Short communication

Kinetic behaviour of Duolite ES 468 in the cosorption of non-ionic surfactant and copper(II)

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Abstract

Kinetic behaviour of the hydrogen form of Duolite ES 468 polyacrylic acid-functionalised cation exchanger with respect to the sorption of non-ionic surfactant alkylmonoethers (ALM-10) and copper(II) has been investigated; kinetic curves have been obtained, using spectrophotometric determination for ALM-10 and complexometric one for copper(II). Kinetic coefficient (B), intraparticle diffusion coefficient (D; $m^2 s^{-1}$) and overall rate constant (k_o; s^{-1}) for non-ionic surfactant and copper(II) depend on the solution composition, pH and the maximum sorption at the equilibrium. On increasing the solution acidity from pH 5 to pH 3 a decrease in both D and the equilibrium sorption for copper(II) although an increase in D for ALM-10 is observed. The action of copper(II) results in an increase in both D for ALM-10 and the maximum sorption at the equilibrium, whereas the action of ALM-10 leads to a decrease in the corresponding parameters for copper(II). Hydrogen form of Duolite ES 468 polyacrylic acid-functionalised cation exchanger is suitable for the simultaneous removal of non-ionic surfactant and copper(II) from waste water.

1. Introduction

Non-ionic surfactants including alkylmonoethers (ALM-10) are widely used in various fields of industry, such as plating processes, because of their wetting, degreasing, emulsifying, lubricating, dispersing, stabilising and other surface active properties. Copper plating processes generate a large volume of rinse water, containing not only cancerous copper(II), but also toxic non-ionic surfactants. The permitted concentration of these contaminants in

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waste water effluents is $0.1 \, \text{mg dm}^{-3}$ for copper(II) and $2 \, \text{mg dm}^{-3}$ for non-ionic surfactant [1].

The purification and recycling of waste water by ion exchange is one of the ways to minimise the toxic discharges and to prevent the environmental contamination. Weak acid cation exchangers are used for the sorption of copper(II) (transition metal) to almost detection limit [2]. Whereas the hydrogen form of polyacrylic acid-functionalised cation exchangers, including Duolite ES 468, can also remove non-ionic surfactant. The principal use of Duolite ES 468 is the removal of non-ionic surfactants from water [2]. Although the simultaneous sorption of copper(II) cations and the molecules of non-ionic surfactant in Duolite ES 468 may be of environmental interest with respect to the prevention of the pollution by toxic copper(II) and non-ionic surfactant, and also of industrial interest with respect to both the quality of the recycled copper plating rinse water and the quality of copper coatings. The data concerning kinetics of the sorption of non-ionic surfactant and copper(II) should be required prior to the integration of Duolite ES 468 into the system of waste water purification [3].

The purpose of this study was to determine the kinetic behaviour of the hydrogen form of polyacrylic acid-functionalised cation exchanger Duolite ES 468 with respect to the simultaneous sorption of non-ionic surfactant alkylmonoethers and copper(II) from aqueous solutions.

2. Experimental

Duolite ES 468 (Fluka Chemie AG, Switzerland) is an acrylic-based weak acid cation exchanger [4]. The concentration of carboxyl groups –COOH in the fraction from 0.2 to 0.5 mm, 7.1 meq. per gram of the cation exchanger (dry mass).

Non-ionic surfactant alkylmonoethers (Russia) represents the oxyethylated higher fatty alcohols [5]. The structure of ALM-10 corresponds to the formula $C_nH_{2n+1}O(C_2H_4O)_mH$, where n is from 12 to 14; $m \sim 10$; mean molecular mass ~643. The concentration of ALM-10 and $CuCl_2$ in the solutions used for the kinetic study was $6 \, \text{mmol dm}^{-3}$ in both the separate solutions and the mixtures.

Copper(II) was determined complexometrically with EDTA disodium salt, using murexide [6], ALM-10 spectrophotometrically, using chromazurol S [7]. KFK spectrophotometer (Russia) with 5 cm path-length cells was applied. The solution pH was measured using pH-121 model pH meter–millivoltmeter (Russia), supplied by glass and silver chloride electrodes and by an automatic thermo compensator. Stirring was carried out with magnetic stirrer R5 (Poland) at the intensity 400 rpm.

