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EQUILIBRIUM AND KINETIC ANALYSIS OF SORPTION OF COPPER ONTO DIATOMACEOUS EARTH

Abstract

In developing new materials for the sorption of mercury from hydrocarbon mixtures, based on copper-modified diatomaceous earth, sorption of copper from aqueous solutions of Cu^{2+} ions on natural (Dz) as well as on conditioned diatomaceous earth was investigated. Dz was conditioned in two ways, by rinsing (Dz-I) and by hydration (Dz-H-48). Equilibrium and kinetic sorption analysis was performed by a simple batch procedure at 25, 40 and 60 °C; concentration of Cu in solution was measured by atomic absorption spectroscopy. It was found that Dz-I was capable of binding significantly more copper (79.10 mg g⁻¹) than Dz (44.8 mg g⁻¹); increasing temperature diminished the mass of bound copper. Equilibrium sorption of water on Dz, Dz-I and Dz-H-48 was successfully described by the Freundlich model. Sorption kinetics was well approximated by the Lagergren 1st order pseudokinetic model.

1. Introduction

Diatomaceous earth has a distinct capability of binding trace elements and therefore influences the cycling of many ecotoxic metals and regulating their concentration in the entire ecosystem [1–4]. It is used for various purposes, e.g. as filtration medium, abrasive, filler, catalyst carrier, sorbent or sorbent carrier [5–7]. Diatomaceous earth is the material of biological origin, formed by sedimentation of skeletons of diatom algae and therefore consists of a major mineral part and some organic matter. Its efficiency in removing ecotoxic metal cannot be explained by a single mechanism because there is a number of various physico-chemical and biosorption processes occurring at the phase boundary and various surface complexes are being formed. One of the basic processes is the exchange of metal ions from the surroundings with the surface H^+ ions of silanol groups (SiOH) [8]. The other process, active in sorption of copper, is the coordinative binding of Cu^{2+} ions with amino and/or carboxy groups of polysaccharides that are the integral part of diatom algae cell walls [9]. Polysaccharides, proteins and lipids found in natural diatomaceous earth contain Group I and II cations, like Na^+ , K^+ , Ca^{2+} and Mg^{2+} , which can be successfully exchanged with metal ions from the environment (e.g. Cu^{2+} , Cd^{2+} , Zn^{2+} , Hg^{2+} and others).

A wider framework of these investigations is the development of new materials for sorption of mercury from hydrocarbon raw materials or process streams of petroleum industry. With this in mind, preliminary investigations were performed where diatomaceous earth was modified with different metal cations (Na^+ , K^+ , Ca^{2+} , Zn^{2+} and Cu^{2+}). The potential of mercury sorption was tested using obtained materials and best results were obtained with copper-modified sorbents. Therefore, in this work the part of investigations that deals with the thermodynamic and kinetic characterization of sorption of copper onto natural diatomaceous earth (Dz) and its preconditioned variants is described. Such a sorption significantly increases the potential of Dz for subsequent binding of mercury in the above mentioned applications.

2. Equilibrium and kinetic sorption models

In order to understand the nature and kinetics of binding ecotoxic metals on sorbent surface, it is important to perform equilibrium and kinetic analysis to determine the governing process parameters. The distribution of solute between liquid and solid phase is commonly described by equilibrium sorption models. Mass of a bound component depends on its concentration in solution in contact with sorbent as well as on nature of other components, their concentration, nature of the solvent, temperature, etc. Several empirical and theoretical expressions of equilibrium sorption models have been proposed [10, 11], however none is universally applicable. It is common to test several different equilibrium models to describe metal sorption on soils [12–14], (Table 1); the most frequently used models are that of Langmuir and Freundlich. The models relate the mass of sorbed component per unit mass of sorbent (q_e , commonly in mg/g) with the mass concentration of solution (γ_e , commonly in mg/L) in the equilibrium state.

