Bulgarian Chemical Communications, Volume 50, Issue 2, (pp. 274 – 280) 2018

Study on copper ions adsorption from aqueous solution by Emeraldine

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Received December 7, 2017; Revised February 5, 2018

The influence of *in situ* synthesized emeraldine (salt and base) on the removal of copper ions from aqueous media is discussed. Physicochemical parameters such as initial copper ion concentration, emeraldine dosage and contact time between adsorbent and Cu(II) ions in aqueous solution were studied. An assessment of the equilibrium and the kinetics of sorption of copper ions was made. The experimental results were fitted to the isotherms of Langmuir, Freundlich, Toth and Baudu. It was established that the Toth and Baudu isotherms are suitable for the case of emeraldine salt. The Langmuir model gave satisfactory correlation with the experimental results only in the low concentration range of copper ion sorption using emeraldine base. The maximum sorption capacity of emeraldine base at 50 mg.dm^{-3} initial copper ions concentration (q_e^{max} 7.5 mg.g^{-1}) was higher than that of the emeraldine salt. Probably, the mechanism of copper ions sorption includes physisorption, chemisorptions, as well as intraparticle diffusion during the later stages of the process.

Keywords: *In situ* polymerization, Emeraldine, Copper ions removal, Aqueous medium.

INTRODUCTION

The wastewaters generated from printed board manufacturing, metal finishing and plating, semiconductor manufacturing, textile dyes production, and others, as well as the landfill leachates, contain toxic heavy metals such as arsenic, lead, mercury, cadmium, chromium, copper, nickel, and zinc. Many heavy metals are essential trace elements for humans, animals and plants in small amounts, but in larger amounts cause acute and chronic toxicity. Despite the treatment processes used, some quantities of the heavy metals remain in the treated industrial wastewater [1]. The widely used processes for industrial wastewater treatment are chemical precipitation, ion exchange, adsorption, membrane filtration, photocatalysis, flotation and electrochemical processes [2]. Among them adsorption and complexation are the most convenient and simple methods. It is well known that the adsorption efficiency depends on the type and properties of the sorbent. Different polymeric compounds such as polyaniline, polypyrrole, chitosan, etc., are used [3-6]. The aniline polymerization leads to production of polyaniline in three idealized oxidation states – leucoemeraldine, emeraldine and (per)nigraniline [7, 8]. Emeraldine exists as emeraldine salt and emeraldine base. The deprotonated emeraldine base has more free electron pairs in its structure in comparison with the protonated emeraldine salt, which contributes to the better complexation ability of this polyaniline form [9, 10].

The aim of this study was to synthesize both emeraldine salt and base, and to study their application for copper ions removal from aqueous media.

EXPERIMENTAL

The experiments were carried out with pure for analysis aniline ($C_6H_5NH_2$), hydrochloric acid (HCl), ammonium persulfate ($(NH_4)_2S_2O_8$), sodium hydroxide (NaOH), $CuSO_4.5H_2O$, sodium acetate ($C_2H_3NaO_2$) and acetic acid (CH_3COOH). Distilled water was used throughout.

Emeraldine salt synthesis

Emeraldine was synthesized through oxidative polymerization using aniline monomer ($C_6H_5NH_2$) and ammonium persulfate ($(NH_4)_2S_2O_8$) as an oxidant. Distilled aniline was diluted with 1 M HCl to 2 l in a volumetric flask. Ammonium persulfate was diluted with distilled water to 800 ml and both solutions were cooled in a refrigerator at 5 ºC. After that the oxidant solution was added dropwise to the 0.5 M aniline solution. The mixture was stirred at room temperature for 1 h and then was left to polymerize. The greenish-black suspension of emeraldine salt was filtered and the precipitate was washed several times with distilled water. After dewatering it was dried in an oven at 40 ºC to constant mass. The dried polymer was ground to a fine homogeneous powder.

