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KINETIC AND ISOTHERM STUDY OF CUPPER ADSORPTION FROM AQUEOUS SOLUTION USING WASTE EGGSHELL

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Abstract. The sorption of Cu^{2+} ions from aqueous solutions by eggshell was investigated in a batch experimental system with respect to the temperature, initial Cu^{2+} concentrations, pH, and biosorbent doses. The adsorption equilibrium was well described by the Langmuir isotherm model with the maximum adsorption capacity of 5.05 mg Cu^{2+}/g eggshell at 25 °C. The value of q_e increased with increasing the temperature while also increases the release of Ca^{2+} and HCO^{-}_3 ions from the eggshell. The highest sorption of Cu^{2+} onto the waste eggshell was determined at the initial pH value of 4.0. The results confirming that the adsorption reaction of Cu^{2+} on the eggshell was thought to be endothermic. A comparison of the kinetic models such as pseudo first and second-order kinetics, intraparticle diffusion, and Elovich on the sorption rate demonstrated that the system was best described by the pseudo second-order kinetic model.

Keywords: eggshells, adsorption, copper, water cleaning technologies.

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Introduction

Industrial wastewaters contained various kinds of pollutants including heavy metals are commonly produced from many industrial processes. High concentrations of heavy metals affect negatively human, animal and vegetation in the water body. Because of unique characteristics of heavy metals, which are non-biodegradable and accumulated by living organisms, are the main environmental concerns (Ghazy *et al.* 2011).

Treatment of the wastewater including heavy metal ions became particularly difficult due to implementation of more restrict law regulations that control the concentration of pollutants in effluents discharged into waters and soil on the level lower than 1 mg/kg (Chojnacka 2005). The traditional treatment processes such as chemical precipitation and coagulation-flocculation for the removal of metal ions became inefficient to achieve below this concentration.

Several methods such as ion exchange, solvent extraction, phytoextraction, ultrafiltration, reverse osmosis, and adsorption have been widely used in order to remove heavy metals from industrial wastewaters. However, adsorption method is widely applied to eliminate heavy metals due to the some limitations like requirements of pretreatments, low removal efficiency and high capital cost of the other methods (Jai *et al.* 2007).

The application of adsorption is one of the effective, simple and low cost methods to remove low concentration heavy metal from industrial wastewater. Low cost sorbents are investigated for heavy metal elimination. The most frequently studied biosorbents are bacteria, fungi, and algae (Yeddou, Bensmaili 2007), grape stalks, crop milling waste, olive stone, sawdust (Zheng *et al.* 2007; Ozacar, Sengil 2005), peanut hull pellets, dried sunflower leaves, sugar beet pulp, *capsicum annuum* seeds (Slijvic *et al.* 2009), fish bones (Kizilkaya *et al.* 2010), and bone char (Cheung *et al.* 2000).

One cheap and easily available material having possibilities as suitable sorbent for heavy metal is eggshell. Due to their low cost and high calcium content, after these materials have been expended, they can be disposed without

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expensive regeneration. Disposal of eggshells is also a serious problem for egg processing industries due to stricter environmental regulations and high landfill costs (Rao *et al.* 2010).

Copper is considered as one of the most toxic metal and poses a potential threat to the human health and environment, even at low concentrations (Ahmad *et al.* 2010). However, low concentrations of cupper is essential for living organisms and additionally deficiency of it may cause effects on human health like, anemia osteoporosis, decreased glucose tolerance, arthritis, cardiac arrhythmias and neurological problems. On the contrary, high concentrations of cupper causes toxicity, as the redox properties, essential for its function in excess copper in cells causes cuproenzymes, can also result in marked reactive oxygen species formation that can damage lipids, nucleic acids and proteins (Sljivic *et al.* 2009). Because of the toxic effects on the living organisms, cupper containing wastewaters from industries require treatment before their discharge into the environment.

The main objective of the experimental study was to investigate the adsorption of Cu^{2+} ions in the synthetic wastewater by using waste eggshells. The removal efficiency of Cu^{2+} on the eggshell was investigated as a function of temperature, pH, contact time, initial Cu^{2+} concentrations, and adsorbent doses. Various models were applied to determine the adsorption isotherms with the best fit to the experimental data. The kinetic models, pseudo first and second order kinetics, intraparticle diffusion, and Elovich were applied in order to investigate the mechanisms of eggshell sorption.