Table 1: Common equilibrium models for the description of sorption of ecotoxic metals on soils

MODEL	EXPRESSION
Langmuir	$q_e = \frac{q_m K_L \gamma_e}{1 + K_L \gamma_e}$
Freundlich	$q_e = K_F \gamma_e^{n_F}$
Langmuir-Freundlich	$q_e = \frac{q_m K_L \gamma_e^{1/n}}{1 + K_L \gamma_e^{1/n}}$
Redlich-Peterson	$q_e = \frac{A \gamma_e}{1 + B}$

Sorption of ecotoxic metals onto sorbent surface is a process that consists of several stages. The first one is the transfer of components to be sorbed (ecotoxic

metals) to the outer surface of sorbent by interphase diffusion. The second one is the diffusion of sorbate within the inner porous structure of sorbent. This process is usually much slower and occurs within the mesopores, micropores and capillaries; only a small fraction of sorbate is bound to the outer surface of sorbent. The third stage is the very binding of components to be sorbed with the outer or inner surface of sorbent by physical or chemical bonds. The rate of sorption of ecotoxic metals on soils is often described [15] by several simple models (Table 2).

Table 2: Common kinetic models for the description of sorption of ecotoxic metals on soils

MODEL	DIFFERENTIAL FORM	INTEGRAL FORM
Pseudokinetic model of the 1 st order (Lagergren)	$\frac{dq_t}{dt} = k_1 (q_e - q_t)$	$q_t = q_e (1 - e^{-k_1 t})$
Pseudokinetic model of the 2 nd order (Hoo)	$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2$	$q_t = q_e \left(\frac{q_e k_2 t}{1 + q_e k_2 t} \right)$
Intraparticle diffusion mode (Weber-Morris)	$\frac{dq_t}{dt} = \frac{k_{int}}{2} t^{-1/2}$	$q_t = k_{int} t^{1/2}$

3. Experimental part

3.1. Materials

Diatomaceous earth (Dz) Celatom[®] is obtained from Eaglepicher Filtration & Minerals, USA; its declared oxide content is: SiO₂ 89.70 %; Al₂O₃ 5.60 %; Fe₂O₃ 2.20 %; CaO 0.90 %; MgO 0.10 % and other oxides 1.90 %; its pour density is 175 g L⁻¹; its equivalent particle diameter is 14 μm and its water content is less than 5 mass %. Saturated CuSO₄ solution was prepared by weighing 150,00 g of the salt, CuSO₄ × 5 H₂O, *p.a.*, Kemika, Zagreb, and adding 100 mL of deionized water at a temperature of 80 °C, followed by cooling to the ambient temperature. Dilute CuSO₄ solutions were prepared by diluting the prepared saturated solution with deionized water.

3.2. Preconditioning of natural diatomaceous earth

Preconditioning of Dz before the sorption of copper was done in two ways: by rinsing with water (Dz-I) and by immersion hydration of natural diatomaceous earth for 48 h (Dz-H-48). Rinsed diatomaceous earth (Dz-I) was prepared by repeated rinsing of 10 g of Dz with a total of 250 mL of distilled water, followed by drying at a temperature of 100 °C. Hydration of natural diatomaceous earth was done by immersing 10 g of Dz in 250 mL of distilled water for the declared time interval, followed by decanting the excess water and drying at a temperature of 100 °C.

3.3. Sorption experiments

Equilibrium analysis of binding of copper onto original and preconditioned Dz was done by a batch procedure, using sorbent mass concentration of 1 g L^{-1} and different concentrations of CuSO_4 in water solutions within the span of $50 - 400 \text{ mg L}^{-1}$. Different contact times were applied: 5, 10, 15, 20, 25, 30, 40, 50, 60, 120, 180 and 240 min, as well as different temperatures: 25, 40 and $60 \text{ }^\circ\text{C}$. After separating supernatant solution from the sorbent by filtration with the filter paper (Black Ribbon, 5891), the concentration of remaining copper in solutions was determined.