Kinetic curves were obtained by batch experiment [2,8]. The samples of the cation exchanger (0.5 g dry mass) were equilibrated with 100 ml solution at 20 °C during predetermined time. Repetitive measurements of kinetic curves yielded the reproducibility at mean relative deviation $\bar{d}/\bar{x} \leq 2$ and standard relative deviation $s/\bar{x} \leq 2.5$ (expressed in percentage), calculated in accordance with [6]. The concentration of copper(II) and ALM-10 in the separate solutions and the mixture, $6 \, \text{mmol dm}^{-3}$, is within the limits (up to $10 \, \text{mmol dm}^{-3}$) inherent to industrial waste water prior its recycling by ion exchangers [8,9].

At the solute concentration <3 mmol dm^{-3} the sorption is usually limited by the diffusion across the immobile film, surrounding the bead (film diffusion) whereas at the concentration >100 mmol dm^{-3} it is limited by the diffusion within a bead (intraparticle diffusion). At the concentration from 3 to 100 mmol dm^{-3}, including 6 mmol dm^{-3} of the solutions investigated, the sorption is controlled by the mixed diffusion (film diffusion and intraparticle one at the same time). The coefficient of the intraparticle diffusion (D, m^2 s^{-1}) were calculated using Eq. (1) [9]:

$$D = \frac{Br^2}{\pi^2 t} \tag{1}$$

where r is the radius of bead (m); t the duration of interaction (s); B the kinetic coefficient, calculated on the ground of the degree (F) of the cation exchanger saturation (dimensionless). $F = a/a_{max}$, here a is the comparative sorption at the equilibration during the predetermined time (mmol g^{-1}), a_{max} the maximum sorption at the equilibrium (mmol g^{-1}). B values for the predetermined time (t) of the interaction between the cation exchanger and solution were calculated as follows: the graph $F = f(Bt)$ was plotted for the F interval from 0.0035 to 0.98 using the table, where the correlation between Bt and F has been presented [9]. To prevent the effect of the film diffusion the kinetic experiment was carried out when stirring solution at 400 rpm [10].

The overall rate constant (k_o, s^{-1}), as a parameter indicating the effect of the film diffusion onto the sorption rate, was calculated after [9,11]:

$$\ln(1 - F) = -k_o t \tag{2}$$

where t is the duration of interaction (s).

3. Results and discussion

The attempts to fit the Duolite ES 468 kinetic data with Bt versus t test provided better results than the attempts to fit the film diffusion control Eq. (2). We tentatively conclude, therefore, that in our experimental conditions, intraparticle diffusion controls the sorption of both copper(II) and ALM-10 at least for 90% of the process.

On increasing the degree of the saturation of the cation exchanger (F) a decrease in D values for both copper(II) and ALM-10 was observed at the two pH investigated. At high F value ion exchange, accompanied by complex formation or other chemical reactions, can be described by the so-called "shell-progressive" ("shrinking core", or "moving boundary") model [2]. In the absence of copper(II) D value (Table 1) and the comparative sorption (a) of ALM-10 (Figs. 1 and 2) are higher at pH 3 when compared to the corresponding parameters at pH 5. This is because the sorption of non-ionic surfactant takes place on the ground of hydrogen bonding between –C$_2$H$_4$O– units contained in the surfactant and the protonated carboxyl groups in the cation exchanger, consequently the sorption of ALM-10 is favoured by an increase in the concentration of unionised carboxyl groups, following the displacement of equilibrium (3) to the left:

$$RCH_2COOH \leftrightarrow RCH_2COO^- + H^+ \tag{3}$$

Table 1
The dependence of the mean value of maximum sorption (a_{max}), the coefficient of intraparticle diffusion (D) and correlation coefficient (R^2) for copper(II) and ALM-10 on the solution composition and pH

Solution composition	pH	a_{max} (mmol g^{-1})	F[a]	D ($\times 10^{13}$; m^2 s^{-1})	R^2
Cu(II) + H$_2$O	3	0.25	0.2–0.5	36.41	0.9926
	5	0.50	0.2–0.5	41.35	0.9940
Cu(II) + (ALM-10) + H$_2$O	3	0.12	0.1–0.3	0.99	0.9988
	5	0.25	0.1–0.5	3.68	0.9857
(ALM-10) + H$_2$O	3	0.74	0.1–0.3	0.47	0.9948
	5	0.74	0.05–0.2	0.14	0.9945
(ALM-10) + Cu(II) + H$_2$O	3	1.07	0.1–0.4	1.39	0.9943
	5	1.39	0.1–0.4	2.11	0.9932

