Cadmium(II) Removal from Aqueous Solution Using Microporous Eggshell: Kinetic and Equilibrium Studies

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ABSTRACT

Heavy metals are soluble in the environment and can be dangerous for many species. So, removal of heavy metals from the water and wastewater is an important process. In this study, an adsorbent made of eggshell powder was employed to remove cadmium ions from aqueous solution. A number of parameters were studied including pH of the aqueous solution, adsorbent dosage, contact time, the initial concentration of cadmium ion and mixing rate. The best efficiency for the removal of Cd(II) was obtained 96% using this adsorbent. The optimal parameters were ambient temperature of 30 °C, mixing rate of 200 rpm, pH of 9, an adsorbent dosage of 5 g/L and initial concentration of cadmium was 200 ppm. In order to study the kinetics of adsorbent, the pseudo-first-order and pseudo-second-order kinetic models and intra-particle diffusion model were applied. According to the pre-determined correlation coefficients (R^2), the pseudo-second-order kinetic model showed a better correlation between the kinetic behaviors of the adsorbent. Furthermore, to study the equilibrium behavior of adsorbent, Langmuir and Freundlich models used and both models showed high efficiency in isotherm behavior of the adsorbent. So, this adsorbent can be used as a natural and cheap adsorbent.

Keywords: *cadmium ions; kinetic models; isotherm models; eggshell powder; aqueous solution*

ABSTRAK

Logam berat tidak larut dalam lingkungan dan bisa berbahaya bagi banyak spesies. Jadi, penghilangan logam berat dari air dan air limbah merupakan proses yang penting. Dalam penelitian ini, adsorben yang terbuat dari serbuk kulit telur digunakan untuk menghilangkan ion kadmium dari larutan. Sejumlah parameter dipelajari meliputi pH larutan, dosis adsorben, waktu kontak, konsentrasi awal ion kadmium dan laju pencampuran. Efisiensi terbaik untuk menghilangkan Cd(II) diperoleh 96% dengan menggunakan adsorben ini. Parameter yang optimal adalah suhu sekitar 30 °C, laju pencampuran 200 rpm, pH 9, dosis adsorben 5 g/L dan konsentrasi awal kadmium adalah 200 ppm. Untuk mempelajari kinetika adsorben, diterapkan model kinetik orde pertama semu dan orde kedua semu dan model difusi intra-partikel. Berdasarkan koefisien korelasi yang telah ditentukan sebelumnya (R^2), model kinetik orde kedua semu menunjukkan korelasi yang lebih baik antara perilaku kinetik adsorben. Selanjutnya, untuk mempelajari perilaku kesetimbangan adsorben, digunakan model Langmuir dan Freundlich dan kedua model menunjukkan efisiensi tinggi dalam perilaku isoterm adsorben. Jadi, adsorben ini bisa digunakan sebagai adsorben alami dan murah.

Kata Kunci: *ion cadmium; model kinetik; model isoterm; bedak telur; larutan encer*

INTRODUCTION

Heavy metals are not dissoluble in the environment and can be dangerous for many species [1]. Heavy metals can also lead to changes in physical, chemical and biological properties of water [2]. Rapid improvements in economical industries like forgery, production of fertilizers, battery manufacturing and etc. are leading to direct and indirect increase in production rate of heavy metals into the environments of developing countries [3]. There are other industries which have heavy metals as byproducts including the automotive industry, dyes for the textile industry and mining operations [4]. As a result, recovery and removal of heavy metals from the water and the wastewater is a significant process to maintain general and environmental health [1]. Cadmium is one of the most dangerous heavy metals and can be hazardous to human health causing serious diseases like kidney failures, hypertension, hepatitis and damage to the lungs and bones cancer [5]. The amount of cadmium in

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sewage water and drinking water is reported to be equal to 0.1 and 0.05 mg/L, respectively [6].