Kinetic analysis of binding copper onto rinsed diatomaceous earth (Dz-I) was performed with a similar batch procedure as well. The total mass of sorbent of 1 g was poured into 1 L of CuSO_4 solution, stirred with magnetic stirrer at 240 rpm . After declared times, 5 mL aliquots were withdrawn, filtered (Black Ribbon, 5891) and concentration of remaining copper in solution was determined.

Copper concentrations in solutions were determined with the atomic absorption spectroscopy method, using a Perkin Elmer 3110 instrument, UK. The mass of copper bound onto sorbent, both in equilibrium and kinetic experiments, was calculated by:

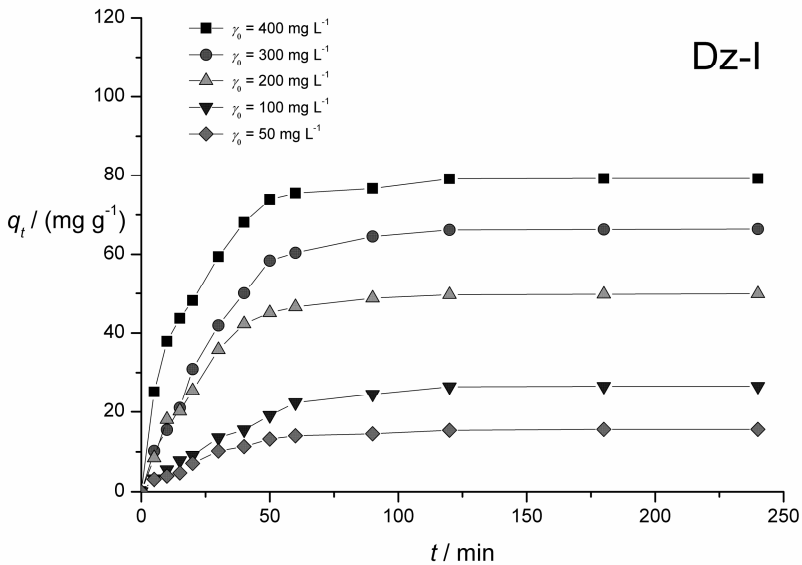
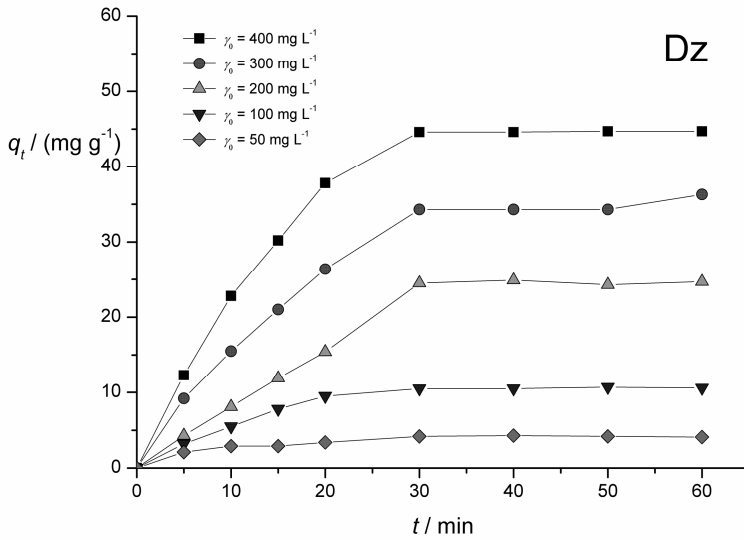
$$q_t = \frac{(\gamma_0 - \gamma_t)V}{m}$$

where q_t stands for the mass of sorbed component per unit mass of sorbent [mg/g], γ_0 is the initial mass concentration of copper [mg/L], γ_t is the mass concentration of copper in supernatant solution [mg/L], V is the volume of solution that is treated [L], and m denotes the mass of sorbent. The equilibrium mass of bound copper q_e is the constant value of q_t observed at the end of each kinetic experiment.