1. Materials and methods

1.1. Preparation of eggshell

The chicken eggshells were collected from bakeries in Sivas, Turkey. After the eggshells were rinsed several times with tap and distilled water to remove impurities like organics and salts, it was dried at 60 °C for 24 hours in an oven. The eggshells were crushed and screened through a set of sieves to get the size of 106–250 μm.

1.2. Sorption studies

All solutions were prepared from analytical reagent chemicals. The synthetic solutions were prepared by diluting Cu^{2+} standard stock solutions (250 mg/L) obtained by dissolving $CuCl_2$ in the distilled water. Fresh dilutions of the synthetic wastewater were used in the experiments.

The sorption studies of Cu^{2+} from aqueous solution onto the eggshells were carried out using batch equilibrium techniques. Experiments were performed in 250 mL Erlenmeyer flasks containing Cu^{2+} and eggshells. Cu^{2+} analyses were performed in the initial solutions and clear samples at the end of batch tests. A sample of 0.25 g eggshell was added to 100 mL solution which was contained desired concentrations of Cu^{2+}.

The effects of experimental parameters such as, initial Cu^{2+} ion concentration (10–50 mg/L), pH (2.0–5.0), adsorbent dosage (0.05–0.5 g/L) and temperature (25–50 °C) on the removal of Cu^{2+} ions were studied. Initial pHs of the solutions were adjusted using H_2SO_4 or NaOH solutions. Various concentrations of Cu^{2+} solutions (15, 25, and 35 mg/L) at a constant initial pH value (≅ 5.0), and adsorbent dosage (2.5 g/L) were used for the kinetic experiments. The batch units were agitated in an orbital incubator shaker (Gerhardt) for a contact time varied in the range 0–2880 min at a speed of 150 rpm at 25 °C. The samples were then centrifuged in NUVE Centrifuge NF800 at 4000 rpm for 10 min to separate the solution from the adsorbent.

Calcination was carried out by increasing the temperature of furnace (REF 150 model, REFSAN) at a rate of 4 °C/min to 1000 °C after crushing the sample.

The initial and final concentrations of Cu^{2+} in the aqueous solutions were determined by using a Merck Spectraquant analytical Cu^{2+} kit (14767) with a Merck photometer PHARO100. The other measurements such as alkalinity, Ca^{2+}, HCO^{-}_{3}, etc. were carried out using the APHA (1998).

1.3. Calculations

The amounts of Cu^{2+} sorbed by eggshells were calculated from the differences between Cu^{2+} quantity added to the sorbent and Cu^{2+} concentration of the supernatant by using following equation:

$$q_e(mg|g) = (C_o - C_e)(mg|L) \times V / M(mL|g), \quad (1)$$

The efficiency of Cu^{2+} removal (E) (%) is calculated by using Eqn (2):

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100, \quad (2)$$

where: q_e (mg/g) is the maximum amount of Cu^{2+} adsorbed at equilibrium; C_o and C_e (mg/L) are the initial and equilibrium concentrations of Cu^{2+} in the solution, M is the mass of eggshell (g); and V is the volume of the solution, respectively.

Sorption experiments were performed in triplicate and the average values of samples were presented. Also, blank samples (without Cu^{2+}) were used to compare the results through all batch procedures. Data presented are the mean values from the experiments, standard deviation (≤6%) and error bars are indicated in figures.

2. Results and discussion

The surface of adsorbent characterized by scanning electron microscopy (SEM) was determined in the