There are a number of different methods for recovery and removal of heavy metals in soil and aqueous solutions like electrochemical processes, ion exchange, chemical scaling, osmosis, evaporation and surface adsorption [7]. Some of these methods have disadvantages like high capital costs and/or inapplicability in industrial scale [8]. Therefore, some researchers have focused on low cost and available adsorbent with agricultural and biological origins [9]. Some of these materials are sunflower wastes [10], orange peel [11], tea factory wastes [12], soybean straw [13], olive stone [14-15] and etc. These materials have been utilized by researchers for recovery and removal of heavy metals.

The aim of this study is to investigate the removal of cadmium ion from aqueous solutions using eggshell powder. To do so, the effect of several parameters such as pH, adsorbent dosage, the initial concentration of cadmium ion in the solution, mixing rate and contact time on adsorption process were investigated. In addition, kinetic and equilibrium behavior of bio-adsorbent was examined.

MATERIALS AND METHODS

Preparation of Cadmium Solution

In order to prepare cadmium aqueous solution, 2.744 g of cadmium nitrate Cd $(NO_3)_2.4H_2O$ is dissolved in one liter of distilled water. This solution is used for the preparation of different concentrations of cadmium (3, 10, 15 and 20 ppm). In all experiments, diluted solution and distilled water were employed.

Preparation of Adsorbent

To prepare eggshell adsorbent, the shells were gathered and washed and then heated up in the oven at 60 °C for one hour. The dried product was milled with the above-mentioned milling machine and made into powder passing sieve No. 25 (ASTM E 11) and stored in the same containers as above.

The changes on the surfaces of the adsorbent were investigated by Scanning Electron Microscopy (SEM) before and after surface adsorption process.

Batch Adsorption Test and Optimized Conditions

The adsorption experiment was carried out as batch inside 250 mL Erlenmeyer flasks containing 100 mL of synthetic cadmium solution. Initial pH of the samples was set by 0.1 molar NaOH and HCl in the range of 2–10. Afterwards, 2 g/L of adsorbent were added up to the solutions with cadmium initial concentration of 10 ppm. The final solution was stirred at 30 °C and 200 rpm for 80 min. The solutes were filtered through filter paper and 5 mL of the solution was analyzed to measure adsorbed cadmium ion concentration. The optimization process repeated for other parameters as well as pH. These parameters were adsorbent dosage (1–8 g/L), mixing rate (0–200 rpm), and initial concentration of cadmium ion in the solution (3–20 ppm). The pH of the solution was adjusted to optimum condition and one of the parameters considered variable while others were constant. The optimized condition of each parameter was selected and the investigation continued to define the optimum condition of other parameters. The cadmium ion concentration was identified by flame atomic adsorption spectroscopy Model SpectrAA-10 Plus made by Varian.

The amount of adsorbed ions by bio-adsorbent for each gram of adsorbent is identified by Eq. (1) [16]:

$$q = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where q_e is the amount of adsorbed material per gram of bio-adsorbent (mg/g) in the equilibrium state, C_0 and C_e are initial and equilibrium concentrations of cadmium (mg/L), V is the solution volume and W is the weight of the adsorbent. In the present study, the recovery of lead ion adsorption in different conditions of the reaction is identified using Eq. (2):

$$\%\ \text{Adsorption} = \frac{C_i - C_o}{C_i} \times 100 \quad (2)$$

C_i and C_o are the initial and final concentration of lead concentration, respectively in aqueous solution after equilibrium. In this research, all of the tests performed twice and the best results were reported.

SEM Analysis

The changes on the surface eggshell powder were studied before and after cadmium ion adsorption using SEM of Hitachi type (S4160). For scanning the surface of the adsorbent, this surface was covered with a thin layer of gold both before and after adsorption. The SEM images showed the apparent surface of the adsorbent. Fig. 1 shows the surface of eggshell powder before and after cadmium ion adsorption.

