main characteristics of this sorbent, in this paper, the Cd (II) ion concentration, kinetic and process equilibrium were analysed. Mathematical models were also proposed for sorption kinetics description.

The aim of this work was to study the kinetic aspects of Cd(II) adsorption on eggshell. Further, the applicability of common isotherm models (*i.e.* Langmuir, Freundlich, Dubinin-Radushkevich and Temkin) was evaluated in relation to Cd(II) adsorption capacities at room temperatures. TEM and SEM image studies were used for biomass surface morphology characterization. EDS analysis was used in order to determine the elemental composition of eggshell waste before and after Cd(II) adsorption.

Experimental part

Sorbent preparation

Hen eggshells were collected from a grocery shop (Cluj County, Romania). The eggshells were washed with tap water for several times and afterwards with redistilled water for three times in order to eliminate surface impurities. Then they were transferred to the oven at 80°C for 24 h in order to dry. The dried eggshells were crushed and milled. Finally, the dried biomass was grinded and sieved (315 μm). The sieved eggshell powder was then stored in an airtight box before its utilization.

Metal solution

The stock solution, 1 g/L of Cd (II), was prepared by dissolving $Cd(NO_3)_2 \cdot 4H_2O$ in distilled water. The required concentrations were obtained by diluting the stock solution to the desired concentrations, in the 11-157 mg/L range. All chemicals used were of analytical grade. The Cd (II) ions concentration from different samples was determined using a flame atomic absorption spectrophotometer (SensAA Dual GBS Scientific Equipment, Australia).

Metal bioadsorption studies

The batch equilibrium technique was used to determine the Cd(II) sorption on the eggshells.

Different initial heavy metal concentrations were tested in the range of 11-157 mg/L. All biosorption experiments were carried out in 250 mL Erlenmeyer flasks containing 1 g dried biosorbent in 100 mL metal ion solution.

This suspension was stirred for 3 h at room temperature on a rotary shaker at 200 rpm. In order to determine the exact concentration of metal ions and to establish the evolution of the removal process, the samples were collected at different time intervals for up to 180 min (preliminary experiments showed that this time is sufficient for attaining the equilibrium). The biomass was separated by centrifugation at 12.000 rpm for 5 min and the residual metal ion concentration was measured in the supernatant.

The amount of adsorbed heavy metal (at equilibrium) was calculated using the following equation of Volesky and May-Phillips [48, 49]:

$$q_e = \frac{(C_0 - C_t)}{m} \cdot \frac{V}{1000} \quad (1)$$

where: q_e is time t adsorption capacity at equilibrium (mg/g), C_0 is the initial heavy metal concentration (mg/L), C_t is time t heavy metal concentration (mg/L), V = 100 mL, and m is the adsorbent quantity (g).

Experimental data were used to determine the effect of contact time on ion biosorption onto eggshell and the adsorption capacity, in order to establish the equilibrium time, and to describe the kinetic models. The evaluation of Cd (II) uptake at equilibrium for the eggshell samples was realised using the adsorption capacity, q_e (mg/g) and removal efficiency, E (%) values.

Microscopy investigations

Transmission electron microscopy (TEM) for eggshell based adsorbent were performed using a Hitachi Automatic TEM H7650 equipment (accelerating voltage 40-120 kV, zoom 200x-600000x) by dipping a holey-carbon TEM grid into a biomass suspension. Samples were imaged using an Olympus KeenView G2 camera, with the transmission electron microscope operating at 120 kV.

SEM

The morphology of eggshell waste was analysed using JEOL (USA) JSM 5510 LV SEM microscope. Prior to the surface observation, the samples were coated with a thin layer (10 nm) of gold under vacuum of 1.33×10-6 mBar in order to improve electron conductivity hence image quality.

Energy-dispersive X-ray spectroscopy (EDS) analysis

The elemental composition of eggshell waste biomass before and after adsorption of Cd(II) was analysed with Scanning Jeol JEM 5510 LV analyser coupled with Oxford Instruments EDS Analysis System Inca 300 (UK).