Emeraldine base synthesis

Protonated emeraldine salt was converted to emeraldine base through washing with 1 M NaOH to pH 10.0 – 11.0. The polymer was dried at 40 ºC to

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constant mass and after that was ground to a fine homogeneous powder.

Preparation of standard solutions of copper ions

Initial stock solution with concentration of 1 g.dm^{-3} of Cu^{2+} was prepared using $CuSO_4.5H_2O$, diluted with freshly distilled water to 1 l. Then standard solutions with concentrations of 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, 30.0, and 50.0 mg.dm^{-3} were prepared.

Equilibrium study

The adsorption equilibrium for the removal of copper ions was studied using 50 cm^3 of aqueous solutions containing Cu^{2+} from 1 to 50 mg.dm^{-3} contacting with 0.1 g of the two forms of emeraldine (salt and base). Shaking was carried out until equilibrium was achieved.

The amount of adsorption at equilibrium [11] in mg.g^{-1} was computed as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (1)$$

where C_o and C_e are the initial and equilibrium copper ion concentrations (mg.dm^{-3}), respectively, V is the volume of solution (dm^3) and m (g) is the mass of the polymer.

Kinetic study

The adsorption kinetics was studied using 50 cm^3 of aqueous solutions containing 50 mg.dm^{-3} Cu^{2+} contacting with 0.1, 0.5, 1.0 and 1.5 g of two forms of emeraldine (salt and base). The samples were taken for analysis at 1, 3, 5, 7, 10, 15, 30, 60 and 360 min, respectively.

The efficiency of Cu^{2+} removal by polyaniline was calculated according to the formula:

$$RE, \% = 100 - \left(\frac{C_t}{C_o}\right) 100 \qquad (2)$$

where C_o is the initial Cu^{2+} concentration and C_t is the concentration at time t in mg.dm^{-3}.

Instrument and measurements

Inductively coupled plasma – optical emission spectroscope ("Prodigy" High dispersion ICP-OES, Telledyne Leeman Labs) was used for determination of the copper ions concentration. In order to avoid Cu^{2+} precipitation, the pH of the aqueous solutions was adjusted to 5 with acetate buffer [12].

Modelling

In this study the obtained results were fitted into the isotherms of Langmuir, Freundlich, Toth and Baudu, and the kinetic experimental data were analysed by comparative estimation of the applicability of the pseudo-first order (PFO), pseudo-second order (PSO), the mixed pseudo-first/pseudo-second order (MFSO) kinetics models, as well as by the intraparticle diffusion (ID) model [13-18] by non-linear regression analyses.

RESULTS AND DISCUSSION

Equilibrium study

Figures 1 and 2 present the experimental equilibrium data of the copper ions sorption on emeraldine salt and base, respectively, and the applied four isotherm models: Langmuir, Freundlich, Toth and Baudu. The calculated isotherm model parameters for both investigated systems, as well as the values of the error functions are presented in Table 1.

The shape of the experimental isotherm of Cu^{2+} sorption on emeraldine salt outlines two sections: an initial gradual increase of the ions concentration in the solid phase followed by a tendency for equilibrium establishment in the low concentration range (C_0 5-15 mg.dm^{-3}), and a subsequent sharp, almost linear sorption capacity increase in the middle and high concentration range C_0 15-36 mg.dm^{-3}).

The error analyses proved commensurable applicability of the four equilibrium models due to the approximately equal values of R^2, SSE, MSE and RMSE.

Baudu has remarked that the calculation of the Langmuir coefficients, b and q_{mL}, by the measurement of tangents at different equilibrium concentrations shows that they are not constants in a broad concentration range. He has transformed the Langmuir equation to the following expression:

$$q_e = \frac{q_{m0} b_0 C_e^{(1+x+y)}}{1 + b_0 C_e^{(1+x)}} \text{ with } (1+x+y) \text{ and } (1+x) < 1 \qquad (3)$$