RESULT AND DISCUSSION

Effect of pH

Initial pH of aqueous solutions containing heavy metals is one of the most significant parameters in the adsorption process. The capacity of ion metal adsorption

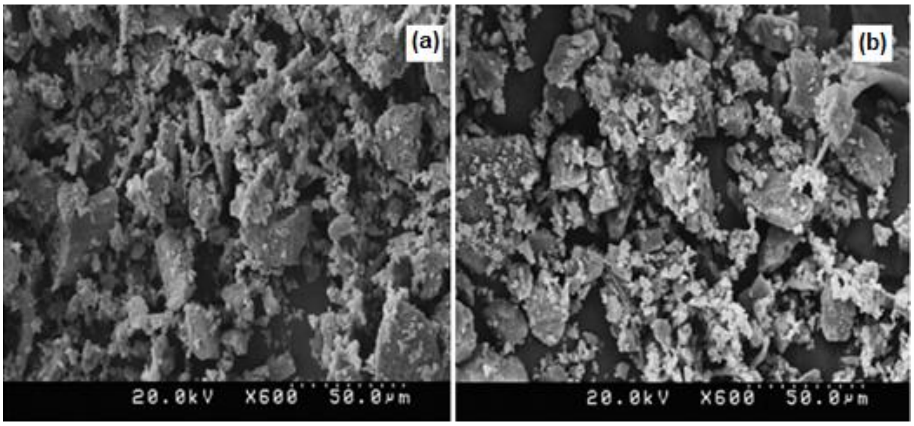

Fig 1. SEM images of the adsorbent a) eggshell before adsorption, b) eggshell after adsorption

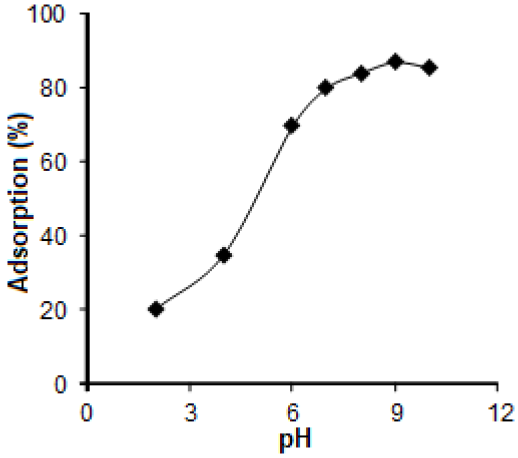

Fig 2. Effect of initial pH on efficiency of cadmium adsorption (initial cadmium concentration 10 ppm, rotation rate 200 rpm, temperature 30 °C, contact time 80 min, adsorbent dosage 2 g/L)

and its mechanism depends on initial pH of the solution [17]. Adsorption recovery is greatly dependent on hydrogen cation in the solution [1]. The effect of initial pH performed in the range of pH = 2–10 and the percentage of removed cadmium ion is shown in Fig. 2. This figure shows that increasing initial pH leads to increase in cadmium ion removal percentage and optimum pH for eggshell is 9. The removal recovery is also 87% of eggshell powder. Low pH means high hydrogen cation content and this cation participates in reactions inside the aqueous solution. In fact, there is a competition between hydrogen cation and cadmium ions to occupy active sites of the adsorbent. If these sites were occupied by hydrogen ions, there would be the less active site for cadmium ions and this reduces the recovery of adsorption. High pH (pH > 7) means low hydrogen cation content and high OH^- content inside the solution. In this case, there is no competition between hydrogen and cadmium ions and active sites are occupied by cadmium ions, resulting in higher recovery. In higher pH values (pH > 9) the adsorption recovery is reduced again. In this case, hydroxide anions compete with cadmium ions to lodge into active sites. Besides, in high pH values, hydroxide anions make a complex with cadmium ions and these ions deposit and accumulate in the solution. As a result, a membrane is made of the cadmium ions and active sites on the surface of the adsorbent. Cadmium removal percentage in pH = 10 is 85.5% for eggshell powder.

