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KINETICS OF MERCURY ADSORPTION

This work is a continuation of the investigations on alkali sulfide regeneration of mercury exhausted ion-exchange resins and on the post-regeneration changes occurring after this treatment. The kinetic behaviours of specific and sulfide-regenerated nonspecific resins toward mercury were studied. It has been found that the kinetics of the sulfide-regenerated resins can be satisfactorily described by a progressive shell model.

DENOTATIONS

$$\varphi_s = \frac{R_s}{3} \left[\frac{kq}{D_{\text{eff}}} \right] - \text{thile modulus, dimensionless,}$$

$$\eta_0 = \frac{1}{\varphi_s} \left[\frac{1}{\tan h3\varphi_s} - \frac{1}{3\varphi_s} \right] - \text{internal effectiveness factor, dimensionless,}$$

$$\varphi_c = \frac{R_c}{3} \left[\frac{Kq}{D_{\text{eff}}} \right] - \text{thile modulus for interior core, dimensionless,}$$

$$\eta_c = \frac{1}{\varphi_c} \left[\frac{1}{\tan h\varphi3_c} - \frac{1}{3\varphi_c} \right] - \text{internal effectiveness factor for the interior core, dimensionless,}$$

C_0 - influent concentration, mg/cm³,

D_{eff} - effective diffusivity, cm²/min,

Q_i - absorbed metal, mg/g,

Q_{max} - maximum binding of the metal, mg/g,

Θ - Q_i/Q_{max} ,

K - adsorption rate constant, cm³/min·mg,

q - adsorbent particle density, g/cm³,

R - radial coordinate within particle (R_s for the entire particle; R_c for the core).

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1. INTRODUCTION

As was shown in our previous investigation [1], [2], the treatment of mercury-exhausted ion-exchange resins by alkali sulfide solutions is a suitable "soft condition" method for regeneration of the resins. The method is based on the formation of soluble mercury polysulfides resulting from the treatment of mercury-exhausted resin by stoichiometric quantities of sulfide.

That approach was found to be applicable only to typical macroporous resins, characterized by a low value of total pore volume and medium pore diameter [3]. This corresponds to the possibilities of diffusion of mercury sulfide and mercury polysulfides formed during regeneration.

It has also been proved that alkali sulfide regeneration of conventional (nonspecific toward mercury) ion-exchange resin yields a lower concentration of residual mercury in effluent and that a filtration cycle can be longer than that of nonsulfide treated resin [3]. This increased selectivity toward mercury of nonspecific resins after sulfide regeneration presents an alternative of the application of ion-specific resin in mercury wastewater treatment.

Following the mentioned line the present work is an attempt at comparing the kinetic behaviour of mercury specific resins and those regenerated by alkali sulfide but nonspecific toward mercury. Furthermore, another purpose was to find a suitable model describing the mercury sorption by sulfide regenerated conventional resin.

2. EXPERIMENTAL

During the experiment three types of resins were examined: (i) ion-specific thiol resin IMAC TMR, in H-form; (ii) conventional weak base anion exchanger WOFATIT AD-41 after alkali sulfide regeneration, in Cl-form; (iii) WOFATIT AD-41 nontreated by alkali sulfide, in Cl-form*. For comparison of the kinetic behaviours of the mentioned resins a laboratory reactor system illustrated in fig. 1. was used.

The resin samples used in the experiments were preswelled for 24 hours in distilled water. A suitable agitation of the system and resulting fluidization of the resin beads were ensured by magnetic stirrer. In this way at a definite stirring rate the external transfer as contributor of the kinetics could be eliminated and equalization of mercury concentration in the system provided. The resin beads were treated by model solutions containing 9-39 mg Hg(II)/dm³ and 5 g NaCl/dm³. The volume rate of the flowing solution (60 cm³/min) was kept constant by means of rotameter. Influent and effluent mercury concentrations were measured by modified colorimetric method [4].

* IMAC TMR and WOFATIT AD-41 are typical macroporous resins.