Bioconcentration factor (BCF)

The BCF provides an index of eggshell biomass ability to accumulate the metal with respect to metal concentration in watery solutions. The BCF was calculated [50] as follows:

BCF = Concentration of metal in eggshell biomass/ Initial concentration of metal in external solution.

Results and discussions

The sorption of Cd(II) on eggshell waste was studied in a batch system and the experimental data were evaluated. Isotherms and kinetic model equations were applied to the experimental data.

Effect of the contact time and initial Cd(II) concentration

Experiments were carried out using a fixed amount of eggshell biosorbent (1 g) and a stirring rate of 200 rpm, but varying the initial Cd(II) concentration between 10-150 mg/L. In order to establish the evolution in time for Cd(II) adsorption on eggshell waste, the cadmium concentration was investigated in relation to contact time, the results being presented in figure 1.

The adsorption was studied for 190 min at room temperature. Considering the initial Cd (II) ion concentration as a parameter in the biosorption process, the following conclusions were drawn:

a) the contact time curve shows that the Cd(II) removal increases rapidly in the first minutes – due to the abundant availability of active binding sites on the eggshell waste adsorbent – followed by a slow decrease;

b) around 90 % of metal ions were removed in the first 120 min with gradual occupancy of porous, vacant sites on the biomass surface. The adsorption became less efficient in the later stages. For equilibrium studies, Cd (II) solution was kept in contact with eggshell waste for 190 min, although no significant variation in the residual Cd (II)

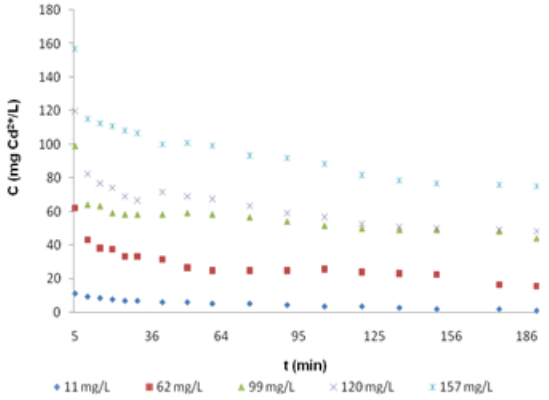

Fig. 1 The influence of initial Cd(II) concentration evolution over time on the eggshell powder; C_i = 11-157 mg/L, 1 g biomass, *d* = 0.315 mm, V = 100 mL, T = 296 K, *p*H = 5.65, v = 200 rpm

concentration was detected after 120 min of the contact time.

Cd (II) adsorption efficiency and sorption capacity on eggshell waste was monitored at various initial concentrations between 10-150 mg/L, as shown on figure 2. The results reveal that at higher initial metal ion concentrations, more metal ions were adsorbed per unit weight at equilibrium. Adsorption capacity increases with the increase in concentration from 1.02 mg/g (C_i= 11 mg/L) to 8.2 mg/g (C_i= 157 mg/L). Meanwhile, adsorption efficiency decreases as the initial metal ion concentration increases from 92.42% (C_i= 11 mg/L) to 52.23% (C_i= 157 mg /L).

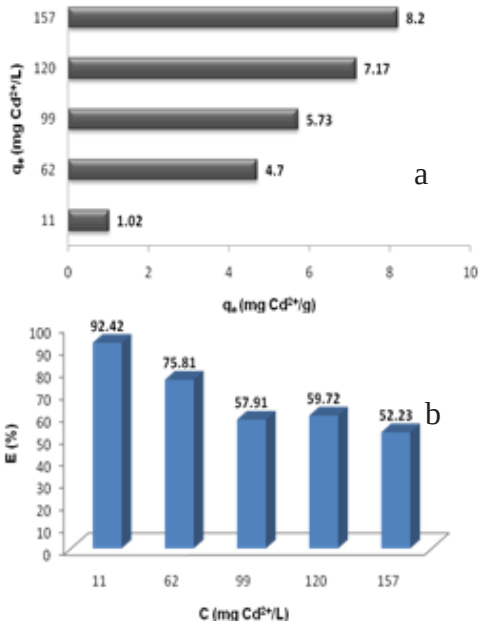

Fig. 2 Influence of the initial Cd(II) concentration on the: (a) adsorption capacity, (b) removal efficiency on eggshell powder; C_i = 11-157 mg/L, 1 g biomass, d = 0.315 mm, V = 100 mL, 296 K, *p*H = 5.65, v = 200 rpm