Effect of Mixing Rate

The mixing rate and turbulence making inside aqueous solution is an important parameter in adsorption process as disturbance increases the possibility of contact between the adsorbent and ions which results in higher recovery [18]. In order to examine mixing rate on adsorption process, the parameters were determined in laboratory conditions as mixing rate 0–200 rpm, initial cadmium ion 10 ppm, time 80 min, temperature 30 °C, adsorbent dosage 2 g/L and pH = 9. The magnetic mixer was used for mixing process and this parameter effect is shown in Fig. 3. According to the Fig. 3, increasing the mixing rate in the range of 0–200 rpm increases the recovery of cadmium adsorption by the adsorbent. Higher mixing rate means higher contact possibility between active sites and cadmium ions. The optimum recovery was at 200 rpm mixing rate equal to 87% for eggshell powder.

Effect of Adsorbent Dose

The amount of used adsorbent is a significant parameter in adsorption process, as it determines the adsorption capacity in a certain concentration of adsorbed material [19-20]. The testing parameters for the range of adsorbent dosage (1–8 g) to remove cadmium

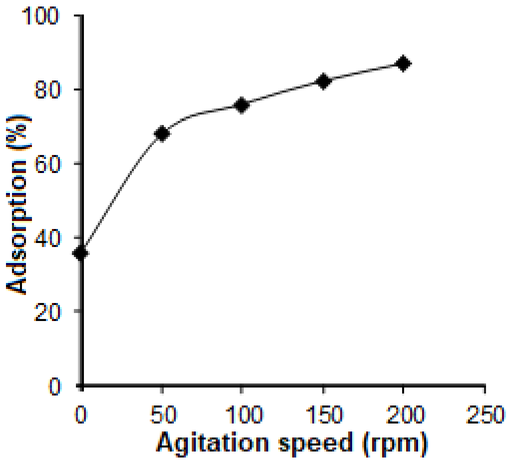

Fig 3. Effect of mixing rate on cadmium adsorption recovery (initial cadmium concentration 10 ppm, temperature 30 °C, contact time 80 min, adsorbent dosage 2 g/L, pH = 9)

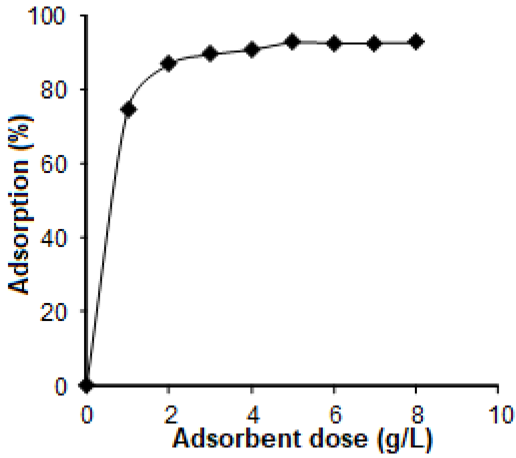

Fig 4. Effect of adsorbent dosage on cadmium adsorption recovery (initial cadmium concentration 10 ppm, temperature 30 °C, contact time 80 min, mixing rate 200 rpm, pH = 9)

ions are initial cadmium concentration 10 ppm, temperature 30 °C, contact time 80 min, mixing rate 200 rpm, pH = 9. The findings revealed that increasing the amount of used adsorbent leads to increase in cadmium adsorption, as higher dosage increases the number of active sites for cadmium ion adsorption. Increase in the amount of adsorbent up to 5 g/L, results in the higher recovery of cadmium removal that is 93%. Higher dosages of adsorbent in aqueous solution, more than 5 g/L, show a negligible increase in recovery because of saturation inactive sites. Even in some cases the final recovery is reduced as there was the higher possibility of contact between adsorbent particles and active sites and this factor makes flocculation on the sites and ultimately decreases the number of active sites and adsorbent surfaces and final recovery as a result.