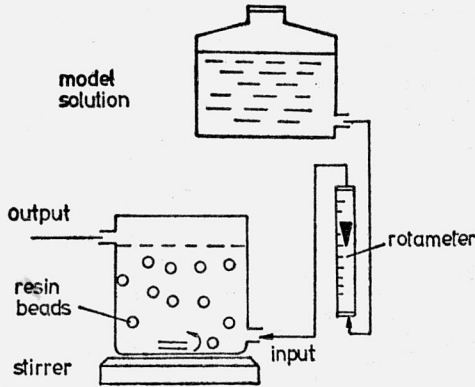


Fig. 1. Experimental reactor system

Rys. 1. Schemat aparatu reakcyjnego

3. DISCUSSION

The data obtained for the corresponding resin at different mercury influent concentrations are shown in figs. 2-4. The results show that the kinetic behaviour of IMAC TMR and sulfide regenerated WOFATIT AD-41 resins is significantly different than that observed for nontreated with alkali sulfide WOFA-

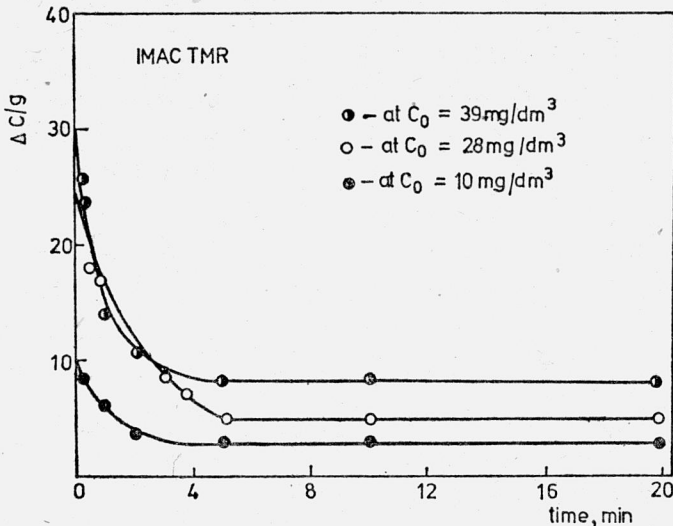


Fig. 2. Mercury decrease (C , mg Hg/dm³) per gram of air-dried resin versus time – for IMAC TMR ($C = C_0 - C_{\text{transitory}}$)

Rys. 2. Zmniejszenie zawartości rtęci (C , mg Hg/dm³) na 1 g powietrznie suchej żywicy w zależności od czasu dla IMAC TMR ($C = C_0 - C_{\text{nietrwały}}$)

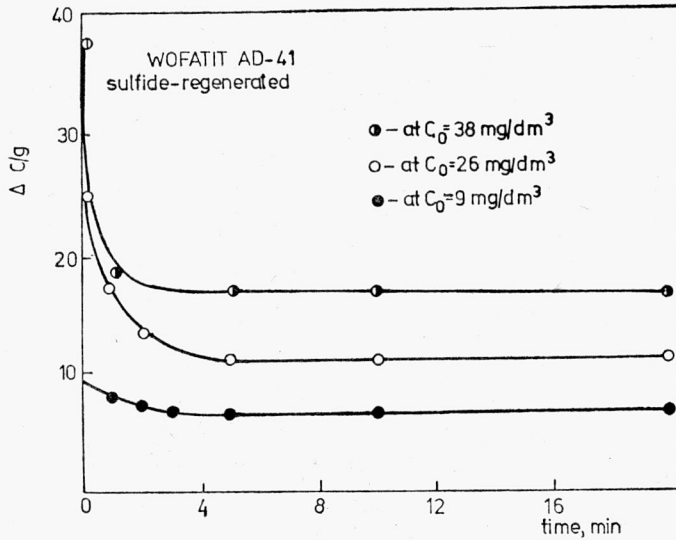


Fig. 3. Mercury decrease (C , mg Hg/dm³) per gram of air-dried resin versus time — for WOFATIT AD-41 regenerated by alkali sulfide

Rys. 3. Zmniejszenie zawartości rtęci (C , mg Hg/dm³) na 1 g powietrznie suchej żywicy w zależności od czasu dla zregenerowanego siarczkim alkalicznym WOFATIT-u AD-41

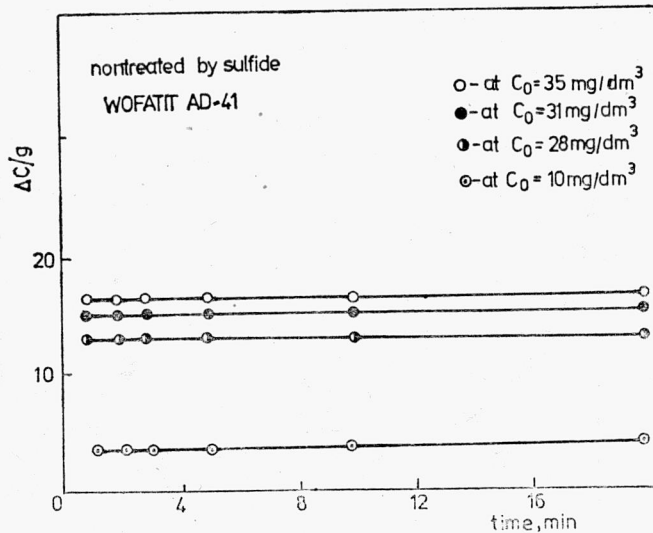


Fig. 4. Mercury decrease (C , mg Hg/dm³) per gram of air-dried resin versus time — for WOFATIT AD-41 nontreated by alkali sulfide