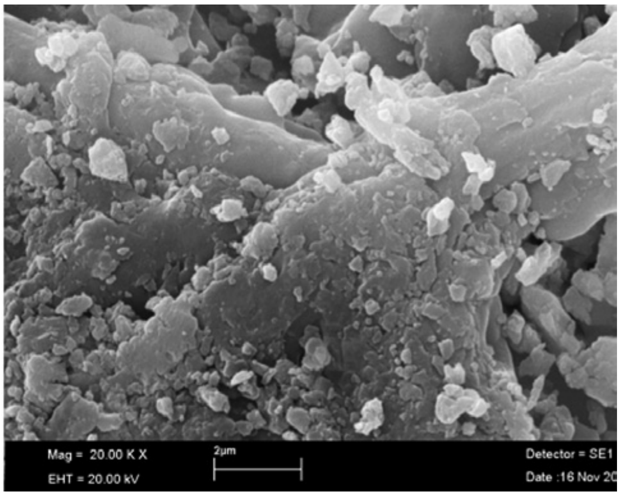

Fig. 1. SEM micrograph of waste eggshell

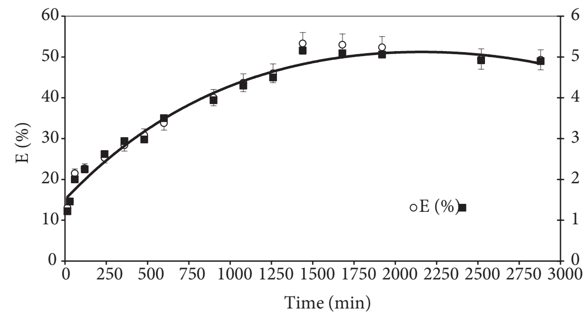

Fig. 2. Effect of contact time on Cu^{2+} sorption onto waste eggshell

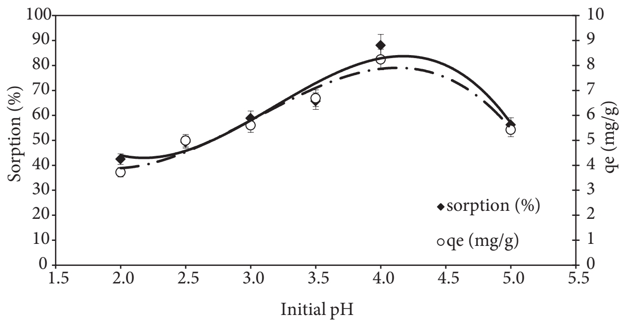

Fig. 3. Effect of initial pH on Cu^{2+} sorption onto eggshell

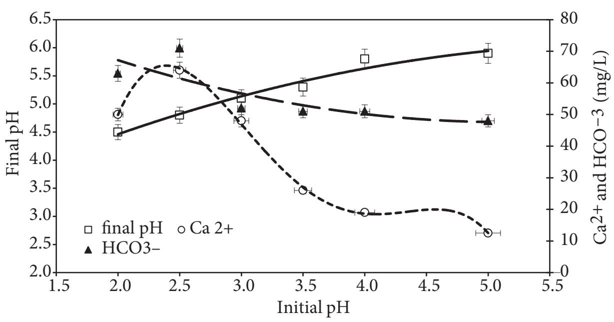

Fig. 4. Effect of initial pH on the release of Ca^{2+} and HCO^{3-} ions from the eggshell

laboratory of Kayseri Teknokent. SEM micrograph shows that eggshell has considerable numbers of pores where the Cu^{2+} ions can be adsorbed (Fig. 1).

2.1. Effect of contact time

The effects of contact time for the initial concentration of 25.0 mg Cu^{2+}/L were studied. The data obtained from the experiments showed that the contact time of 1440 min was sufficient to achieve equilibrium, because the adsorption reached a plateau at this time (Fig. 2). At this point the highest Cu^{2+} sorption efficiency (about 55%) and adsorption value (q_e = 5.2 mg/g) were achieved. Further increase the contact time, the sorption did not take place. Due to the active sites of the eggshell availability and the highest driving force for the mass transfer, rapid Cu^{2+} uptake onto the sorbent was observed at the beginning (zero to 60 min) of the sorption experiments. After this period, Cu^{2+} sorption was slower because of the occupancy of eggshell active sites and the lower concentrations of Cu^{2+} in the solution. Long mixing time was necessary in order to achieve the equilibrium time, due to the removal rate of Cu^{2+} was quite slow.

2.2. Copper sorption at different initial solution pH

The acidity of solution is an important parameter for the sorption of heavy metals from aqueous solutions since the value of pH is responsible for protonation of metal binding sites, calcium carbonate solubility and Cu^{2+} speciation in the solution (Chojnacka 2005). The uptake of Cu^{2+} was investigated as the function of pH in the range of 2.0 to 5.0 with an increment of 0.5 pH units.

Sorption of Cu^{2+} after interaction of Cu^{2+} and eggshell sorbents are presented in Figure 3. It was found that Cu^{2+} uptake by eggshells was a function of initial solution pH. The lowest adsorption efficiency of 42.5% was observed at the pH value of 2.0. Increasing the pH value from 2.0 to 4.0, sorption capacities (q_e) and the removal efficiencies of Cu^{2+} increased significantly from 3.7 mg/g to 8.2 mg/g and 42.5% to 88% respectively. Further increase the pH value to 5.0, the q_e value and removal efficiency decreases to about 5.4 mg/g and 56%, respectively. The ionization degree of heavy metal and the surface property of the eggshell may be affected by the pH. The same experimental results were also observed by Li and Wua (2010) and Ahmad *et al.* (2010). The optimum initial pH value for Cu^{2+} sorption by eggshell was determined to be 4.0. This results are expected as it is established that eggshell operate more efficiently under acidic conditions (Chojnacka 2005; Rao *et al.* 2010).