where q_e is the adsorbed amount at equilibrium (mg.g^{-1}), C_e is the equilibrium concentration of the adsorbate (mg.dm^{-3}), q_m is the Baudu maximum adsorption capacity (mg.g^{-1}), b_0 is the equilibrium constant, and x and y are the Baudu parameters. For lower surface coverage, this equation reduces to the Freundlich model, i.e.:

$$q_e = \frac{q_{m0} b_0 C_e^{(1+x+y)}}{1 + b_0} \qquad (4)$$

The predicted monolayer sorption capacity of the emeraldine salt by the Baudu model was $q_m = 2.117$ mg.g^{-1} (Table 1), while by the Langmuir equation the determined value of the parameter was $q_m = 81.924$ mg.g^{-1}. Considering the fact that the experimentally obtained maximum equilibrium capacity of the sorbent was q_e 6.6 mg.g^{-1}, the Langmuir q_m value is unacceptable. The latter observation questions the accuracy of the two-parameter model, although, according to the plots in Figure 1 and the very close

Table 1. Values of the equilibrium model parameters and error functions.

System	Copper ions-Emeraldine salt				Copper ions-Emeraldine base			
Equilibrium model	Model parameters		Error function		Model parameters		Error function	
Langmuir	q_m	8.251	R^2	0.976	q_m	81.924	R^2	0.987
	b	0.179	SSE	1.555	b	0.003	SSE	1.699
			MSE	0.222			MSE	0.340
			RMSE	0.471			RMSE	0.583
Freundlich	K_f	0.267	R^2	0.986	-		-	
	n_f	0.903	SSE	1.729				
			MSE	0.346				
			RMSE	0.588				
Toth	q_{mT}	249.289	R^2	0.995	$q_{m}t$	390.063	R^2	0.987
	K_T	1.082	SSE	0.232	K_t	85.706	SSE	1.724
	m_T	0.596	MSE	0.039	mt	0.596	MSE	0.431
			RMSE	0.197			RMSE	0.657
Baudu	q_m	4.952	R^2	0.995	q_m	2.117	R^2	0.986
	b_o	0.50	SSE	0.235	b_o	0.135	SSE	1.732
	x	-0.638	MSE	0.047	x	-0.770	MSE	0.577
	y	0.240	RMSE	0.217	y	0.728	RMSE	0.760

values of the calculated by non-linear regression analyses error functions R^2, SSE, MSE and RMSE, the four model isotherms almost overlapped and equally fitted to the experimental equilibrium data of copper sorption on the emeraldine salt.

Besides, the adsorption capacity predicted by the four mathematical models - approximately 6.9 $mg.g^{-1}$, was approximately equal to the experimentally obtained value.

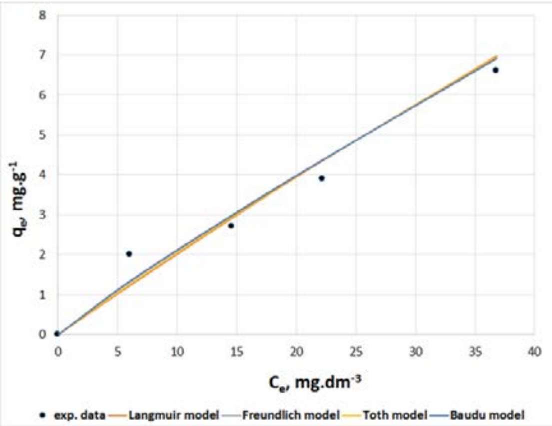

Fig. 1. Experimental and model isotherms of the copper ions sorption on emeraldine salt.

From a statistical point of view, due to the higher number of isotherm parameters in Toth and Baudu empirical models, it could be accepted that they simulate the model variations more accurately. In the absence of a theoretical model that could account for the chemical heterogeneity of the surface, and simultaneous prevalence of different sorption mechanisms, isotherm models having a greater number of model constants are able to better predict the system behavior.