All these results indicate that if the metal ion concentration in the solution increases, the difference in concentration between bulk solution and surface also increases, intensifying the mass transfer processes as this was mentioned by Nagy et al. [33], where they reached an 83.85% efficiency of Cd(II) removal using *Lactarius piperatus* as adsorbent.

Adsorption isotherm models

Several mathematical models were developed to quantitatively express the relationship between the extent of sorption and the residual solute concentration.

In order to characterize the mechanisms of Cd(II) ions interaction with biosorbent site, Dubinin-Radushkevich and Temkin adsorption isotherm models, along with Langmuir and Freundlich isotherms were selected.

Langmuir is the most important model for describing monolayer adsorption, based on the assumption that there are a fixed number of adsorption sites, and each site can hold one adsorbate molecule [34]. All sites are equivalent and there is no interaction between adsorbed molecules.

The Langmuir equation can be expressed as follows:

$$\log q_e = \log k + \frac{1}{n} \cdot \log C_e \qquad (2)$$

where: q_e is the solid-phase adsorbate concentration at equilibrium (mg/g), q_{max} is the maximum adsorption capacity corresponding to the monolayer adsorption capacity (mg/g), C_e is the concentration of heavy metals solution at equilibrium (mg/L) and K_l is the adsorption equilibrium constant that is related to the apparent energy of adsorption. Isotherm parameters q_{max} and b can be obtained by plotting $1/q_e$ against C_e.

The values of the Langmuir parameters (table 1), q_{max} and K_L, were 7.14 (mg/g) and 0.098 (L/mg). Also, the correlation coefficient R^2 was found to be 0.9963 (table 1). The Freundlich isotherm was also employed to explain the observed phenomena [35]. The Freundlich isotherm is represented by the following equation:

$$\log q_e = \log k + \frac{1}{n} \cdot \log C_e \qquad (3)$$

where: k is the Freundlich constants related to adsorption capacity, C_e equilibrium concentartrion (mg/L), and n is the Freundlich constants related to adsorption intensity. The $\ln q_e$ versus $\ln C_e$ plot allows the determination of the Freundlich constants presented in (table 1).

The value of n, which is related to the distribution of bonded ions on the adsorbent surface, represents beneficial adsorption if it is between 1 and 10 [8]. The n value for the used biosorbent was found to be greater than one, indicating that adsorption of Cd(II) was favorable. The correlation coefficients R^2 were found to be 0.9853 (table 1). Comparing the correlation coefficients of these two models, the obtained results indicate that the equilibrium data in case of Cd(II) removal were better fitted well the Langmuir isotherm model.

The linearized forms of Langmuir and Freundlich isotherms are shown in figure 3 and figure 4.

The Dubinin-Radushkevich isotherm expresses the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. This model was applied to understand the equilibrium process better, and to determine if adsorption had occurred by physical or chemical processes [36].

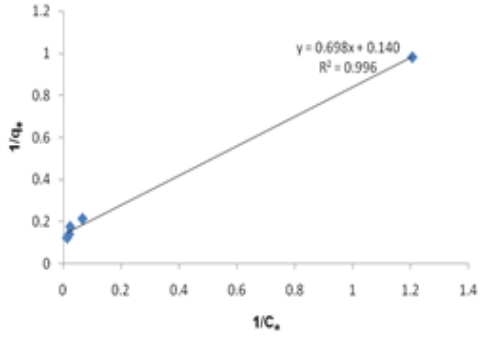

Fig. 3. Langmuir isotherm for the adsorption of cadmium on eggshell biomass; C_i = 11-157 mg/L, 1 g biomass, d = 315 µm, 296 K, *p*H = 5.65, v = 200 rpm