Experimental results showed that all the studied initial pH values were gradually increased and the highest final pH of about 6.0 was determined at the end of experiments (Fig. 4). Due to the release of HCO_3^- ions from the eggshells, the pH in the solutions increased. As can be seen in the Figure 4 that the initial pHs significantly affects the release of Ca^{2+} and HCO^{-}_{3} ions from the eggshell.

The chemical composition of eggshell was mainly calcium carbonate (Jai *et al.* 2007; Tsai 2006, 2008; Arunlertaree *et al.* 2007). In order to determine the CaO contents of the eggshell, calcinations experiments were carried out. The following reaction was happened in the calcinations (Zhang *et al.* 2011):

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow. \quad (3)$$

After calcinations of 550 g pre-treated eggshell, the sample weight was 300 g and corresponding mass loss was as 45.5%. As most of the impurities such as organics and humidity were removed by the pretreatment process, it was assumed that a major composition (55.5%) of the eggshell was identified as CaO when the temperature was ascending to 1000 °C. A similar result was determined by Jai *et al.* (2007).

The chemical composition (by weight) of by-products eggshell has been reported as follows $CaCO_3$ (94%), magnesium carbonate (1%), calcium phosphate (1%), and organic matter (4%) (Tsai 2008). The principal components of eggshell are $CaCO_3$ and HCO^{-}_{3}, Ca^{2+}, $CaHCO^{+}_{3}$, and $CaHO^{+}$. They are formed in the solution and their proportion is dependent on the pH value (Ghazy *et al.* 2011).

It was expected that any water equilibrated with the eggshell became basic that confirmed with following mechanisms (Arunlertaree *et al.* 2007):

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-};$$
$$CO_3^{2-} \leftrightarrow HCO_3^{-} + OH^{-}. \quad (4)$$

As can be seen in the Eqn (4), the solution has become more basic due to the hydrolysis reaction of $CaCO_3$ which gives OH^- and Ca^{2+} content of the solution is also increased.

In general, sorption of divalent metal cations on metal oxides, hydroxides and oxyhydroxides is known to be promoted by increasing pH. When divalent metal cations adsorb on these materials, the cations undergo a reaction with a surface hydroxyl group (Kuh, Kim 2000). Adsorption or precipitation mechanisms involve characteristic reactions of some metals with CaO and MgO surfaces, with adsorption occurring at low concentration of metals solution, and precipitation dominating at high concentrations (Pehlivan *et al.* 2009). Carbonates formed by $CaCO_3$ dissolution increase the pH values in the solution and therefore may be formation of precipitate form of cupper precipitate near the surface of eggshell and then these forms adsorb on the eggshell (Kuh, Kim 2000).

Because of the eggshell composition, the final pHs of the solutions were higher than the initial value. The precipitation forms of Cu^{2+} are formed when the pH value is higher than 6.0. However, the final pHs of the solutions were lower than 6.0 in this study.

2.3. Effect of temperature

It was found that the value of q_e increases with increasing the temperature while also increase the release of Ca^{2+} from the eggshell. When the temperature increases from 25 to 50 °C, the adsorption capacity increased from 5.16 to 9.94 mg/g indicating that the adsorption was endothermic in nature. At the temperature of 25 °C and 50 °C, the removal efficiency of Cu^{2+} ion at equilibrium was 54.5% and 97.5%, respectively (Fig. 5). It was probably related with the increase of Ca^{2+} release from the eggshells at higher temperature. Elevating the temperature from 25 to 50 °C, the release of Ca^{2+} ions into the aqueous solution was increased (about two times). Results might be attributed to the creation of some new active sites on the eggshell and increase in collision frequency between adsorbent and Cu^{2+} ions at high temperatures. In addition to that, the rise of adsorption with temperature may enlarge the pore size to some extent which may also affect the adsorption capacity (Demirbas *et al.* 2009).

As mentioned at above, eggshells are composed mainly of calcium carbonate. Calcium ions are bound via ion-exchange and can be thus exchanged by other cations – in this case Cu^{2+}. The experimental results and previous studies confirming that the release of Ca^{2+} from the various adsorbents were a part of the sorption mechanisms (Sljivic *et al.* 2009; Arunlertaree *et al.* 2007; Cheung *et al.* 2000; Kuh, Kim 2000). This situation can be explained by the fact that at higher temperature, the kinetic energy of Cu^{2+} is high; therefore, contact between Cu^{2+} and the eggshell is sufficient, leading to an increase in adsorption efficiencies. The results are consistent with the results of Ghazy *et al.* (2011). Results indicating that the adsorption of Cu^{2+} ions was favored at higher temperatures.

