

# SORPTION AND SEPARATION OF METALS FROM AQUEOUS SOLUTION BY A MACROMOLECULAR RESIN CONTAINING TRI-*n*-OCTYLAMINE

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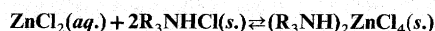
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**Key Words:** Sorption, Separation, Zinc, Copper, Tri-*n*-octylamine, Distribution Equilibrium, TOA Impregnated Sorbent

Experiments were conducted on the equilibrium distribution of divalent zinc between hydrochloric acid medium and macromolecular resin containing tri-*n*-octylamine (TOA) as an active component. The sorption of zinc on the impregnated sorbent can be expressed by the following stoichiometric relation:



where the equilibrium constant was found to be  $3.59 \times 10^5 \text{ kg-sorbent} \cdot \text{dm}^3/\text{mol}^2$ .

Furthermore the separation of zinc and copper in aqueous solution by use of the sorbent was examined in a batch operation with hydrochloric acid concentrations over 5M. It was found that the sorbent gives high selective separation of zinc to copper, and they can be separated satisfactorily from a  $1.0 \text{ mol/dm}^3$  hydrochloric acid solution. The applicability of the TOA-impregnated sorbent to column operation is also reported.

## Introduction

The selective separation and concentration of metal ions from aqueous solutions are of great importance in hydrometallurgy and wastewater treatment. Solvent extraction processes for metal separation are, in general, considered to be economical for aqueous feeds in the metal concentration range of  $10^{-2} \sim 1M$ . The need for separating metal ions from a dilute solution has led to the development of ion exchange resins and chelating resins. In comparison with solvent extraction, though allowing greater simplicity in equipment and operation, ion exchange resins have low selectivity to metal ions; chelating resins show a relatively slow complexation of metal ions, and also are high in price since their synthesis is rather difficult.

To overcome these problems, new types of sorbent have been developed as impregnated resins.<sup>2,4,7)</sup> The sorbent can be obtained in a simple manner by impregnating gel-type or cross-linked polymer matrices with liquid ion-exchanger or chelating reagent. The development of such impregnated resins is expected to lead to the technique of chromatographic separation of metal ions<sup>5)</sup> and has been covered extensively by Warshawsky.<sup>8)</sup>

The properties of impregnated resins mainly depend on the extractant and polymer matrix selected; the ion

exchange behavior of the reagent in the resin is expected to resemble solvent extraction, provided that the reagent is not chemically bonded to the polymer matrix.

Tri-*n*-octylamine (TOA) is a long-chain aliphatic amine and a representative of ionic extractants; the mechanism of metal extraction with TOA has been investigated extensively.<sup>3,6)</sup> The present study was made to elucidate the mechanism of sorption of zinc ion from acidic media by a macromolecular resin containing TOA as an active component. It was also expected that the sorbent might prove useful in developing separation processes in column operation.

## 1. Experimental

### 1.1 Reagents

Reagent-grade tri-*n*-octylamine (TOA or  $\text{R}_3\text{N}$ , Tokyo Kasei Co., Ltd.) was used as an active component without further purification. Amberlite XAD-2, obtained from Organo Co., Ltd., is a macromolecular resin made of styrene-divinylbenzene copolymer with a specific surface area of 280–320  $\text{m}^2/\text{g}$ , an average pore diameter of 9 nm, and a particle size of 250–850  $\mu\text{m}$ . This resin was washed by acetone and *n*-hexane and dried at 50°C in a vacuum for 2 hr.

Aqueous solutions of divalent zinc and copper were prepared by dissolving an appropriate amount of these chlorides ( $\text{ZnCl}_2$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) in hydrochloric acid and/or potassium chloride solutions. All chemicals

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used were of SG grade.

## 1.2 Preparation of the resin containing TOA

Amberlite XAD-2 resin was impregnated with a *n*-hexane solution of TOA by the following procedures. The impregnating solution was prepared by diluting an appropriate volume of 0.2M solution of TOA in *n*-hexane with fresh *n*-hexane. The organic solution (10 cm<sup>3</sup>) was mixed with the resin (1.0 g) for 1 hr. The diluent was then evaporated at 50°C in a vacuum for 2 hr. The resin thus treated contains TOA, and we call it TOA-impregnated sorbent. The content of TOA in the sorbent was determined by titrating the amount of TOA eluted with *n*-hexane from the sorbent, according to the procedures of Kakihana and Nakagawa,<sup>3)</sup> using Bromophenol Blue instead of Bromocresol Green as an indicator.