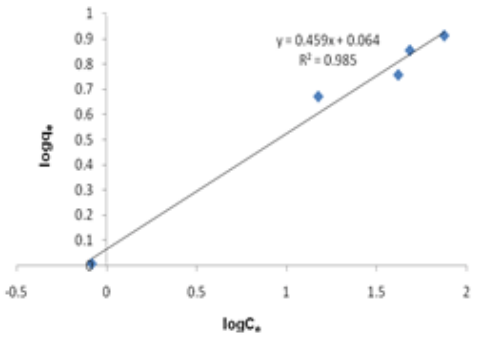

Fig. 4. Freundlich isotherm for the adsorption of cadmium on eggshell biomass; C_i = 11-157 mg/L, 1 g biomass, d = 315 µm, 296 K, *p*H = 5.65, v = 200 rpm

The linear form of this adsorption isotherm equation can be expressed as:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (4)$$

where: q_m is the theoretical adsorption capacity (mg/g), β is Dubinin-Radushkevich model constant (mol^2 kJ^2), ε is equal to:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (5)$$

where: R is the gas constant (8.314 J mol/K) and T is absolute temperature (K).

Free energy E per molecule, eq. 5, of adsorbate, which helps to distinguish between physical and chemical adsorption of metal ions is given below:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (6)$$

The isotherm constants q_m and β were obtained from the intercept and the slope of the plot lnq_e *vs.* ε^2.

If E value is between 8 and 16 kJ/mol, the adsorption process takes place by ion-exchange and if E < 8 kJ/mol, the adsorption process is physical [37]. In our case, with eggshell biomass the mean free energy was 1 kJ/mol (table 1), which corresponds to physical adsorption.

The Temkin isotherm assumes that the adsorption heat of all the molecules in the layer decreases linearly with the coverage of molecules due to the adsorbate-adsorbent repulsions and the adsorption of cadmium ions uniformly realized on the surface [38].

The equation of this model can be expressed as:

$$q_e = B \ln A_t + B \ln C_e \quad (7)$$

$$B = \frac{RT}{b_T} \quad (8)$$

where: T is absolute temperature (K) and R is the universal gas constant (8.314 kJ/K mol), A_T is Temkin isotherm equilibrium constant (L/g), b_T is the Temkin isotherm constant, B is a constant related to heat of sorption (J/mol). From the q_e *vs.* lnC_e plot, A_T and B constants were determined.

Atkins, 1999 revealed that if the mean free energy and heat of adsorption values (kJ/mol) are lower than 20 kJ/mol physical sorption process can occur [39]. Taking into consideration that in our study, the calculated value of the constant related to sorption heat, B has a value smaller than 20 kJ/mol (table 1) we concluded that according to this isotherm the adsorption process takes place as physical sorption.

Kinetics studies

In order to examine the mechanism of Cd(II) ions biosorption process on the eggshell waste biomass, such as mass transfer and chemical reaction onto eggshell waste powder biomass, pseudo-first- and pseudo-second order, intra particle and film diffusion were used to examine the experimental data. Linear regression was used to determine the correlation coefficients.

In order to analyze the adsorption kinetics of Cd(II) ions onto eggshell waste biomass, experimental data were tested with the most widely used Lagergren's pseudo-first-order [40] and Ho's and McKay pseudo-second-order models [41]. The values of k_1 and R^2 along with the calculated uptake capacity $q_e(calc)$, are provided in table 2.

As the table shows, low correlation coefficients values were obtained (in range of 0.7798-0.9600). Also, the calculated uptake capacities of adsorption equilibrium were much lower than the experimental uptake capacity $q_e(exp)$ values.

Therefore, it can be concluded that Lagergren pseudo-first-order model is not suitable for describing the heavy metal adsorption on eggshell waste biomass. By plotting t/q_t versus t, the rate constant k_2, the calculated uptake capacity $q_e(calc)$ and the correlation constant R^2 were calculated and summarized in table 2. The calculated uptake capacity values agree very well with the experimental values and the R^2 values also exceed 0.9932. This indicates the applicability of Ho and McKay pseudo-second-order model for describing Cd(II) adsorption on the selected adsorbent.