2.4. Effect of sorbent amount

The dosage of adsorbent is an important parameter in the sorption studies because it provides the capacity of an adsorbent for a given initial concentration of the adsorbate. Figure 6 shows that the absorbability diminished as the adsorbent dosages increased, resulting in that the

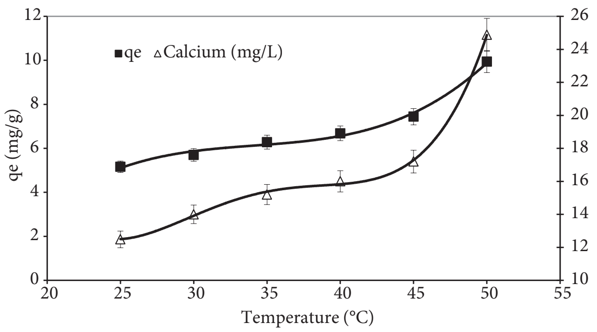

Fig. 5. Temperature effects on Cu^{2+} adsorption onto eggshell

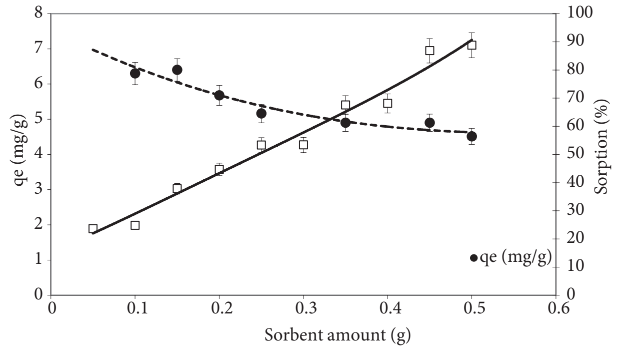

Fig. 6. The effect of sorbent amount on Cu^{2+} adsorption

amount of Cu^{2+} adsorbed per unit mass of eggshell decreased. While the amount of Cu^{2+} sorbed increase from about 24% to 89% with an increase in sorbent dosage from 0.05 to 0.5 g, the absorbability of Cu^{2+} was decreased from about 6.5 to 4.5 mg/g. The decrease in unit adsorption with increase in the dosage of adsorbent was due to adsorption sites remaining unsaturated during the adsorption process (Demirbas *et al.* 2009). This leads to make a suggestion that, higher Cu^{2+} concentrations should be tested in conjunction with an appropriate adsorbent dosage in order to determine the optimal eggshell dosage.

2.5. Modeling of sorption equilibrium depending on Cu^{2+} concentrations

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms. After determining the data with respect to the initial concentrations of Cu^{2+}, the results were verified with the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich (D-R) adsorption isotherm models.

Langmuir, (Eqn (5)) Freundlich, (Eqn (7)), Temkin (Eqn (8)), D–R (Eqn (10)) isotherms were plotted by using standard straight-line equations and corresponding two parameters for Cu^{2+} were calculated from their respective graphs.

A basic assumption of the Langmuir theory is that sorption takes place at specific homogenous sites within the sorbent (Baig *et al.* 2010). The Langmuir isotherm equation is represented by the following equation (Tsai *et al.* 2008).

$$q_e\,(mg/g) = q_m \frac{K_L C_e}{1 + K_L C_e}, \quad (5)$$

where q_m indicates the monolayer sorption capacity of adsorbate (mg/g).

In order to predict the affinity between the waste eggshells and Cu^{2+} ions, the Langmuir parameters of the dimensionless separation factor R_L can be used. The value of R_L can be calculated by the following equation:

$$R_L = \frac{1}{1 + K_L C_0}. \quad (6)$$

The value of R_L indicates that the shape of the sorption process is; unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Kilic *et al.* 2011; Sljivic *et al.* 2009).

The Freundlich isotherm model is considered to be appropriate for describing both multilayer sorption and sorption on heterogeneous surfaces (Coles, Yong 2006). The Freundlich isotherm equation is represented by the following equation (Tsai *et al.* 2008).

Freundlich

$$q_e\,(mg/g) = K_{Fi} C_e^{\frac{1}{n}}. \quad (7)$$

Temkin and Pyzhev considered the effects of indirect adsorbent/adsorbate interactions on adsorption isotherms (Kilic *et al.* 2011).