4. Results and discussion

4.1. Equilibrium analysis – type of sorbent

The time needed for establishing the equilibrium binding of copper onto sorbent in the investigated system was determined from Figure 1, where mass of bound copper onto sorbents Dz, Dz-I and Dz-H-48 was plotted as a function of contact time and initial solution concentration at $25 \text{ }^\circ\text{C}$. The mass of bound copper increased with increasing the initial solution concentration in all the experiments. The time required for establishing the thermodynamic equilibrium was found different for differently preconditioned diatomaceous earth samples; it was 30 min for Dz and Dz-H-48 sorbents, and 120 min for Dz-I sorbents. The time required for establishing the equilibrium did not depend on the initial concentration of Cu^{2+} ions in solution.



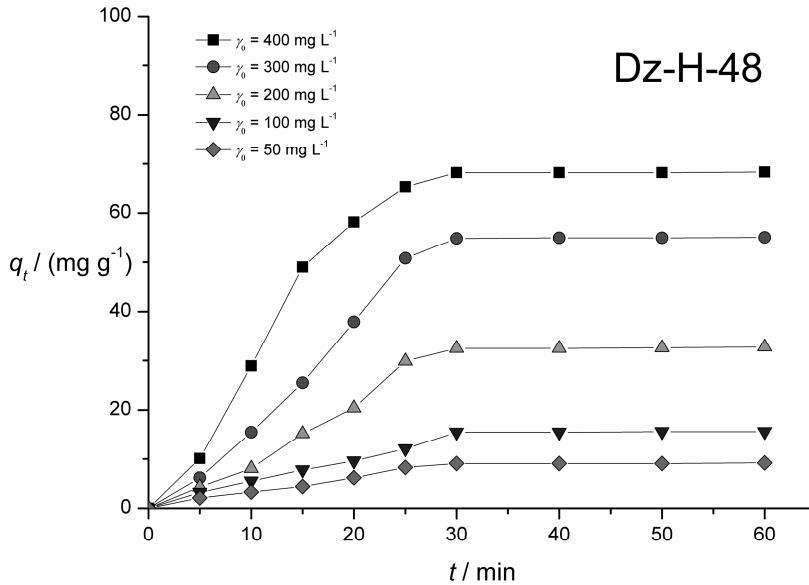


Figure 1: Mass of copper sorbed onto Dz, Dz-H-48 and Dz-I, q_t , as dependent on contact time, t , and initial solution concentration, γ_0 , at 25 °C. Lines are added for the sake of clarity

Unconditioned diatomaceous earth Dz showed the least potential for binding copper of 44,5 mg g⁻¹ for the maximal initial concentration of Cu of 400 mg L⁻¹; for the same initial concentration 68,5 mg g⁻¹ of copper was bound at Dz-H-48 and the largest mass of 79,1 mg g⁻¹ was found to bind onto Dz-I. Proportionally less copper was bound for all other initial concentrations, without any significant deviations between the individual experiments.

Figure 2 shows the equilibrium mass of bound copper as a function of the concentration of remaining copper in solution (sorption isotherm) at 25 °C for all the investigated sorbents. The plateau of maximum sorbed mass (maximum sorbent capacity) was not found within the investigated concentration range (50 – 400 mg L⁻¹). Therefore, it did not make sense to test experimental data against Langmuir model as well as other models that include maximum sorbent capacity as a parameter. So, data were described with Freundlich isotherm only, shown in Figure 2 as well.