Effect of Ion Concentration and Contact Time

In batch adsorption processes, the initial concentration of metals plays an important role in providing appropriate force for transferring stable mass between solid and liquid phases [21]. The testing conditions of different initial concentration of lead ion (3–20 ppm) were: temperature 30 °C, contact time 0–150 min, mixing rate 200 rpm, pH = 9 by eggshell powder. Fig. 5 shows the effect of initial cadmium ion (3, 10, 15, and 20 ppm) in different contact times (0–150 min) for adsorption using eggshell powder. This figure confirms that increasing both initial concentrations of cadmium ion and contact time, amplifies the recovery; due to appropriate produced forces for mass transfer between solid and liquid phases. In addition, Fig. 5 shows that longer contact time increases adsorption recovery. Cadmium ion adsorption rate by the adsorbent is higher during initial time intervals that because of activity of adsorption sites. Equilibrium time of adsorption by eggshell is 40 min. After this period, the percentage of total adsorbed metal changes negligibly, since active sites were occupied by cadmium ions and adsorption continued through ions penetration into adsorbent layers.

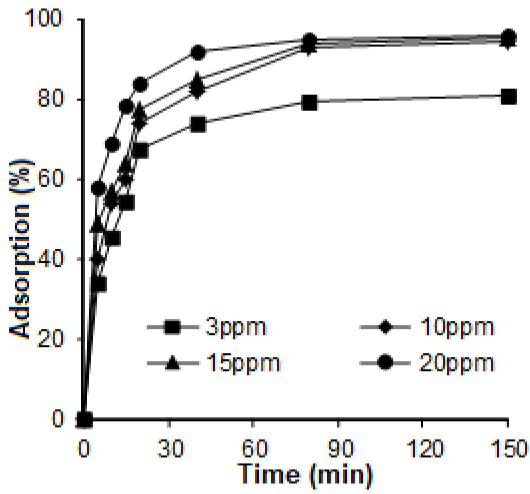

Fig 5. Effect of initial concentration of cadmium ion on adsorption recovery using eggshell powder (temperature 30 °C, mixing rate 200 rpm, pH = 9, adsorbent dosage 5 g/L)

The results of this stage of the experiments were applied to investigate the kinetic behavior of adsorbent.

Kinetic Studies

Adsorption kinetics is used for identification and control mechanisms of surface adsorption processes.

Table 1. Constants and correlation coefficient of kinetic models for cadmium ion adsorption in different concentrations using eggshell powder

Kinetic models and the parameters	Adsorbate concentration (mg/L)			
	3	10	15	20
Pseudo-first order				
$q_{e\ cal}$	0.282	1.35	1.783	1.524
K_1	0.0422	0.0487	0.0482	0.0479
$q_{e.exp}$	0.486	1.8854	2.856	3.84
R^2	0.9618	0.9874	0.9902	0.9724
Pseudo-second order				
$q_{e.cal}$	0.512	1.999	2.994	3.943
K_2	0.267	0.0616	0.0501	0.0707
R^2	0.9994	0.9993	0.9994	0.9999
H	0.0699	0.246	0.449	1.099
$q_{e.exp}$	0.486	1.8854	2.856	3.84
Intraparticle diffusion				
K_{in}	0.0261	0.1036	0.1383	0.136
C	0.2187	0.8097	1.4195	2.4672
R^2	0.7479	0.8157	0.8187	0.7248

This mechanism depends on physical and chemical properties of adsorbent. In the present study, kinetics and cadmium adsorption mechanism of the adsorbent were modeled by pseudo-first and pseudo-second-order kinetic models and intra-particle diffusion model. The degree of this correlation was determined by the correlation coefficient (R^2).

The pseudo-first order model is widely used for kinetic behavior of adsorbent in many types of research. In this model, it is assumed that the rate of changes in the solute is directly proportional to the changes in the saturation concentration and the amount of consumed adsorbent versus time. The linear form of the pseudo-first-order model is as Eq. (3) [19,22]:

$$\mathrm{Ln}\left(q_e - q_t\right) = \mathrm{Ln}q_e - K_1 t \qquad (3)$$

In this equation, q_e is the amount of adsorbed ion in the equilibrium state (mg/g) per gram of the adsorbent, q_t is the amount of adsorbed ion (mg/g) per gram of adsorbent versus time and k is the constant rate of adsorption (1/min). This constant value is obtained by plotting Ln (q_e-q_t) versus t.