Temkin

$$q_e(mg/g) = B \ln A_T + B \ln C_e. \quad (8)$$

The linear form of Temkin isotherm equation is as follows:

$$q_e(mg/g) = B \ln K_T + \ln C_e, \quad (9)$$

where: $B = RT/b_T$ (Temkin constant related to heat of sorption, J/mol); $1/b_T$ indicates the adsorption potential of the adsorbent

The experimental data were also analyzed using the Dubinin-Radushkevich (D–R) isotherm model to determine the nature of biosorption processes as physical or chemical (Baig *et al.* 2010) by applying the following equation:

$$\ln q_e = \ln q_{max} - \beta\varepsilon^2, \quad (10)$$

and ε can be correlated as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right). \quad (11)$$

The constants β and E are the mean free energy and sorption per molecule of the sorbate, respectively. They can be computed using the following relationship (Kose, Kivanc 2011).

$$E = \frac{1}{\sqrt{-2\beta}}. \quad (12)$$

Sorption parameters for the isotherms are as follows: K_L (L/mg) Langmuir constant related to the energy of sorption; K_{Fi} (L/mg) Freundlich constant related to sorption capacity of adsorbent; q_{max} (mg/g) is the maximum biosorption capacity of D–R. b_T and A_T (L/mg) Temkin isotherm parameters; R is the gas constant (8.314 joule.mol/K); T is the absolute temperature (K).

The constants of all isotherms equation are presented in Table 1. As a result of the experiments, the highest correlation coefficient of 0.999 was determined using the Langmuir model than the others; it is suggesting that the Cu^{2+} ions were adsorbed onto the eggshell in a monolayer. Additionally, the calculated q_{cal} value of the Langmuir model equation corresponded well with the experimentally obtained. The amounts of sorbed Cu^{2+} increased with the increase of initial Cu^{2+} concentration in the solution until the equilibrium was achieved. Further increase, the removal of Cu^{2+} became independent of the initial cation concentration, due to occupancy of all active sites on the adsorbent surface (Sljivic *et al.* 2009). The experimentally obtained maximum capacity for monolayer saturation was 5.05 mg Cu^{2+}/g eggshell at 25±1 °C. The calculated R_L values were between 2.27×10^{-3} and 11×10^{-2} which indicated that the Cu^{2+} sorption by waste eggshell sample was favorable.

Table 1. Correlation coefficient and sorption parameters for various models

Model	Equation	Sorption Parameters	
Freundlich	$q_e(mg/g) = K_{Fi}C_e^{\frac{1}{n}}$	R^2	0.6958
		n	15.9
		K_F	4.08
Langmuir	$q_e(mg/g) = q_m \frac{K_L C_e}{1+K_L C_e}$	R^2	0.9995
		R_L	11×10^{-2} 2.27×10^{-3}
		q_m	5.05
		K_L	70,7
Temkin	q_e (mg/g) = $B_T \ln A_T + B_T \ln C_e$	R^2	0.720
		b_T	7485
		A_T (L/g)	248
R–D	$\ln q_e = \ln q_{max} - \beta\varepsilon^2$	R^2	0.994
		q_0 (mg/g)	5.083
		β (mol²/j²)	−0.063
		E (kj/mol)	2.82

2.6. Kinetics of sorption

In order to determine the uptake rate of adsorbate at the solid-phase interface, adsorption kinetics study is important. Various kinetic models including, pseudo first and second order kinetics, intraparticle diffusion, and Elovich were applied to the experimental data in order to investigate the mechanisms of eggshell sorption.

The adsorption kinetic models were investigated at three adsorbate dosages of 15, 25, and 35 mg Cu^{2+}/L. Lagergren and Annadurai and Krishan presented the first (Eqn (13)) and second order (Eqn (14)) rates expression for the first and second pseudo order kinetics (Chiou, Li 2002; Rao *et al.* 2010; Chairat *et al.* 2005):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t; \quad (13)$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (14)$$

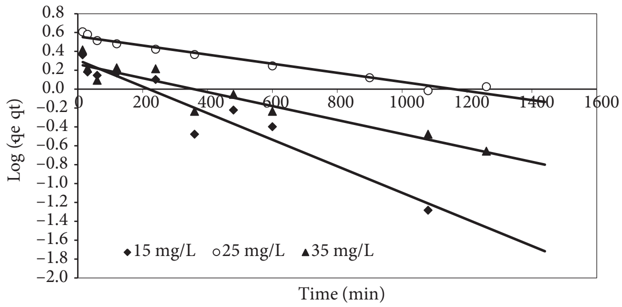

Fig. 7. Pseudo-first order kinetics of Cu^{2+} adsorption onto the eggshell at various adsorbate amounts