Rys. 4. Zmniejszenie zawartości rtęci (C , mg Hg/dm³) na 1 g powietrznie suchej żywicy w zależności od czasu dla niezregenerowanego siarczkim alkalicznym WOFATIT-u AD-41

TIT AD-41. As it can be seen for the first two mentioned resins (see figs. 2 and 3), the rate of mercury removal is during the initial 3–5 min high and it subsequently decreases.

Comparatively similar kinetic behaviours of IMAC TMR and alkali sulfide treated WOFATIT AD-41 differing from that of sulfide nontreated WOFATIT AD-41 (see fig. 4), clearly indicate that the modified (regenerated by alkali sulfide) resin possesses a specific characteristic with respect to mercury.

When examining the total quantities of IMAC TMR and alkali sulfide regenerated WOFATIT AD-41 (at influent concentration of 28 and 26 mg Hg/dm³, respectively) binding mercury per 1 g of sorbent for a definite time (fig. 5), it seems that the course of mercury binding follows a different pattern.

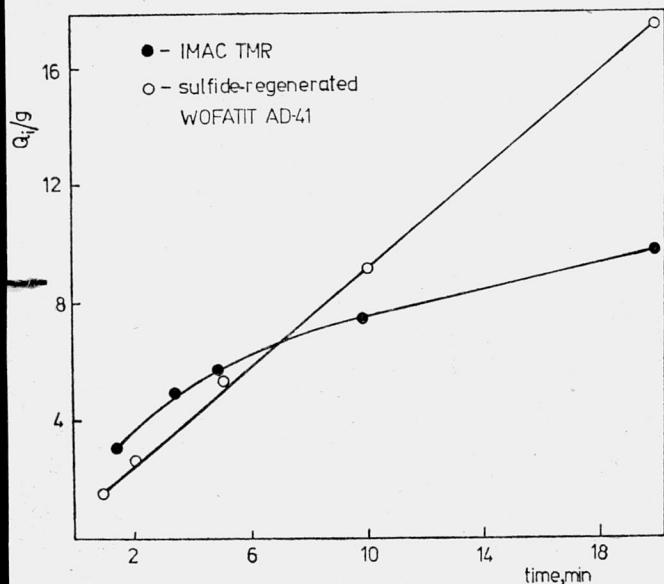


Fig. 5. Binding of mercury (Q_i) per gram of resin for a definite time

Rys. 5. Wiązanie rtęci (Q_i) na 1 g żywicy w określonym czasie

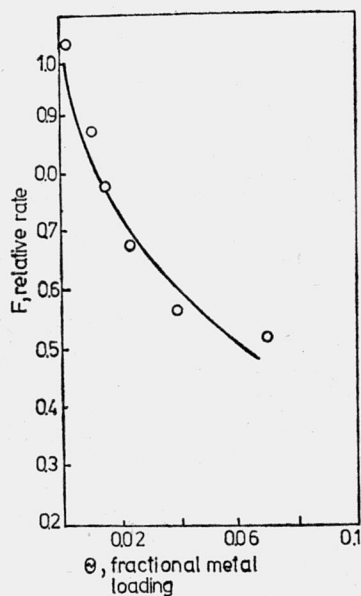


Fig. 6. Comparison of experimental results with the model predicted ones

Rys. 6. Porównanie danych doświadczalnych z modelowymi

From the concentration curves obtained experimentally it has been found that the sorption of mercury by WOFATIT AD-41 regenerated with sulfide corresponds to first order reaction, being between first and second order in the case of IMAC TMR. That phenomenon can be explained by the nature and localization of the residual mercury polysulfide species obtained by alkali sulfide regeneration. As it has been mentioned, mercury polysulfides can be well

transported only in typical macroporous media. Therefore for macroporous WOFATIT AD-41 it might be assumed that the residual post-regeneration polysulfide species which give rise to sorption capacity [3] are located on the surface or in near depth of the gel nature microreticular particles of the resin. Consequently, the sulfide-regenerated ion-exchanger is completely "open" to the mercury-active residual mercury polysulfides, because the available macropores do not create any diffusion resistances.