The pore diffusion coefficient, D (cm^2/s) for the removal of Cd(II) ions by eggshell waste biomass was calculated (assuming a spherical geometry of the adsorbent, and an average size of 0.315 mm) using the following equation [42]:

$$D = 0.003 \cdot \frac{r_0^2}{t_{1/2}} \quad (9)$$

Based on the pseudo-second-order model, $t_{1/2}$ was estimated using the equation:

Table 1

LANGMUIR, FREUNDLICH, DUBININ-RADUSHKEVICH AND TEMKIN CALCULATED COEFFICIENTS USING LINEAR REGRESSION ANALYSIS FOR CD(II) BIOSORPTION ON EGGSHELL POWDER; C_i = 11-157 mg/L, 1 g biomass, d = 0.315 mm, V = 100 mL, 296 K, pH = 5.65, v = 200 rpm

	Langmuir			Freundlich			Dubinin-Radushkevich			Temkin		
	K_L (L/mg)	q_{max} (mg/g)	R^2	n	K_f (mg$^{(1-1/n)}$L$^{1/n}$/g)	R^2	β (mol^2 kJ^2)	E (kJ/mol)	R^2	A_T (L/g)	B (J/mol)	R^2
Cd(II)	0.098	7.14	0.9963	2.17	1.16	0.9853	5×10^{-7}	1	0.9386	2.10	2×10^{-4}	0.9477

Table 2

PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER RATE CONSTANTS, CALCULATED AND EXPERIMENTAL q_e VALUES FOR Cd(II) BIOSORPTION ON EGGSHELL POWDER BIOMASS USING DIFFERENT INITIAL CONCENTRATIONS; C_i = 11-157 mg/L, 1 g BIOMASS, d = 0.315 mm, V = 100 mL, 296 K, pH = 5.65, v = 200 rpm.

C (mg/L)	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
11	1.02	1.51×10^{-2}	0.90	0.96	1.92×10^{-2}	1.20	0.9729
62	4.7	1.34×10^{-2}	2.78	0.7798	1.27×10^{-2}	4.78	0.9816
99	5.73	0.98×10^{-2}	2.57	0.7996	1.45×10^{-2}	5.65	0.987
120	7.17	2.4×10^{-2}	4.72	0.9414	0.97×10^{-2}	7.60	0.9932
157	8.2	2.47×10^{-2}	6.42	0.9234	0.65×10^{-2}	8.86	0.9901

$$t_{1/2} = \frac{1}{k_2 q_e} \quad (10)$$

The heavy metal sorption is governed usually by either the liquid phase mass transport rate or the intra-particle mass transport rate. Hence, diffusive mass transfer is incorporated into the adsorption process.

Intra-particle diffusion (Weber and Morris intra-particle diffusion equation) [43] plots for Cd(II) biosorption on eggshell waste biomass are shown is figure 5a. It can be observed that the data present multilinear plots comprising three regions.

The first region (from 10 to 40 min), is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or boundary layer diffusion of solid molecules. The second, linear portion (region from 40 - 135 min) is the gradual equilibrium stage with intra-particle diffusion dominating.

The third portion is attributed to the final equilibrium stage for which the intra-particle diffusion starts to slow down due to the extremely low adsorbate concentration left in the solution [44]. Plots of q_t against $t_{1/2}$ are linear (R^2-values, table 3) but with intercepts ranging between +0.0023 and +7.42 (plots do not pass through origin). The calculated intra-particle diffusion rate constants and pore diffusion coefficients (assuming spherical geometry for the adsorbent) are also listed in table 3.

The pore diffusion coefficients are values in the 1.14×10^{-9} – 4.07×10^{-9} cm^2/s range. Therefore, it can be concluded that the intra-particle is not the rate determining stage for Cd(II) biosorption on eggshell waste biomass.

