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Assessment of adsorption kinetics for removal Copper Ions from aqueous solutions using Egg Shells as a Bioabsorbent

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Abstract.

Adsorption process kinetics study showed the possibility of using egg shell as a natural adsorbent, and this has had a high effectiveness in eliminating ions of Cu ion from water solution. The experiments were conducted in a temperature range of 293 - 323 K, with the initial concentration of Cu ions of 5 mg/L and adsorbent of 5 mg/L. At during in experiments, pH Solution value was set to 6, and the amount of absorbed ions was determined the following time interactions: 10, 30, 40, 60, and 120 minutes. The experiments were conducted in an electric shaker, at 200 rpm speed.

The data the pseudo-second row model depends on the value of the correlation coefficient (R^2), The results data suggest that this model describes the adsorption system well when the correlation coefficient R^2 > 0.900. which indicates that this model is more applicable and better describes the examined adsorption processes in this study and speed of interacting with adsorbent and active places present on the surface of the biosphere.

Keywords: Kinetics; Cu; Pseudo-second; Egg shell; Adsorption

Introduction

Intensive technological and industrial development has led to excessive exploitation of water resources and an increase in the level of pollution of surface and underground water surfaces. Due to increased exploitation and processing of ore, the burden of water flows on toxic metals (Cd, Mn, Cu, Pb, Ni, Co, Cr) has become a leading environmental problem, which is further contributed by the inefficiency or inefficiency method of treating (Njoku, VO, 2014).

Scientific studies suggest that the egg shell itself can bind different metal ions from water solution (Ishikawa, SIK, 2002). The shell of the egg biomaterial, which has great potential in the process of removing heavy metal ions from the water solution, is industrial and waste from households, restaurants and hotels - easily accessible. The egg shell shows the best adsorption properties. In addition to the low cost of applying this material, the advantage is that the material is in accordance with the environment, its application does not produce chemical seeding, there is secondary pollution; material is easy to work and use compared to other methods (Rathnakumar, SR, 2009).

The kinetic study is considered important for determining the constant speed of reaction and getting to know the speed of the reaction. In this study, kinetic models of adsorption processes were discussed and parameters of these models were defined that determine the speed the removal of pollutants. The importance of the kinetic study is also reflected in defining the possibility of using adsorbent (biomass) in the removal of heavy metals and other water pollutants (Aksu, 2008 & Bayramoglu, G, 2009).

2. MATERIALS AND METHODS

2.1 Material

- Egg shell powder was used, which was collected from hotels and restaurants in the city of Belgrade (Serbia).
- Cu, (BDH), Deionized water, Sodium hydroxide and nitric acid.
- Mill for grinding eggshells, Sieve to separate the eggshell powder particles.
- Whatman filter paper No. 41.
- Regular containers of 1000.00 ml for preparing standard solutions.
- Volume containers (100 ml) for experimental samples.
- pH meter, Analytical balance, Electric drying oven, Electric Shaker (Orbi-Shaker ™ Orbital Shaker)
- Centrifuge (Megafuga1.0 / Herouse Sepatech), Atomic Absorption Spectroscopy (AAS).

2.2 Methods

The collected shells were first washed with hot water to wash them off the stuck dirt, and then washed several times with deionized water to remove all ionic impurities (Ghani, A. & Ibrahim, N. 2007). Thereafter, the shells were sintered in an annealing furnace at 900 ° C for four hours. The stated temperature was chosen on the basis of literature data, ie studies that studied the influence of temperature on the increase of the surface area of natural materials (Ahmed, M, 2010). depending on the applied treatment temperature. Surface development is an important characteristic of the adsorbent and has an active role in binding the adsorbate (Panagiotou, E, 2018). After annealing, the shell was crushed and finally sifted through a sieve. In this way, a fine powder was obtained, the particle size of which is less than 100 µm. The samples were stored in dry and clean bottles, until the moment of use in adsorption experiments.