Toth has modified the Langmuir equation to reduce the error between experimental data and predicted values of equilibrium adsorption data. The application of his equation is best suited to multilayer adsorption similar to BET isotherms which is a special type of Langmuir isotherm and has very restrictive validity. The Toth correlation is given as:

$$q_e = \frac{q_{m_T} C_e}{(1/K_T + C_e^{m_T})^{1/m_T}} \qquad (5)$$

where q_e is the adsorbed amount at equilibrium ($mg.g^{-1}$), C_e is the equilibrium concentration of the adsorbate ($mg.dm^{-3}$), q_{mT} is the Toth maximum adsorption capacity ($mg.g^{-1}$), K_T is the Toth equilibrium constant, and m_T is the Toth model exponent. Besides, the model is useful in describing heterogeneous adsorption systems, which satisfy both low- and high-end boundaries of the concentration.

The experimental isotherm for the system copper ions/emeraldine base (Figure 2) is characterized with well-balanced tendency towards equilibrium establishment. The Langmuir adsorption isotherm is based on the assumption that maximum adsorption occurs when a saturated monolayer of adsorbate molecules is present on the adsorbent surface, the energy of adsorption is constant, and there is no migration or interaction between the adsorbate molecules in the surface plane. However, according to the shapes of the experimental and model isotherms presented in Figure 2, obviously, the Langmuir model gave satisfactory correlation with the experimental results only in the low concentration range. A tendency similar to the one observed for the system copper ions/emeraldine salt with regard to the values of the monolayer capacity predicted by the Langmuir and Baudu models was outlined. The comparative analyses of the experimentally determined maximum equilibrium capacity (q_e^{exp} = 7.5 mg.g^{-1}) and the q_m values of 8.251 mg.g^{-1} (Langmuir model) and 4.952 mg.g^{-1} (Baudu model) (Table 1) proved the predominant accuracy of the four-parameter model. The isotherms in Figure 2 display unsatisfactory correlation between the experimental equilibrium data and the Freundlich model in the high concentration region due to the observed significant deviation between the modes of both isotherms. The latter conclusion was proved by the power value of the regression coefficient and the higher values of the SSE, MSE and RMSE functions (Table 1) as compared to these of the Toth and Baudu models.

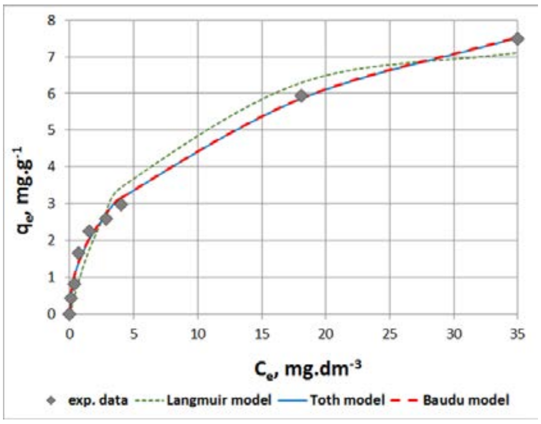

Fig. 2. Experimental and model isotherms of the copper ions sorption on emeraldine base.

Thus, according to the modes of the four model isotherms and the values of the error functions calculated by non-linear regression analyses (Table 1), it could be concluded that the sorption behavior of the copper ions on emeraldine base at equilibrium conditions was best represented by the three- and four-parameter models of Toth and Baudu, respectively, as they are characterized with the highest correlation coefficients (R^2 0.995) and the lowest SSE, MSE and RMSE values.

Kinetic study

The kinetics behaviour of copper ions during their adsorption on emeraldine salt and base was described by four kinetics models: the pseudo-first, pseudo-second, mixed pseudo-first/pseudo-second order models, and the intraparticle diffusion model (Table 2).

The experimental kinetic curve of the copper ions sorption on emeraldine salt, plotted as C_t = f (t) (Figure 3), revealed the highest sorption rate in the initial stages of the process. The system reached equilibrium within the first 10 min after the beginning of the process. The highest adsorption capacity attained was q_t = 7.1 mg.g^{-1} and the highest removal efficiency of the copper ions was 29.6 %. The experimental data were modelled by the pseudo-first order, pseudo-second order, the mixed pseudo-first/pseudo-second order kinetics models, as well as by the intraparticle diffusion model. The values of the calculated kinetic parameters and error functions are presented in Table 2.