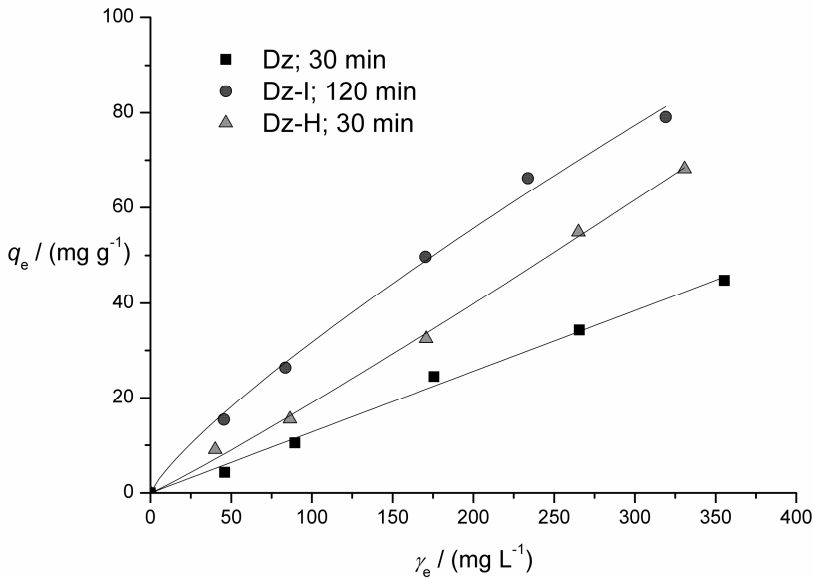


Figure 2: Equilibrium mass of copper sorbed onto Dz, Dz-I and Dz-H, q_e , as dependent on equilibrium concentration of copper in solution, γ_e , at 25 °C. Lines are Freundlich sorption isotherms

Table 3: Parameters of the Freundlich equilibrium model, K_F and n_F , for the sorption of copper, and corresponding regression coefficients, R^2 , at 25 °C

SORBENT	K_F	n_F	R^2
Dz	0.128±2.027	1.000±0.065	0.9949
Dz-I	0.761±0.179	1.234±0.067	0.9963
Dz-H	0.135±0.032	0.932±0.038	0.9982

Table 3 shows the corresponding parameter values and correlation coefficients. According to the results shown, including the correlation coefficient values, the description of experiment with Freundlich isotherm is satisfactory. The largest value of Freundlich parameter K_F for Dz-I indicates its largest potential for sorption binding of copper. The investigated concentration range is too narrow to allow for drawing any significant conclusions from the curvature parameter n . According to literature [16, 17], Freundlich isotherm is found very often in systems where sorption is achieved by physical forces and where it is not limited to a monomolecular layer on sorbent surface, but there is a possibility for further binding of molecules onto a previously formed layer.

4.2. Equilibrium analysis – effect of temperature

According to shown results, diatomaceous earth preconditioned by rinsing, Dz-I, can bind the largest amounts of copper, though in the longest sorption times. It is presumed that the large amount of bound Cu is a more important property than the slow rate of copper binding, from the standpoint of potential application of Cu-modified diatomaceous earth for sorption of mercury from the hydrocarbon raw materials or refinery process streams. Therefore Dz-I sorbent was selected for testing the influence of temperature on sorption of Cu.

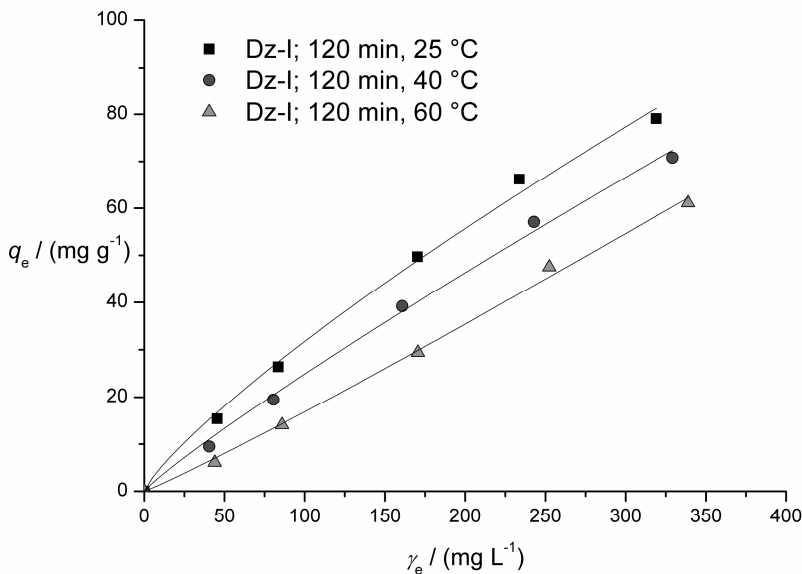


Figure 3: Equilibrium mass of copper sorbed onto Dz-I, q_e , as dependent on equilibrium concentration of copper in solution, γ_e , and temperature. Lines are Freundlich sorption isotherms