The mass of the 5mg/L egg shell was used in a 100 ml solution volume containing initial concentrations of copper (5mg/L); the experiment was performed in an electric shaker, at a rotation rate of 200 rpm (200 rpm), at 40°C and at pH = 6. The samples were analyzed after the predetermined time (10 – 120 minutes), And the concentration of copper ions in the solution after the selected time was determined by (AAS), Atomic Absorption Spectroscopy. The results were expressed over the size of the quilt, which represents the amount of adhesive substance in it. Each measurement has been repeated three times.

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3. RESULTS AND DISCUSSION

3.1 Adsorption process kinetics study (Pseudo-Second Model)

This model was developed on the assumption that the absorption process and the ion exchange, modification are unfolding simultaneously on the surface of biomaterial's, and the process itself is limited by the speed at which the polluter reaches active places to surface. This model involves multiple active sites (Coleman, NT, 1956).

The amount of adhesive metal ions is calculated at a time based on **Eqn. 1**:

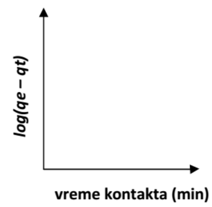
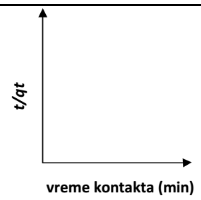
$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad \text{(Eqn. 1)}$$

Eqn. 2 is the pseudo-first and **Eqn. 3** pseudo-second kinetic model, was given in **Table 1.** It found that absorption systems where heavy metal ions are absorbed by ions on cinemas can be described by listing kinetic models (Saeed, A, 2005).

$$\log(qe - qt) = \log(qe) - (k_1/2.303).t \quad \text{(Eqn. 2)}$$

$$t/qt = 1 / k_2\, qe^2 + (1 / qe)\, t \quad \text{(Eqn. 3)}$$

Table 1. kinetics models (Pseudo-first line and Pseudo -second line) (Saeed, A, 2005)

Kinetic model	linear shape (Eqn)	Graph view
Pseudo-first line	$log(qe - qt) = log(qe) - (k_1/2.303).t$	
Pseudo-second line	$t/qt = 1 / k_2\, qe^2 + (1 / qe)\, t$	

Where *qt* (mg/g) and *qe* (mg/g) are the quantities of adorning metal ions in time, or in balance state. K_1 is the constant speed of reaction in the first row and is determined based on the linear curve obtained as a ratio (*qe* - *qt*) of the time to *t*. The literature data suggest that this model depends on the value of the correlation coefficient (R^2) and can only be applied during a certain period of time at the start of the absorption process (in the first 20 to 30 minutes), before a more balanced time (Ho, YS, 1998). The K_2 displayed is a second-row reaction constant; K_2 and qe values are determined from the snip and the slope of the curve obtained when *T* is expressed in *t*/quit function. The literature data suggest that this model describes the adsorption system well when the correlation coefficient R^2 > 0.900 is high and when a good match is being made between the values of ***Qe*** obtained from this model and the values obtained from the experimental results qe^{exp} **(**Gupta, VK 2007, Azouaou, N, 2010**)**.

3.2 Experimental and calculated values q_e^{exp} and q_e^{cal}

Table 2. compares the experimental values obtained for the amount of adsorbed copper ions on the eggshell biosorbent qe^{exp} and the calculated values qe^{cal} based on the application of the pseudo-first and pseudo-second order models.

pseudo-first model was not satisfactory for the explanation of the experimental data, and cannot be considered appropriate for the description of the examined adsorption processes, because the values of eqel derived from this model differ significantly from the experimental ones. the calculated values of the qe^{cal} for pseudo-second order model are very close to the values obtained in the experiments, which indicates that this model is more applicable and better describes the adsorption processes examined in this study. The obtained results are in accordance with previously published scientific studies, which describe the use of egg shell as a biosorbent in the process of removing copper ions (Rao, HJ, 2010).