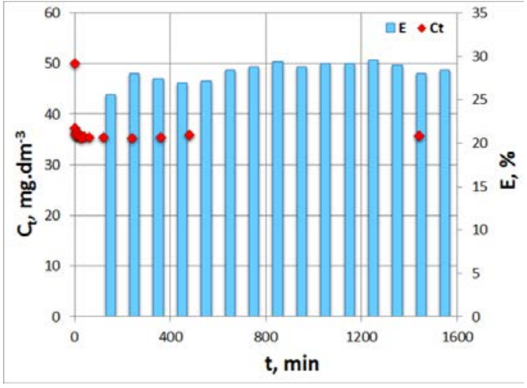

Fig. 3. Experimental kinetic curve and efficiency of the copper ions sorption on emeraldine salt.

The analyses of the experimental data, model parameters and error functions proved that the mixed order model satisfactorily correlated the kinetic experimental data of the copper ions sorption on emeraldine salt (Table 2, Figure 4).

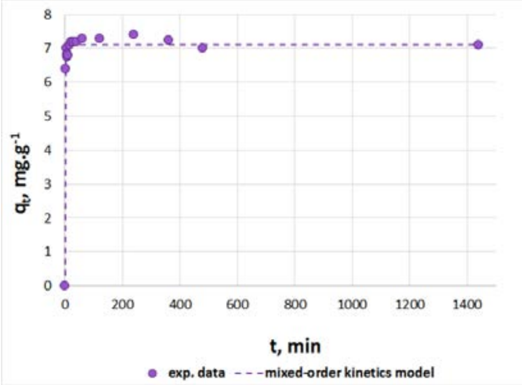

Fig. 4. Mixed order kinetics model for the system copper ions-emeraldine salt; a) initial kinetics curve section.

Table 2. Values of the kinetic model parameters and error functions for the systems copper ions-emeraldine base and copper ions-emeraldine salt.

		PFO model					PSO model					Intraparticle diffusion model				Mixed order model				
		Non-linear form $\frac{dq_t}{dt} = k_1(q_e - q_t)$ (6) Linear expression $\log(q_e - q_t) = log q_e - \frac{k_1}{2.303} t$ (7)					Non-linear form $\frac{dq_t}{dt} = k_2(q_e - q_t)^2$ (8) $\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t$ (9) Linear expression $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$ (10)					Non-linear form $q_t = k_i t^{0.5} + I$ (11)				Non-linear form $q = q_e \left(\frac{1-\exp(-k_1 t)}{1-f_2 \exp(-k_1 t)}\right)$ (12) Linear expression $ln\left(\frac{1-F}{1-f_2 F} = -k_1 t\right)$ (13) $F = \frac{q_t}{q_e}$ (14) $f_2 = \frac{k_2 q_e}{k_1 + k_2 q_e}$ (15)				
Polymer	Mass, g	Model parameter		Error function			Model parameter		Error function			Model parameter		Error function		Model parameter		Error function		
		k_1	q_{e1}	R_1^2	MSE	RMSE	k_2	q_{e2}	R_2^2	MSE	RMSE	k_{i1}	k_{i2}	R_{i1}^2	R_{i2}^2	k_1	f	R^2	MSE	RMSE
Polyaniline salt	0.1	0.01	0.871	0.458	2.198	1.512	0.0240	7.0323	0.9113	0.064	0.325	0.1972	0.0182	0.6223	0.8905	1.471	0.991	**0.990**	0.048	0.219
Polyaniline base	0.1	4.483×10^{-4}	0.595	0.488	0.098	0.312	1.416×10^{-2}	0.591	0.504	84.929	9.216	0.0232	0.0109	0.7726	0.6507	0.2904	0.3712	**0.998**	0.016	0.128
	0.5	1.552×10^{-3}	0.593	0.594	0.763	0.873	8.915×10^{-2}	1.913	0.961	104.751	10.235	0.0521	0.0004	**0.9914**	0.9716	0.1920	0.2297	0.918	0.094	0.307
	1.0	1.309×10^{-3}	0.942	**0.991**	0.007	0.083	4.822×10^{-2}	0.218	0.911	62.788	7.924	0.0469	0.0095	0.9466	0.9640	0.039	1.2×10^{4}	0.923	0.053	0.230
	1.5	1.315×10^{-3}	0.555	0.912	0.077	0.278	0.234	0.0407	0.759	7.492×10^{2}	86.557	0.0388	0.0018	**0.9832**	0.9122	0.081	422.39	0.959	0.015	0.122