By examining the mass of bound copper onto Dz-I sorbent vs. equilibrium concentration of copper solution at various temperatures (Figure 3), a good agreement with Freundlich equilibrium model was observed at all temperatures. It was found that binding of copper is promoted by lowering the temperature, as well. The parameters of Freundlich isotherms are shown in Table 4.

Table 4: Parameters of the Freundlich equilibrium model, K_F and n_F , for the sorption of copper onto Dz-I, and corresponding regression coefficients, R^2 , at various temperatures T

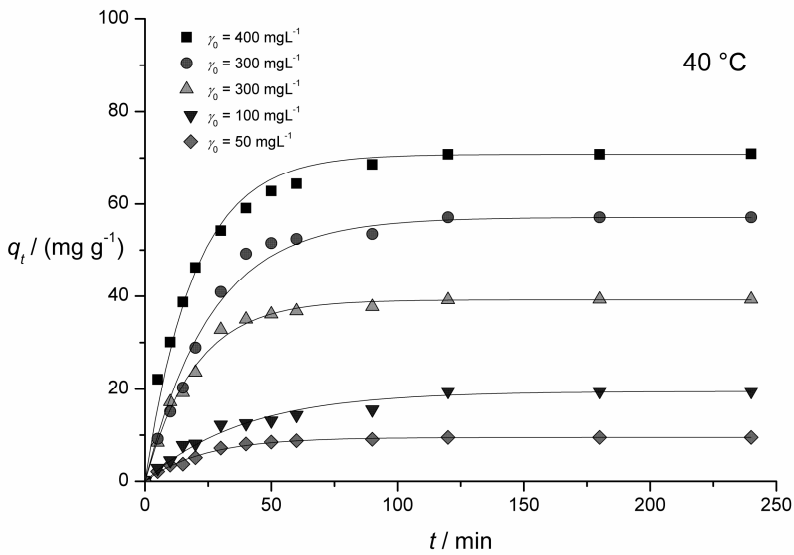
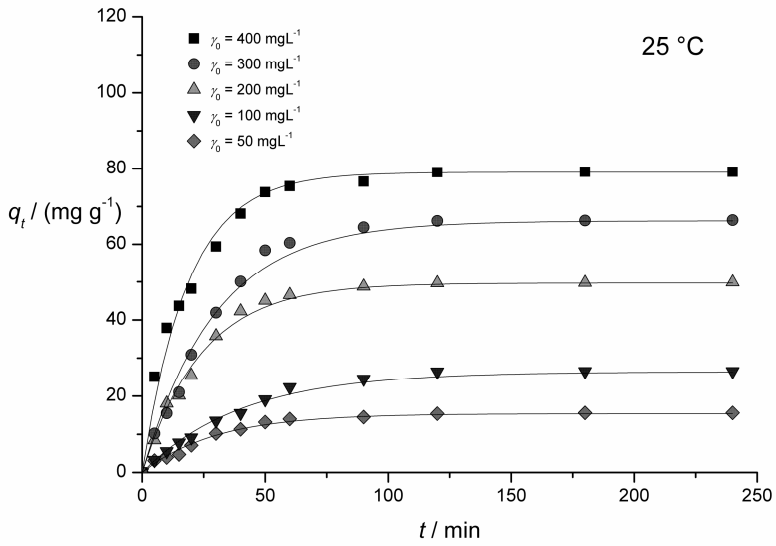
$T / ^\circ\text{C}$	K_F	n_F	R^2
25	0.761±0.179	1.234±0.067	0.9963
40	0.400±0.092	1.115±0.053	0.9971
60	0.123±0.031	0.936±0.040	0.9977