Table 3

INTRA-PARTICLE DIFFUSION RATE COEFFICIENTS FOR CD(II) BIOSORPTION USING EGGSHELL WASTE BIOMASS; C_i = 11-157 mg/L, 1 g of biomass, d = 0.315 mm, V = 100 mL, 296 K, pH 5.65, 200 rpm

C (mg/L)	D (cm^2/s)	Region 1, 10-40 minutes		Region 2, 40-135 minutes		Region 3, 135-190 minutes	
		k_{ip} (mg/g-$min^{1/2}$)	R^2	k_{ip} (mg/g-$min^{1/2}$)	R^2	k_{ip} (mg/g-$min^{1/2}$)	R^2
11	1.14×10^{-9}	0.088	0.9496	0.073	0.9586	0.59×10^{-2}	0.7677
62	3.02×10^{-9}	0.378	0.9676	0.052	0.5792	10.58×10^{-2}	0.7677
99	4.07×10^{-9}	0.147	0.6624	0.217	0.9564	43.28×10^{-2}	0.7677
120	3.67×10^{-9}	0.330	0.7234	0.390	0.9749	0.58×10^{-2}	0.7619
157	2.84×10^{-9}	0.388	0.9094	0.495	0.9748	0.58×10^{-2}	0.7677
Intercept:		0.0023 – 3.23		0.06 – 2.34		0.23 – 7.42	

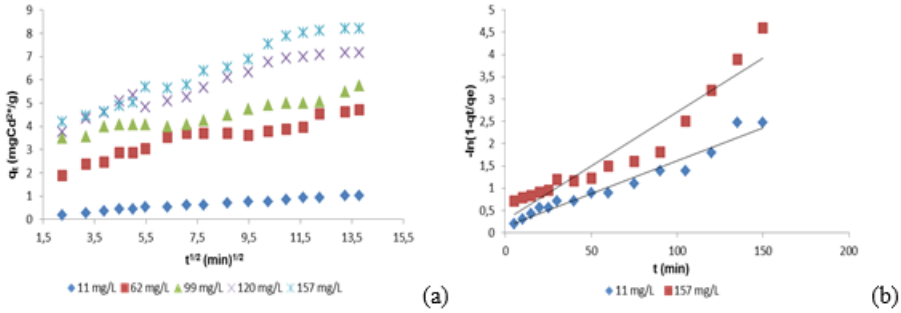

Fig.5. Plots of the intra-particle diffusion (a) and liquid film diffusion (b) models for Cd(II) biosorption using eggshell waste biomass; C_i = 11-157 mg/L, 1 g of biomass, d = 0.315 mm, *V* = 100 mL, 296 K, *p*H = 5.65, v = 200 rpm.

Liquid film model [45] was also applied to Cd(II) ions biosorption on eggshell waste biomass (fig. 5b) for two concentrations (11 and 157 mg/L). Linear plots of –ln(1-F) against *t* were obtained, and rate constants and intercepts were calculated (table 4). As none of these plots exhibit a zero intercept, it could be suggested that kinetics of the considered process is not controlled by diffusion through the liquid surrounding the adsorbent grains.

Table 4

LIQUID FILM DIFFUSION RATE COEFFICIENTS FOR CD(II) BIOSORPTION ON EGGSHELL WASTE BIOMASS AT DIFFERENT INITIAL CONCENTRATIONS; C_i = 11-157 mg/L, 1 g OF BIOMASS *d* = 0.315 mm, *V* = 100 mL, 296 K, pH 5.65, 200 rpm

C (mg/L)	k_{fd} (1/min)	Intercept	R^2
11	0.015	- 0.14	0.9579
62	0.012	- 0.62	0.7685
99	0.008	- 0.95	0.9545
120	0.023	- 0.50	0.9427
157	0.024	- 0.29	0.9157

Taking into consideration all the results obtained by applying kinetic models on Cd(II) biosorption by eggshell waste biomass experimental data, it can be concluded that the rate-determining step is the biosorption process.

TEM analysis

The TEM micrographs show progressive changes on the textural structure of the eggshell particles, enabling the direct observation of the surface morphological structure of the adsorbent. Comparing figure 6 control biomass (a) and Cd(II) adsorbed biomass (b) the differences between two samples become evident. Figure 6b shows morphology changes on surface; the biomass surface changes obviously after Cd(II) adsorption, having a tendency to form dark blots and agglomerates, which can be attributed to the metal ions. These surface structure modifications can be explained by the fact that the Cd ions are bound onto the eggshell waste biomass.