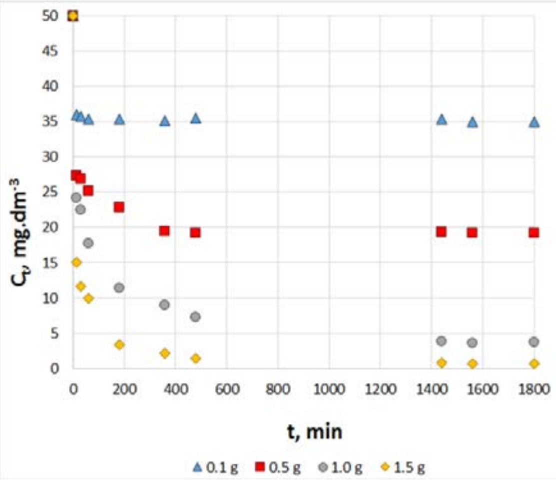

Fig. 5. Experimental kinetic curves of copper ions sorption on emeraldine base – effect of adsorbent mass.

The experimental kinetic curves of the copper ions sorption on polyaniline base, plotted as $C_t = f(t)$ (Figure 5), displayed that the sorption rate in the initial stages of the process was the highest.

The removal efficiency at the fifteenth min was 28, 45.4, 51.6 and 70 %, using 0.1, 0.5, 1.0 and 1.5 g of emeraldine base, respectively. The system reached equilibrium approximately 400 min after the beginning of the process. The highest adsorption capacity attained was $q_t = 7.5$ mg.g^{-1} with 0.1 g emeraldine base. An increase in removal efficiency with increasing adsorbent mass was observed. The increase in the sorbent mass contributes to the increase in surface area and number of active sites. The optimal removal efficiency of 97.14 %, using 1.5 g of emeraldine base was achieved after approximately 400 min. Simultaneously, with emeraldine mass increasing, its adsorption capacity decreased. The lowest adsorption capacity attained was $q_t = 1.6$ mg.g^{-1} with 1.5 g emeraldine base after 1800 min. After that, no significant removal was observed, probably due to the saturation of the active sites. The experimental data were modelled by the pseudo-first order, pseudo-second order, the mixed pseudo-first/pseudo-second order kinetics models, as well as by the intraparticle diffusion (ID) model. The values of the calculated kinetic parameters and error functions are presented in Table 2. According to the experimental results and model data, the kinetics behavior of the studied system with 0.1 g of emeraldine base was best described by the mixed order model (Table 2, Figure 6). The experimental series with 0.5 g and 1.5 g emeraldine base were best represented by the intraparticle diffusion model. The highest values of the correlation coefficient (R_1^2 0.991) and the lowest values of the error functions SSE, MSE and RMSE characterized the pseudo-first order model applied to the system copper ions-emeraldine base (1.0 g) (Table 2, Figure 7).