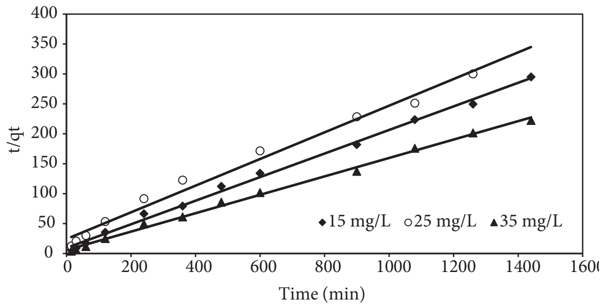

Fig. 8. Pseudo-second order kinetics of Cu^{2+} adsorption onto the eggshell at various adsorbate amounts

where: q_e and q_t (mg/g) are the amount of Cu^{2+} adsorbed onto the eggshell at equilibrium and at time t (min), respectively, the first and second order rate constants $(min)^{-1}$ are k_1 and k_2 (mg/g·min), respectively. In order to determine the value of k_1 and q_e, the plot of log $(q_e - q_t)$ against t is employed for the first pseudo order kinetic constants. The second pseudo order kinetics constants k_2 and q_e are calculated by the slope and intercept of (t/qt) versus t (Figs 7 and 8).

The initial sorption rate h (mg/g.min) is determined by using the Eqn (15):

$$h = k_2 \times q_e^2. \quad (15)$$

The uptake of adsorbate by the sorbent from solutions involves bulk, film, and intraparticle diffusion in the solid phase and within the pores, and finally adsorption on the sites. In order to determine the rate-controlling step, intraparticle diffusion model was applied to adsorption kinetic data by applying the Eqn (16) (Ghasemi *et al.* 2012).

$$q_t = k_{id}t^{\frac{1}{2}} + C, \quad (16)$$

where: q_t is the amount of Cu^{2+} ions adsorbed onto the eggshell at time t and k_{id} (g/mg.min) is the intraparticle diffusion rate constant and C presents an idea on the thickness of the boundary layer (Ahmad *et al.* 2010).

The value of rate constant of Morris–Weber transport, K_{id}, calculated from the slope of the linear plot are shown in Figure 9.

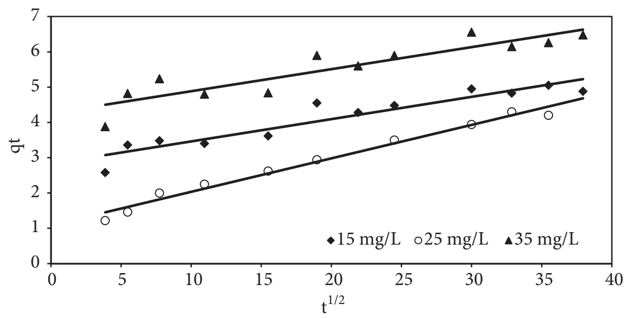

Fig. 9. Intraparticle diffusion for the adsorption of Cu^{2+} onto the eggshell at various adsorbate amounts

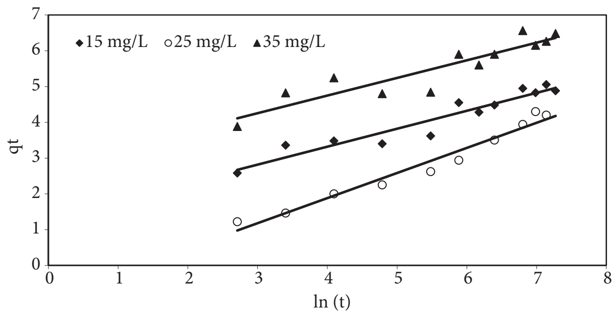

Fig. 10. Elovich Model for Cu^{2+} adsorption onto the eggshell at various adsorbate amounts

The integrated Elovich equation is given as:

$$q_t = \frac{1}{\beta}\ln\alpha\beta + \frac{1}{\beta}\ \ln t\,, \tag{17}$$

where: α (mg/g.min) is the initial sorption rate and β (g/mg) is related to the extent of surface coverage and activation energy for chemisorption (Ozacar, Sengil 2005). A plot of q_t versus ln (t) should yield a linear relationship with a slope of (1/b) and an intercept of (1/b) ln (αb) (Demirbas *et al.* 2009). The values of rate constants of Elovich model are shown in Figure 10.