In contrast to sulfide-regenerated WOFATIT AD-41, the functional groups of IMAC TMR are situated in the resin macropores as well as in the microge (microreticular) particles. It makes diffusion more difficult affecting the order of reaction. This fact was confirmed by the values of effective diffusion coefficient $D_{\text{eff}} = 1.15 \times 10^{-4}$ and $D_{\text{eff}} = 6.48 \times 10^{-4}$ obtained at influent concentrations $C_0 = 28 \text{ mg Hg/dm}^3$ and $C_0 = 26 \text{ mg Hg/dm}^3$ for IMAC TMR and WOFATIT AD-41, respectively. It has been found that the kinetic behaviour of the sulfide regenerated resin can be satisfactorily explained by the model developed by SWAN et al. [5] based on the progressive shell theory involving irreversible equilibrium. The model is based on the hypothesis that the rate of metal diffusion r_D through the outer shell fully loaded with the metal is equal to the rate of reaction r_c in the interior core of that particle. The net reaction rate is defined as

$$r = r_D = r_c = \frac{\eta_c k C_s}{\left(\frac{1}{1-\Theta} \right) + 3\eta_c \varphi_s^2 \left[\frac{1-(1-\Theta)^{1/3}}{(1-\Theta)^{1/3}} \right]} \quad (1)$$

The practical rate, when the metal loading $\Theta = 0$, is

$$r_0 = \eta_0 k C_s \quad (2)$$

The effect of metal loading is expressed by factor F which is an r to r_0 ratio. This factor is equal to unity for metal-free adsorbent and decreases to zero as Θ approaches unity.

From the experimental concentration curves for mercury sorption by sulfide-regenerated WOFATIT AD-41, the rate constant k was calculated from

Table

Kinetic parameters of sulfide-regenerated
WOFATIT AD-41
Parametry kinetyczne dla WOFATIT-u AD-41
zregenerowanego siarczkiem

Diameter cm	Capacity mg Hg/dm ³	k cm ³ /min · g	D_{eff} cm ² /min
0.0715	204	0.81	6.48×10^{-4}

the digital simulation through the eq. (1). The value obtained for k (table, the kinetic parameters of the sulfide-regenerated WOFATIT AD-41) was then used to calculate η_0 and r_0 respectively. Thus the estimated values of assessed k permit also to define F as a function of Θ both for the experimental and mathematical simulated rates. The results obtained are presented in fig. 6.

Solid line represents F as a function of Θ predicted by the progressive shell model, in accordance with eq. (1). The points state for the results from the treatment of sulfide-regenerated WOFATIT Ad-41 at influent mercury concentration of 26 mg/dm³. As it can be seen from fig. 6, the predicted and experimental data are in a good agreement.

4. CONCLUSIONS

Based on the comparative kinetic investigations a high specificity of sulfide-regenerated resin (conventional type) toward mercury has been proved. The progressive shell model was found to be a suitable model to describe the kinetics of the sulfide-regenerated ion-exchange resins.

REFERENCES

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KINETYKA ADSORPCJI RTĘCI

Prezentowana praca stanowi kontynuację badań nad regeneracją siarczkiem alkalicznym wymienniczy jonowych w formie rtęciowej oraz zmian poregeneracyjnych zachodzących w tych wymienniczach. Zbadano zachowanie się specyficznych dla rtęci wymienniczy jonowych oraz wymienniczy konwencjonalnych, regenerowanych siarczkiem. Stwierdzono, że kinetyka regeneracji może być dobrze opisana modelem postępującej otoczki (ang.: *progressive shell model*).

DIE KINETIK DER QUECKSILBERADSORPTION

Berichtet wird eine fortgesetzte Studie zur Regeneration von Ionenaustauschern (die speziell für Quecksilber geeignet sind) mit alkalischem Sulfid. Betrachtet werden die Veränderungen, die nach dem Regenerationsverfahren auftreten. Die untersuchten Ionenaustauscher werden mit konventionellen, sulfid-regenerierten Austauschern verglichen. Die Kinetik der Regeneration kann mit dem Modell der progressiven Hülle beschrieben werden.

КИНЕТИКА АДСОРБЦИИ РТУТИ

Предлагаемая работа представляет собой продолжение исследований по регенерации щёлочным сульфидом ионообменников в ртутной форме, а также послерегенерационных изменений, происходящих в этих ионообменниках. Исследовано поведение специфических для ртути ионообменников, а также традиционных ионообменников, регенерированных сульфидом. Отмечено, что кинетика регенерации может быть хорошо описана с помощью модели прогрессивной оболочки (*progressive shell model*).