[a] The degree of the cation exchanger saturation.

whereas, in the presence of copper(II) D values, the maximum sorption (a_{max}) at the equilibrium (Table 1) and the comparative sorption for ALM-10 are higher compared to the corresponding values obtained without copper(II) at both pH investigated (Figs. 1 and 2). This is presumably because of the additional sorption of ALM-10, contained in the complex compounds. It is known that in aqueous solutions metal ions and non-ionic surfactant molecules can form complex compounds [12]. The sorption of these compounds, containing the surfactant molecules and the copper(II) cations, can proceed on the ground of the hydrogen bond between –C$_2$H$_4$O– units and the protonated carboxyl group on one hand and the ground of the complexation of metal cations with carboxyl groups on the other
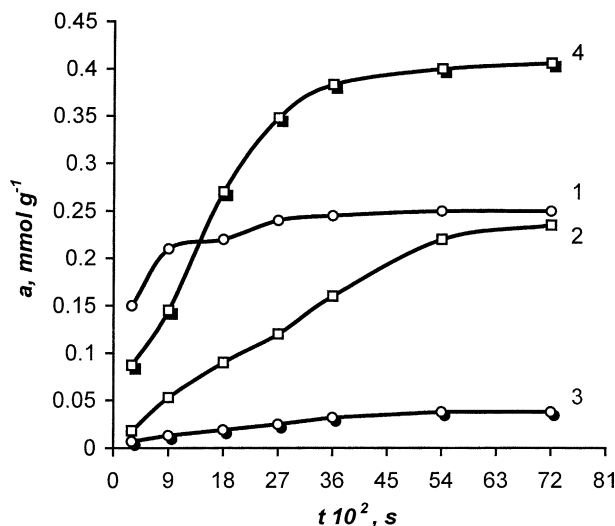

Fig. 1. Kinetic curves for the comparative sorption (a) at the solution pH 3: (1) copper(II) without ALM-10; (2) ALM-10 without copper(II); (3) copper(II) in the presence of ALM-10; (4) ALM-10 in the presence of copper(II).

Fig. 2. Kinetic curves for the comparative sorption (a) at the solution pH 5: (1) copper(II) without ALM-10; (2) ALM-10 without copper(II); (3) copper(II) in the presence of ALM-10; (4) ALM-10 in the presence of copper(II).
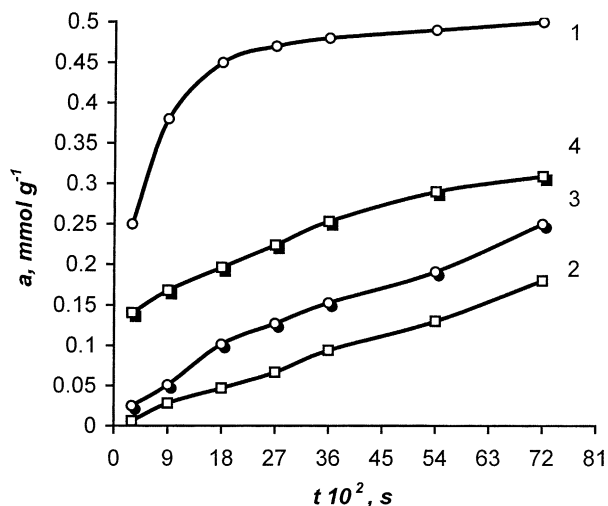
hand. Accordingly to D and k_o values the sorption of ALM-10 without copper(II) proceeds slower than the sorption of copper (Tables 1 and 2).

D and a_{max} values (Table 1), as well as the comparative sorption (a) (Figs. 1 and 2) for copper(II) are higher at pH 5 when compared to the corresponding parameters at pH 3. This is because at pH 5 equilibrium (3) is displaced to the right more significantly than that at pH 3. The displacement is followed by an increase in both the concentration of deprotonated carboxyl groups and swelling of the cation exchanger. Swelling favours the intraparticle diffusion of copper(II) (Table 1) resulting in an increase in the comparative sorption (Figs. 1 and 2, curves 1 and 3).