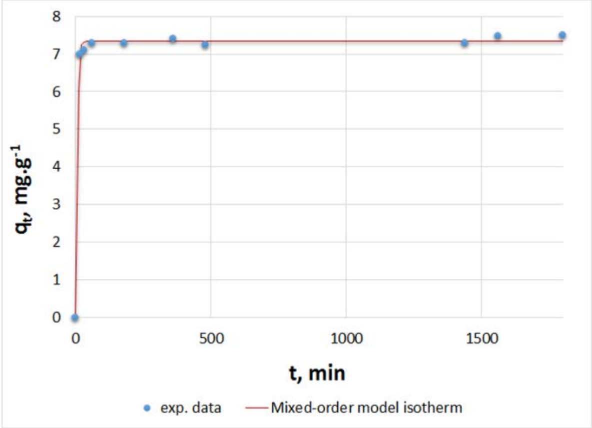

Fig. 6. Mixed order kinetic model for the system copper ions-emeraldine base (0.1 g emeraldine base); a) initial kinetics curve section.

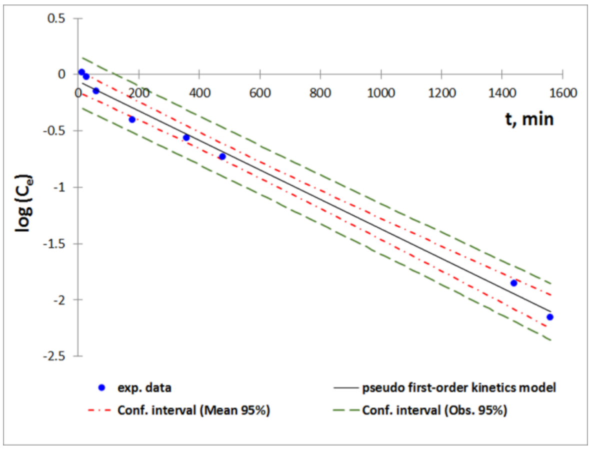

Fig. 7. Linear regression of the pseudo first-order kinetics model for the system copper ions-emeraldine base (1.0 g emeraldine base).

CONCLUSIONS

The comparative analyses of the equilibrium experimental data for the sorption behavior of the copper ions on emeraldine salt and base outlined that the base displayed higher affinity, as the attained maximum sorption capacity at 50 mg.dm^{-3} initial copper ions concentration (q_e^{max} 7.5 mg.g^{-1}) was approximately 1.14 times higher than that for the salt compound.

Based on the above stated observations for the sorption behaviour of both investigated systems, an explicit conclusion whether chemisorption or intraparticle diffusion was the general rate controlling mechanism during the copper ions sorption on emeraldine base and salt could not be withdrawn due to the close values of the statistical errors. Probably, the mechanism of sorption included physisorption, chemisorption and intraparticle diffusion during the later stages of the process.

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ИЗСЛЕДВАНЕ НА АДСОРБЦИЯТА НА МЕДНИ ЙОНИ ОТ ВОДЕН РАЗТВОР С ИЗПОЛЗВАНЕ НА ЕМЕРАЛДИН

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Постъпила на 7 декември, 2017 г.; коригирана на 5 февруари, 2018 г.

(Резюме)

Обсъдено е влиянието на *in situ* синтезиран емералдин (сол и база) върху отстраняването на медни йони от водни разтвори. Определени са физикохимични параметри като начална концентрация на медни йони, количество емералдин и време на контакт между адсорбента и Cu(II) йони във воден разтвор. Оценени са равновесието и кинетиката на сорбция на медните йони. Експерименталните резултати са приложени към изотермите на Langmuir, Freundlich, Toth и Baudu. Установено е, че изотермите на Toth и Baudu са подходящи за описване на сорбцията с емералдинова сол. Моделът на Langmuir дава задоволителна корелация с експерименталните резултати само при ниски концентрации на медни йони с използване на емералдинова база. Максималният сорбционен капацитет на емералдиновата база при начална концентрация на медните йони 50 mg.dm^{-3} (q_e^{max} 7.5 mg.g^{-1}) е по-висок от този на емералдиновата сол. Най-вероятно, сорбционният механизъм на медните йони включва физисорбция, хемисорбция и дифузия в частиците при последните етапи на процеса.