Another kinetic model frequently used is pseudo-second-order model and the linear form of this equation is like Eq. (4) [19]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

In this equation, K_2 is the constant rate of pseudo-second-order equation (g/mg.min), q_e is the maximum adsorption capacity (mg/g) and q_t is the adsorbed amount during the time t (min).

The initial rate of adsorption is determined using Eq. (5) [19]:

$$H = Kq_e^2 \qquad (5)$$

The values of q_e and K_2 are obtained by plotting t/q_t versus t. q_e is the slope of the linear plot and K_2 is the intercept of the line.

Another kinetic model is intra-particle diffusion model which is as Eq. (6):

$$q_t = K_{id} t^{1/2} + C \qquad (6)$$

q_t (mg/L) is the amount of adsorption time t (min) and k_{id} (mg/g.min) is the rate constant of intra-particle diffusion. Table 1 displays the parameters and constants of pseudo-first, pseudo-second and intra-particle diffusion models for adsorbent in optimum conditions and for different concentrations of cadmium ion (3, 10, 15, 20 ppm). Based on the correlation coefficient for mentioned adsorbent, the pseudo-second-order kinetic model is more appropriate in comparison with other models to describe the kinetic behavior of adsorbent and best matches with laboratory data.

Equilibrium Study

The isotherm models are usually investigated for the description of adsorption process and related mechanisms [23]. Langmuir and Freundlich are two isotherm models that are widely used. Langmuir isotherm is widely used for the description of laboratory data in previous studies. The linear form of this model is like Eq. (7) [19,22-24]:

$$\frac{1}{q_e} = \frac{1}{k_L q_{max} C_e} + \frac{1}{q_{max}} \qquad (7)$$

C_e is the concentration of metal ion in the equilibrium state (mg/L), q_e is the adsorbed ion in equilibrium state per gram of adsorbent. q_{max} and k_L are the capacity of surface adsorption (mg/g) and

Table 2. Constants and parameters of Langmuir and Freundlich isotherm models for eggshell adsorbent

Adsorption isotherm	Isotherm constants	value
Langmuir	K_L(L/g)	0.121
	q_{max}(mg/g)	20.16
	R_L	0.452
	R^2	0.9707
Freundlich	K_f(mg/g)(L/mg)$^{1/n}$	2.813
	n	0.9
	R^2	0.971

adsorption energy (l/g), respectively which are the constants of Langmuir model. The values are obtained by calculating the slope and intercept of linear Langmuir equation in C_e/q_e versus C_e diagram. Another effective parameter in Langmuir equation is R_L that describes the properties of the equation. The value of R_L is the representative of the state and quality of adsorption isotherm model. If $R_L > 1$, $R_L = 0$, $R_L = 1$ and $0 < R_L < 1$, the process is non-desired, irreversible, linear and desirable, respectively [19,24]. The value of R_L is identified using Eq. (8):

$$R_L = \frac{1}{1+K_L C_0} \quad (8)$$

C_0 in Eq. (8) is the initial concentration of cadmium ion in aqueous solution in mg/L.

Another typical isotherm model frequently used is Freundlich isotherm model. This model is empirical and able to describe adsorption of organic and inorganic compounds by different adsorbents. The non-linear Freundlich isotherm model is like Eq. (9):

$$q_e = K_f C_e^{1/n} \quad (9)$$

The linear form of this equation is like Eq. (10) which is used in this study:

$$Lnq_e = LnK_f + \frac{1}{n} LnC_e \quad (10)$$

q_e is the capacity of equilibrium adsorption (mg/g), C_e is the equilibrium concentration of cadmium ion in the solution (mg/L), K_f and n are the constants of Freundlich model that shows the relationship between adsorption capacity and adsorption intensity, respectively. In order to identify these parameters (K_f and 1/n), Lnq_e is plotted versus LnC_e and the slope of the line is 1/n and the intercept is K_f. The value of n in many types of research is in the range of 1-10. High values of n represent the high interactions between the adsorbent and metal ions and n = 1 shows the linear adsorption for all active sites of the adsorbent [24].