3.3 Values of adsorption rate constants K_1 and K_2

The values of the adsorption rate constants K_1 and K_2 in **Table 2.** determined for the pseudo-first and pseudo-second order models, indicate the rate of interaction of adsorbates and active sites present on the surface of biosorbents. Constant values were obtained for each temperature at which adsorption was performed. It has been observed that with increasing temperature, the values of the given constants decrease, which is in accordance with the literature (Coleman, NT, 1956, Gupta, VK 2007, Azouaou, N, 2010). In addition, the constants of the pseudo-first order model - K_1, decrease significantly with temperature, in relation to the constants of the pseudo-second order - K_2.

3.4 Correlation coefficient values (R^2)

The applicability of a particular model to describe the tested adsorption system is determined on the basis of the value of the correlation coefficient (R^2), obtained on the basis of the linear equations of the model. **Table 2.** shows the calculated parameters of the kinetic models, together with the correlation coefficients obtained for each adsorption experiment of adsorption of copper ions on the egg shell biosorbent. By comparing the values of the correlation coefficients (R^2), it is noticed that these values for the pseudo-first order model are significantly lower compared to the correlation coefficients obtained for the pseudo-second order model. Such results are expected, based on similarities with adsorption systems that have been examined and described in the literature (Gupta, VK 2007, Azouaou, N, 2010).

Table 2. Comparison between speed constants and kinetics absorption of Cu on synchronized egg shells as an adsorbent (first and second line models).

Heavy metal	Temperature		q_e(exp)	Model Pseudo-first line			Model Pseudo- second line		
	°C	K		*(K_1) (1/min)*	*qe(cal) (mg/g)*	R^2	K_2*(g/mg) min*$^{-1/2}$	*qe(cal) (mg/g)*	R^2
Cu	20	293	18.035	-0.015	11.831	0.868	0.033	18.480	0.970
	30	303	60.331	-0.027	52.540	0.828	0.010	62.673	0.919
	50	323	63.731	-0.026	42.930	0.793	0.012	65.167	0.986

Figures 1a-b-c. and **Fig 2a-b-c.** show the equations of model Pseudo-first line and pseudo-second order in linear form, for the adsorption processes of removal of copper ions on the egg shell as a biosorbent, under the described experimental conditions.