4.3. Kinetic analysis

Experimental determination of the amount of sorbed matter vs. time is the basis for kinetic sorption analysis. The kinetics of Cu sorption onto diatomaceous earth preconditioned by rinsing, Dz-I, was determined at various initial concentrations of Cu solutions and at temperatures of 25, 40 and 60 °C. The results in Figure 4 showed that the mass of bound copper increased with time and reached its maximum value after 120 min; the equilibration time did not depend on other experimental conditions. Maximal mass of bound copper increased with the initial solution concentration in batch experiments. The temperature increase produced the lowering of initial sorption rate as well as diminishing the achieved maximum mass of bound copper. This all was in accordance with the previously described observations for equilibrium experiments.

Table 5: Parameters of the Lagergren pseudokinetic model, q_e and k_1 , for the sorption of copper onto Dz-I, and corresponding regression coefficients, R^2 , at various temperatures, T , and various initial concentrations of copper solutions, γ_0

Parameters of Lagergren pseudokinetic model	$T / ^\circ\text{C}$	$\gamma_0 / (\text{mg L}^{-1})$				
		400	300	200	100	50
$q_e / (\text{mg g}^{-1})$	25	79.1	66.2	49.7	26.4	15.4
	40	70.8	57.1	39.2	19.5	9.5
	60	61.1	47.5	29.4	14.1	6.1
k_1 / min^{-1}	25	0.0533±0.0028	0.0336±0.0016	0.0412±0.0015	0.0250±0.0001	0.0334±0.0015
	40	0.0514±0.0022	0.0383±0.0019	0.0510±0.0024	0.0259±0.0013	0.0424±0.0017
	60	0.0589±0.0024	0.0388±0.0008	0.0708±0.0049	0.0352±0.0022	0.0612±0.0056
R^2	25	0.9836	0.9881	0.9925	0.9901	0.9874
	40	0.9885	0.9885	0.9930	0.9744	0.9910
	60	0.9904	0.9972	0.9723	0.9741	0.9428



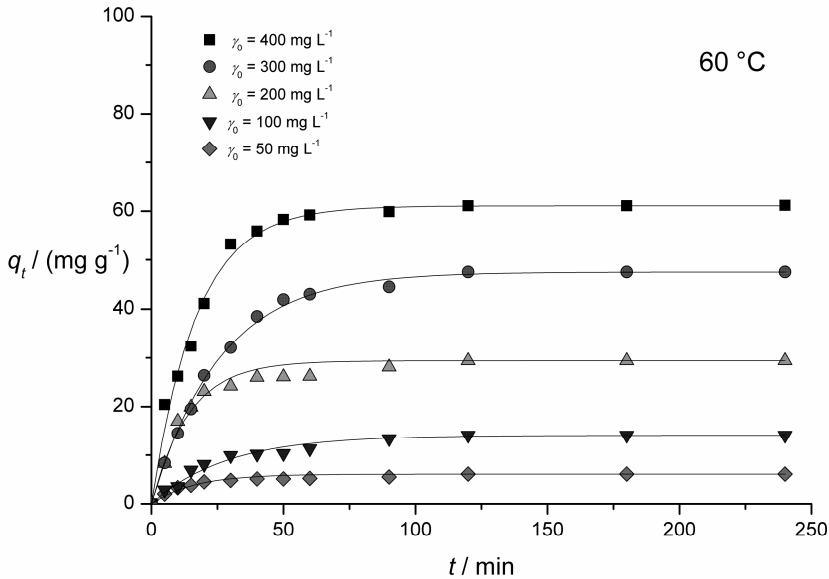


Figure 4: Mass of copper sorbed onto Dz-I, q_t , as dependent on contact time, t , initial solution concentration, γ_0 , and temperature. Lines are Lagergren pseudokinetic model