To investigate the equilibrium behavior of the process, the test performed in the following conditions: initial cadmium ion concentration 10 ppm, temperature 30 °C, contact time 80 min, mixing rate 200 rpm, adsorbent dosage 1–5 g/L and pH = 9. Attained equilibrium data were examined for the adsorbent in Langmuir and Freundlich models. The constant values and other parameters of the models for eggshell powder are listed in Table 2. According to the calculated value of correlation coefficient of the adsorbent in isotherm Langmuir and Freundlich model, it was revealed that both models can describe isotherm behavior of the adsorbent. The correlation coefficient for eggshell adsorbent using Langmuir and Freundlich models was 0.9707 and 0.971, respectively. Both models are good estimators of isotherm behavior of cadmium ion adsorption by the eggshell adsorbent. It should be mentioned that the value of R_L for both adsorbent show desirable adsorption; as it is 0.452.

CONCLUSION

The findings of this research were promoted for adsorption and removal of the Cd^{2+} ion from aqueous solution using bio-adsorbent prepared by eggshell powder. Effective parameters in cadmium ion adsorption were pH, the amount of used adsorbent, the initial concentration of cadmium ion in the solution, contact time and mixing rate. The percentage of cadmium ion removal using eggshell was 96%. The testing conditions were: temperature 30 °C, mixing rate 200 rpm, adsorbent dosage 5 g/L, the initial concentration of cadmium in the aqueous solution 20 ppm and pH 9. Kinetic and isotherm behavior of the adsorbent were investigated by different synthetic and isotherm models and correlation coefficients of the adsorbent showed that pseudo-second-order kinetic model was better for prediction of adsorbent kinetic behavior. Also, the equilibrium study showed that Langmuir and Freundlich isotherm models were similar in data matching. Adsorption process of cadmium ion using eggshell powder showed that the adsorption process was desirable according to the value of R_L which was 0.452. Therefore, the recovery of ions removal and correlation coefficients of the models confirm that eggshell powder can be considered as a natural and cheap adsorbent for cadmium ion removal.

REFERENCES

[1] Sari, A., Tuzen, M., Citak, D., and Soylak, M., 2007, Equilibrium, kinetic and thermodynamic studies of adsorption of Pb(II) from aqueous solution onto Turkish kaolinite clay, *J. Hazard. Mater.*, 149 (2), 283–291.

[2] Barros, A.J.M., Prasad, S., Leite, V.D., and Souza, A.G., 2006, Biosorption of heavy metals in upflow sludge columns, *Bioresour. Technol.*, 98 (7), 1418–1425.

[3] Fu, F., and Wang, Q., 2011, Removal of heavy metal ions from wastewaters: A review, *J. Environ. Manage.*, 92 (3) 407–418.

[4] Li, Q., Zhai, J., Zhang, W., Wang, M., and Zhou, J., 2007, Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk, *J. Hazard. Mater.*, 141 (1), 163–167.

[5] Lodeiro, P., Barriada, J.L., Herrero, R., and de Vicente, M.E.S., 2006, The marine macroalga *Cystoseira baccata* as biosorbent for cadmium(II) and lead(II) removal: Kinetic and equilibrium studies, *Environ. Pollut.*, 142 (2), 264–273.

[6] Jagtap, S., Thakre, D., Wanjari, S., Kamble, S., Labhsetwar, N., and Rayalu, S., 2009, New modified chitosan-based adsorbent for defluoridation of water, *J. Colloid Interface Sci.*, 332 (2), 280–290.

[7] Esmaeili, H., and Foroutan, R., 2015, Investigation into ion exchange and adsorption methods for removing heavy metals from aqueous solutions, *IJBPAS*, 4 (12), 620–629.

[8] Sari, A., and Tuzen, M., 2009, Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass, *J. Hazard. Mater.*, 164 (2-3), 1004–1011.

[9] Han, R., Li, H., Li, Y., Zhang, J., Xiao, H., and Shi, J., 2006, Biosorption of copper and lead ions by waste beer yeast, *J. Hazard. Mater.,* 137 (3), 1569–1576.