The simultaneous sorption of copper(II) and ALM-10 in Duolite ES 468 from the mixture leads to the diminution of copper(II) sorption. An abrupt decrease in D values for copper(II) in the presence of ALM-10 at pH 3 and pH 5, arises presumably from the action of the molecules of ALM-10, having a very complex steric structure.

Table 2

The overall rate constant (k_o) and the correlation coefficient (R^2) for the sorption of copper(II) and ALM-10 from the separate solutions and from their mixtures

Solution composition	pH 3		pH 5	
	k_o ($\times 10^2$; s^{-1})	R^2	k_o ($\times 10^2$; s^{-1})	R^2
Cu(II) + H$_2$O	6.07	0.9947	6.18	0.9772
Cu(II) + (ALM-10) + H$_2$O	0.67	0.9979	2.57	0.9954
(ALM-10) + H$_2$O	0.61	0.9779	0.20	0.9298
(ALM-10) + Cu(II) + H$_2$O	0.75	0.9972	0.83	0.9143

The mean D ($m^2\,s^{-1}$) values for the sorption of both ALM-10 and copper(II) by Duolite ES 468 are comparable with the corresponding values for the sorption of Me^{2+} and organic contaminants by the other polyacrylic acid-functionalised cation exchanger, used in the systems of the waste water purification [8].

k_o values for ALM-10 determined from the slopes of the linear relationship between $\ln(1-F)$ and t accordingly to [9] using Eq. (2), are 10 times less than the corresponding values for copper(II) (Table 2). The presence of ALM-10 in the solution results in a decrease in k_o value for copper(II), whereas the presence of copper(II) results in an increase in k_o for ALM-10. The sequence of k_o values with respect to the solution composition and pH is as follows: at pH 3: Cu(II) $\gg$ (ALM-10) in the presence of Cu(II) > Cu(II) in the presence of (ALM-10) > (ALM-10); at pH 5: Cu(II) $\gg$ Cu(II) in the presence of (ALM-10) > (ALM-10) in the presence of Cu(II) > (ALM-10). Consequently, pH 3 is more favourable for the sorption of ALM-10, whereas pH 5 is more favourable for the sorption of copper(II).

The experimental data shows a deviation from the linearity of relationship between $\ln(1-F)$ and t; the correlation coefficient (R^2) for k_o (Table 2) are lower (especially for ALM-10) when compared to those obtained for the intraparticle diffusion coefficient D (Table 1). Taking into account this and also a small error in the determination of the equilibrium concentration of copper(II) and ALM-10 in solution, which cannot affect the kinetic curves considerably, it may be supposed that on increasing the degree of the cation exchanger saturation the change of rate-controlling processes between the intraparticle diffusion and the film diffusion takes place.

4. Conclusions

Kinetic behaviour of Duolite ES 468 polyacrylic acid-functionalised cation exchanger with respect to the non-ionic surfactant alkylmonoethers and copper(II) can be described sure by the intraparticle diffusion model than by the film diffusion model. On decreasing the solution acidity from pH 3 to pH 5 an increase in the intraparticle diffusion coefficient (D) and in the equilibrium sorption of copper(II), although a decrease in D values for ALM-10 is observed. The action of copper(II) leads to an increase in both the rate of ALM-10 intraparticle diffusion and the maximum sorption at equilibrium. Whereas the action of ALM-10 leads to a decrease in the corresponding parameters for copper(II).

The overall rate constant (k_o), characterising the effect of the film diffusion onto the sorption rate depends on the solution composition and pH. At pH 3 the sequence of k_o is as follows: Cu(II) $\gg$ (ALM-10) in the presence of Cu(II) > Cu(II) in the presence of (ALM-10) > (ALM-10), although at pH 5: Cu(II) $\gg$ Cu(II) in the presence of (ALM-10) > (ALM-10) in the presence of Cu(II) > (ALM-10). pH 3 is more favourable for the sorption of ALM-10, whereas pH 5 is more favourable for the sorption of copper(II).

Hydrogen form of Duolite ES 468 cation exchanger can be applicable for the purification of waste water including copper plating rinse water, from copper(II) and non-ionic surfactant simultaneously; the sorber filled with Duolite ES 468 would not limit the productivity if integrated into the system of waste water purification system, containing other ion exchangers.

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