Three kinetic models from Table 2 were tested for describing sorption of copper. Figure 5 shows the typical comparison of the three models (at 25 °C and initial solution concentration of 400 mg L⁻¹). The results showed that the 1st order pseudokinetic sorption model of Lagergren was capable to describe satisfactorily the experimental data. The 2nd order pseudokinetic sorption model of Hoo predicted too large equilibrium times with respect to experiment, and the intraparticle diffusion model of Weber and Morris completely failed. The results were very much the same for other initial concentrations of copper in solution as well as for all the temperatures. Therefore we show only the results obtained by Lagergren model, in the form of curves included in Figure 4 as well as model parameters and correlation coefficients in Table 5. The results of the pseudokinetic sorption model of Lagergren confirmed its applicability for the description of sorption of copper onto diatomaceous earth preconditioned by rinsing, Dz-I, at all investigated temperatures and solution concentrations. The kinetic coefficient k_1 showed neither definite temperature dependence nor clear dependence on the initial solution concentration, which might be attributed to the uncertainty of measurements.

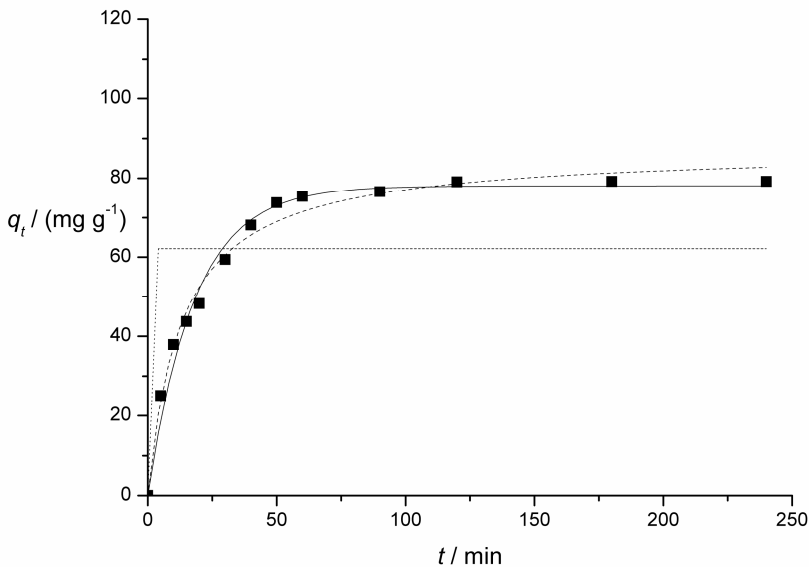


Figure 5: Mass of copper sorbed onto Dz-I, q_t , as dependent on contact time, t , at 25 °C and initial concentration of copper solution, $\gamma_0 = 400 \text{ mg L}^{-1}$. Symbols are experimental data; solid, dashed and dotted lines are Lagergren, Hoo and Weber-Morris model, respectively

5. Conclusion

The sorption of copper onto natural diatomaceous earth and its preconditioned modifications was investigated within the course of preparing copper-modified sorbent for removing mercury from hydrocarbon raw materials and process streams of petroleum industry. Based on the investigations performed, one can conclude that the primary factor that affects the sorption of copper onto diatomaceous earth is its hydrophilicity/hydrophobicity which can be somewhat influenced by preconditioning procedures such as immersion hydration or rinsing with water. Thus, water-rinsed diatomaceous earth (Dz-I) is capable of binding much larger amount of copper (79.10 mg g^{-1}) than the original unconditioned sample Dz (44.8 mg g^{-1}). Sorption is influenced by the temperature as well – the mass of copper sorbed is decreased with the temperature increase for all the investigated sorbents. Equilibrium sorption binding of copper onto Dz and its modifications (Dz-I and Dz-H-48) was described successfully with Freundlich sorption isotherms at all temperatures. For the description of sorption kinetics, the 1st order pseudokinetic model of Lagergren was found most suitable among three tested models.

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