[10] Zhang, Y., and Banks, C., 2006, A comparison of the properties of polyurethane immobilised Sphagnum moss, seaweed, sunflower waste and maize for the biosorption of Cu, Pb, Zn and Ni in continuous flow packed columns, *Water Res.*, 40 (4), 788–798.

[11] Li, X., Tang, Y., Cao, X., Lu, D., Luo, F., and Shao, W., 2008, Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel, *Colloids Surf., A*, 317 (1-3), 512–521.

[12] Malkoc, E., and Nuhoglu, Y., 2005, Investigations of nickel(II) removal from aqueous solutions using tea factory waste, *J. Hazard. Mater.*, 127 (1-3), 120–128.

[13] Zhu, B., Fan, T., and Zhang, D., 2008, Adsorption of copper ions from aqueous solution by citric acid modified soybean straw, *J. Hazard. Mater.*, 153 (1-2), 300–308.

[14] Kula, I., Uğurlu, M., Karaoğlu, H., and Çelik, A., 2008, Adsorption of Cd(II) ions from aqueous solutions using activated carbon prepared from olive stone by $ZnCl_2$ activation, *Bioresour. Technol.*, 99 (3), 492–501.

[15] Fiol, N., Villaescusa, I., Martínez, M., Miralles, N., Poch, J., and Serarols, J., 2006, Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone waste, *Sep. Purif. Technol.*, 50 (1), 132–140.

[16] Foroutan, R., Esmaeili, H., and Kosari Fard, M., 2015, Equilibrium and kinetic studies of Pb(II) biosorption from aqueous solution using shrimp peel, *IRJABS*, 9 (11), 1954–1965.

[17] Hasan, S., Ghosh, T.K., Viswanath, D.S., and Boddu, V.M., 2008, Dispersion of chitosan on perlite for enhancement of copper(II) adsorption capacity, *J. Hazard. Mater.*, 152 (2), 826–837.

[18] Dotto, G.L., and Pinto, L.A., 2011, Adsorption of food dyes acid blue 9 and food yellow 3 onto chitosan: Stirring rate effect in kinetics and mechanism, *J. Hazard. Mater.,* 187 (1-3), 164–170.

[19] Sarvestani, F.S., Esmaeili, H., and Ramavandi, B., 2016, Modification of *Sargassum angustifolium* by molybdate during a facile cultivation for high-rate phosphate removal from wastewater: Structural characterization and adsorptive behavior, *3 Biotech.*, 6 (2), 251.

[20] Khoo, F.S., and Esmaeili, H., 2017, Synthesis of CaO/Fe_3O_4 magnetic composite for the removal of Pb(II) and Co(II) from synthetic wastewater, *J. Serb. Chem. Soc.*, DOI: 10.2298/JSC170704098S.

[21] Rafatullah, M., Sulaiman, O., Hashim, R., and Ahmad, A., 2009, Adsorption of copper(II), chromium(III), nickel(II) and lead(II) ions from aqueous solutions by meranti sawdust, *J. Hazard. Mater.*, 170 (2-3), 969–977.

[22] Foroutan, R., Esmaeili, H., Abbasi, M., Rezakazemi, M., and Mesbah, M., 2017, Adsorption behavior of Cu(II) and Co(II) using chemically modified marine algae, *Environ. Technol.*, DOI: 10.1080/09593330. 2017.1365946.

[23] Yadav, S.K., Singh, D.K., and Sinha, S., 2014, Chemical carbonization of papaya seed originated charcoals for sorption of Pb(II) from aqueous solution, *J. Environ. Chem. Eng.*, 2 (1), 9–19.

[24] Foroutan, R., Esmaeili, H., Rishehri, S.D., Sadeghzadeh, F., Mirahmadi, S., Kosarifard, M., and Ramavandi, B., 2017, Zinc, nickel, and cobalt ions removal from aqueous solution and plating plant wastewater by modified *Aspergillus flavus* biomass: A dataset, *Data Brief*, 12, 485–492.