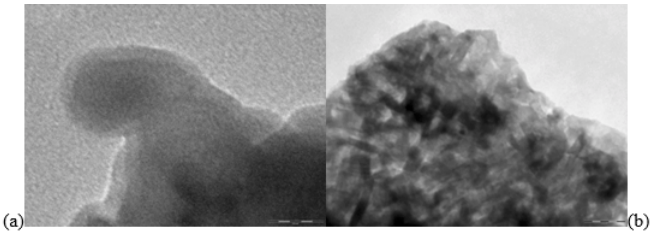

Fig. 6. TEM photographs of (a) control (8000×) and (b) Cd(II) adsorbed (8000×) eggshell biomass.

SEM analysis

Figure 7 exhibits the scanning electron microscopy (SEM) images for the calcareous layer of eggshell waste loaded with Cd(II). In order to examine the textural and surface morphologies of this biomass, micrographs were taken of the biomass before and after metal ion adsorption, at 50 µm magnification. It could be seen with the naked eye that the eggshell waste had a smooth, dense and porous surface texture (fig. 7a) whereas the porous texture disappeared after contact time with Cd(II) (fig. 7b). Interaction of eggshell waste with Cd(II) has resulted in the formation of agglomerates with irregular shape deposits on its surface. During metal sorption the texture of eggshell waste becomes more and more rough and irregular. All in all, we can see a clear change in the surface structure following the sorption experiments. Our results are similar to the experiments of Ahmad [46] and Putra [47] where they studied Pb(II), Cu(II), Zu(II) and Cd(II) adsorption on eggshell waste.

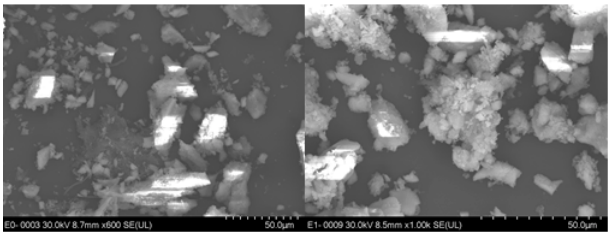

Fig. 7 SEM photographs of (a) control and (b) Cd(II) adsorbed eggshell waste

Results indicate that the adsorption of metal ions on the eggshell waste surface is likely due to the ion exchange reaction [46].

EDS analyses

EDS analysis was performed in order to determine the elemental composition of the eggshell waste, our biosorbent, before and after its exposure to Cd(II) metal ions. Values listed in table 5 indicate that our samples contained large proportions of C, O and Ca (it is known that eggshell consists of $CaCO_3$). After adsorption Cd(II) clearly appears in the elemental composition of the eggshell waste. Figure 8 presents the EDS spectrum of the biosorbent before and after Cd(II) treatment. As shown in figure 8, a new peak appeared around 3keV representing

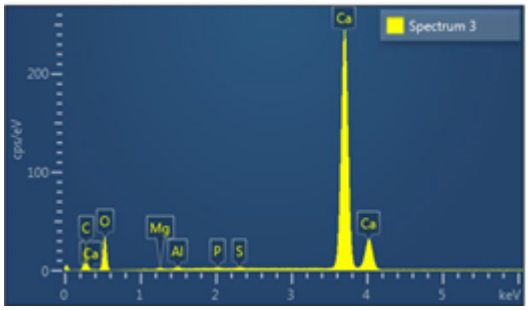

Fig. 8 EDS spectrum of eggshell waste before Cd(II) adsorption

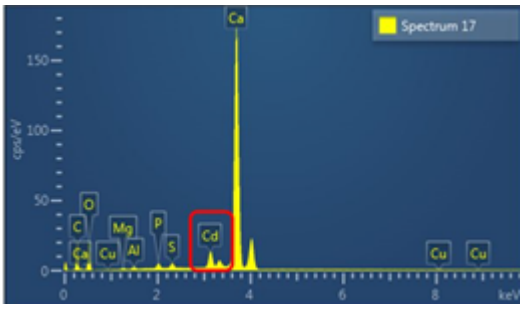

Fig. 8 EDS spectrum of eggshell waste after Cd(II) adsorption

Table 5
THE CONTROL AND TREATED EGGSHELL WASTE ELEMENTAL CONTENT FROM EDS SPECTRA ; VALUES EXPRESSED AS MEANS OF 10 REPLICATES