The values of q_e, k_1, k_2, α, and β with the correlation coefficient (R^2) for various eggshell amounts of 15, 25, and 35 mg/L were calculated by their respected plots and the results are presented in Table 2.

Table 2. Kinetic parameters for the sorption of Cu^{2+} onto the eggshell

Conc mg/L	$q_{e,exp}$ mg/g	Pseudo-first-order			Pseudo-second-order			
		$q_{e,cal}$	$k_1 \cdot 10^{-3}$	R^2	$q_{e,\,cal}$	$k_2 \cdot 10^{-3}$	R^2	h
15	4.88	2.035	3.22	0.92	5.08	4.15	0.99	0.107
25	5.26	3.62	1.15	0.97	4.49	2.04	0.98	0.041
35	6.48	1.836	1.61	0.88	6.51	4.13	0.99	0.175
Conc mg/L	**$q_{e,exp}$ mg/g**	**Intraparticle diffusion**		**Elovich**				
		k_p	R^2	α	β	R^2		
15	4.88	0.0632	0.911	6.83	1.99	0.913		
25	5.26	0.0949	0.981	2.634	1.423	0.966		
35	6.48	0.0624	0.819	36.2	2.03	0.838		

On changing the initial concentration of Cu^{2+} in the solutions from 15 to 35 mg/L, the amount of Cu^{2+} adsorbed onto the eggshell increased experimentally. The correlation coefficient for the pseudo-second orders were relatively higher than the other kinetic models and the experimental q_e (4.88 mg/g and 6.48 mg/g) values are also very close to the calculated q_e values (5.08–6.51 mg/g). The rate constant slightly decreases with an increasing of initial Cu^{2+} concentration while the initial sorption rate increases with an increasing of initial Cu^{2+} concentration for the pseudo second-order model. The similar phenomena have also reported in sorption of Cu^{2+} onto the biowaste materials (Sljivic *et al.* 2009; Kizilkaya *et al.* 2010; Ahmad *et al.* 2010; Demirbas *et al.* 2009). Increase of q_e value is a result of the increase in the driving force of the concentration gradient with the increase in the initial Cu^{2+} concentration. Therefore a higher initial concentration of Cu^{2+} ions may increase the adsorption capacity of eggshell. It means that the biosorption is highly dependent on initial concentration of metal ion.

The results are indicated that the sorption perfectly complies with pseudo-second order reaction and the sorption of Cu^{2+} onto the eggshell appeared to be controlled by the chemisorption process.

Several biosorbents have been used to remove Cu^{2+} from aqueous solutions. A comparison of the adsorbent capacity is presented in Table 3. As can be seen from the table that eggshell shows the comparable sorption capacity for Cu^{2+} with respect to the other biosorbents.

Table 3. Comparison of various biosorbent for Cu^{2+} removal

Biosorbent	mg/g	References
Fish bones	150.7	Kızılkaya *et al.* 2010
Green alga *Spirogyra*	133.3	Gupta *et al.* 2006
Garden grass	58.34	Hossain *et al.* 2012
Iron oxide coated eggshell powder	44.843	Ahmad *et al.* 2010
Sunflower shell	30.30	Onal *et al.* 2008
Sawdust	8.452	Larous *et al.* 2005
Rice straw	8.14	Rocha *et al.* 2009
Modified mangrove barks	6.950	Rozaini *et al.* 2010
Eggshell	6.48	This study
Soybean straw	5.40	Šciban *et al.* 2008
Eggshell	5.03	Vijayarghavan *et al.* 2005
Orange skin	4.96	Onal *et al.* 2008
Barley straws	4.64	Pehlivan *et al.* 2009
Wheat straw	4.448	Šciban *et al.* 2008
Corn stalk	3.749	Šciban *et al.* 2008
Corn cob	2.16	Šciban *et al.* 2008

Conclusions

The present experimental study results showed that the waste eggshells might be applicable successfully as a sorbent of cupper ions from aqueous solution. As a conclusion:

1) The adsorption of cupper onto the waste eggshell was found to be initial Cu^{2+} concentration, pH, temperature, mixing time, and adsorbate dosage depended.
2) The optimum pH value for the experimental study was determined as 4.0.
3) Increasing the temperature, q_e value increased with the increase the release of Ca^{2+} from the eggshell.
4) Sorption of eggshell onto the eggshell was well described by Langmuir model.
5) Results indicated that pseudo second-order kinetic model, which is an agreement with a chemisorption mechanism, provided the best correlation of the experimental data.

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