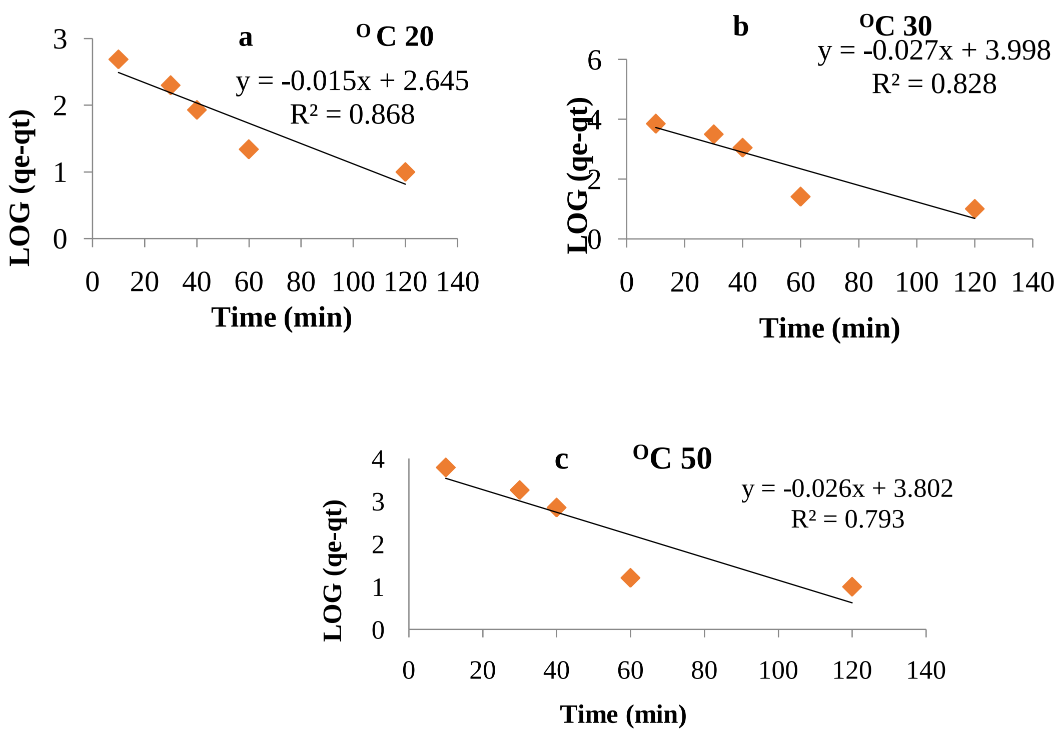


Fig 1. a-b-c. Model Pseudo-first line is shown by the curves a, b, and c for the absorption of copper ions, at temperature = 20, 30, 50 °C.

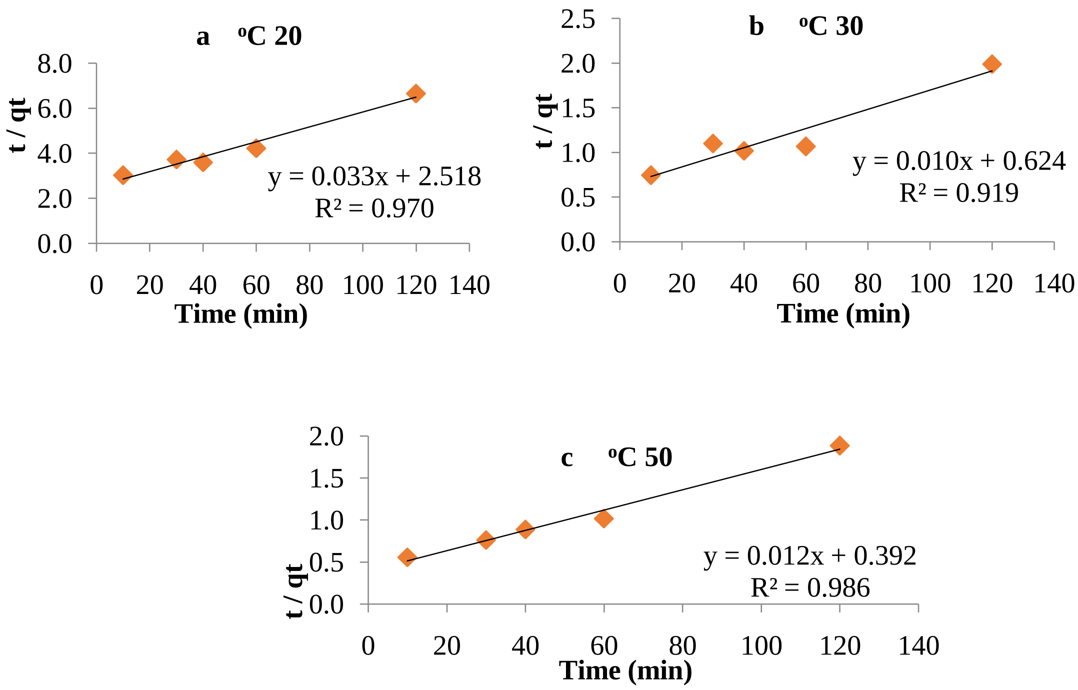


Fig 2. a-b-c. Model Pseudo- second line is shown by the curves a, b, and c for the absorption of copper ions, at temperature = 20, 30, 50 °C.

4. CONCLUSION

Based on the inverse equations of the applied models, the pseudo-second row model was found to better describe the examined adsorption system, and based on the presented results, it is possible to describe the kinetics of the examined adsorption processes under the applied experimental conditions, ie to estimate the rate at which the removal of copper ions from aqueous solutions takes place, when using egg shell as a biosorbent. The kinetic data suggest that there is good interaction between the copper and the surface of the biosphere, and that it is a factor that determines the speed of the adsorption process of the metal ion diffusion on the border layer of the solution by adsorbent.

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