Element	Wt(%) Content of the control eggshell waste	Wt(%) Content of the eggshell waste adsorption of Cd (200 mgLl)
C	32.008 ± 7.494	23.468 ± 7.417
O	44.587 ± 3.388	43.926 ± 4.168
Na	1.969 ± 5.984	0
Mg	0.356 ± 0.064	0.306 ± 0.080
Al	0.265 ± 0.124	0.418 ± 0.370
Si	0	0.025 ± 0.057
P	0.185 ± 0.088	0.210 ± 0.151
S	0.566 ± 0.286	0.514 ± 0.193
Ca	21.949 ± 7.610	28.801 ± 9.282
Cd	0	2.282 ± 0.902
Cu	0	0.072 ± 0.058

the feature of Cd(II). The appearance of the EDS feature of Cd on the surface of eggshell waste implies its ability of metal ion binding [47].

Bioconcentration factor (BCF)

The bioconcentration factor (BCF) was calculated based on the metal concentrations in eggshell waste and the dissolved metal concentrations of water solution. The BCF values for Cd(II) in eggshell waste at different concentrations are shown in figure 9. The BCF values for Cd(II) significantly decreased when Cd(II) concentration was increased in the experimental solution. After equilibrium, the BCF was 12.2 at initial concentration of 11 mg/L. In this case the BCF value at lower Cd(II) concentrations was remarkably higher (about 10 times higher) than with higher metal concentrations. This observation is noteworthy as it strongly suggests that eggshell waste biomass is a promising biosorbent candidate for removing Cd(II) from aqueous solution even at lower Cd concentrations.

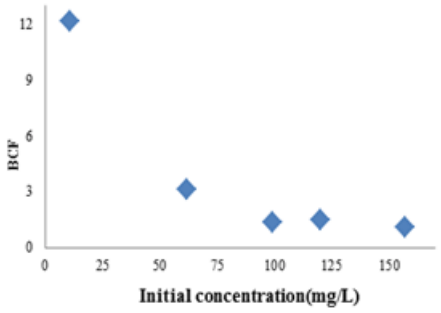

Fig. 9. BCF values for Cd(II) in eggshell waste at different concentrations

Conclusions

The results obtained in this study highlight that eggshell waste can be used as biosorbent for Cd (II) ions removal from aqueous solutions.

During the experiment, in the first 120 min around 90 % of metal ions were removed. As time passed by, initial metal ion concentration decreased. With the increase of initial Cd (II) ions concentration, the quantity at equilibrium increased, whereas the adsorption efficiency decreased.

According to our experimental conditions, the Langmuir isotherm model describes best the adsorption fact which indicates that a monolayer adsorption took place. The Temkin and Dubinin-Radushkevich constants point to physical sorption as the form of the adsorption process.

By comparing various kinetic models, and taking into consideration that pore diffusion coefficients have higher values than rate determining range, that none of the plots of the liquid fill model exhibit a zero intercept and the kinetic data showed that the biosorption of Cd(II) ions onto eggshell waste biomass followed well the pseudo-second-order kinetic model.

TEM and SEM images taken before and after Cd (II) ions adsorption show surface structure modifications on eggshell waste due to ion exchange reactions which took place.

By means of EDS analysis we determined the elemental composition of the eggshell waste during the experiments. EDS spectrum and values prove that eggshell waste is capable of metal ion binding.

Our results indicate that at lower Cd (II) concentration the bioconcentration factor is 10 times higher than at higher metal concentrations.

Based on the results obtained, it can be concluded that eggshell waste is an effective, green and alternative adsorbent for removing Cd (II) from aqueous solutions.

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