## 1.3 Sorption equilibria

In the sorption equilibrium study the sorbent (0.1 g) and aqueous solution (20 cm<sup>3</sup>) were placed in a 50 cm<sup>3</sup> glass-stoppered flask and shaken for 20 hr using a shaker (Yamato, BT-25). After standing for 1 hr, the aqueous phase was separated from the sorbent and then the metal concentration in the aqueous phase was determined by two methods: atomic absorption spectroscopy for lower metal concentrations and titration with EDTA for higher metal concentrations. Both the contents of metal retained in the sorbent and unreacted TOA were calculated from a mass balance.

The initial concentration of hydrochloric acid was determined by titration with a standardized sodium hydroxide solution. When potassium chloride solution was added, the total concentration of chloride ion was determined by argentometry.

## 1.4 Column operation

A column was packed with known amounts of the sorbent in a glass tube, supported between glass wool beds. Fresh sorbent was used for breakthrough curve determination; sorbent preloaded with zinc was used to follow the elution histories. Prior to the sorption run, 1.0M hydrochloric acid solution was passed through the column to chlorinate the TOA in the sorbent. In the sorption experiments a metal-hydrochloric acid solution was fed to the top of the column by a microtube pump at a constant flow rate. The effluent samples were collected at appropriate intervals by a fraction collector (Dainihonseiki, DFC-100); its metal concentrations were determined to follow the change in activity of the sorbent bed with throughput of the solution.

# 2. Results and Discussion

## 2.1 Sorption equilibria

Figure 1 shows the effect of the TOA concentration in the impregnating solution on the content of TOA in the resin. The content is proportional to the solution concentration; it was found that the amount of TOA

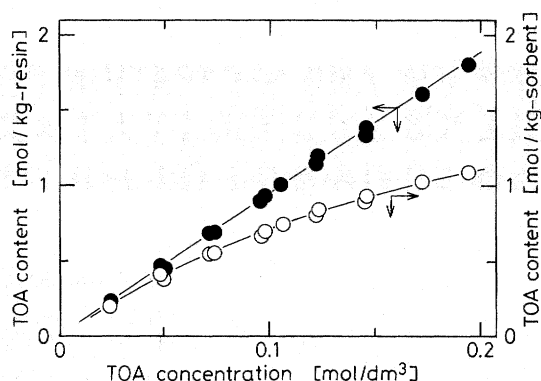
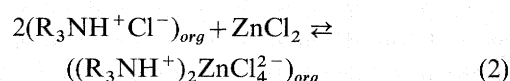
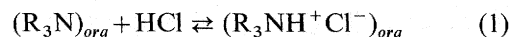


Fig. 1. Effect of TOA concentration in impregnating solution on content of TOA in resin and sorbent

transferred from the organic solution to the resin phase was more than 95% in all impregnations. When exceeding 1.02 mol/kg-sorbent, the sorbent became adhesive even after evaporating the diluent; therefore we used the sorbent at a content of 0.40 to 1.02 mol/kg-sorbent. The TOA content obtained by the titration was in good agreement with the values calculated from the change in the weight of the resin before and after the impregnations.

Solvent extraction of divalent metals from hydrochloric acid solutions with high-molecular weight amines has been studied extensively. Sato *et al.*<sup>6)</sup> have reported on the extraction of zinc chloride, whereby TOA was first converted to its amine salt and the neutral species of zinc ions in the aqueous phase could be extracted according to the following relations:



Assuming that the mechanism of zinc sorption on the TOA-impregnated sorbent is the same as that of the solvent extraction, we can express the equilibrium constant,  $K_{ex}$ , distribution ratio,  $D$ , and percent sorption,  $E$ , from the equilibrium relation by Eq. (2):

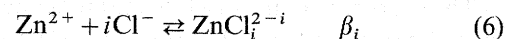
$$K_{ex} = \frac{[(R_3NH^+)_2ZnCl_4^{2-}]_{org}}{[R_3NHCl]^2[ZnCl_2]} \quad (3)$$

$$D = \frac{[Zn]_{total}}{[Zn]_{total}} \quad (4)$$

$$E = \frac{100D}{D + V/W} \quad (5)$$

where the overbar denotes the sorbent phase.

In general, zinc ions in hydrochloric acid medium exist in the form of zinc chloride complexes:



where  $\beta_i$  is the overall stability constant.

Consequently, the total concentration of zinc in the

aqueous phase can be expressed as:

$$\begin{aligned}
 [\text{Zn}]_{\text{total}} &= [\text{Zn}^{2+}] + [\text{ZnCl}^+] + [\text{ZnCl}_2] \\
 &\quad + [\text{ZnCl}_3^-] + [\text{ZnCl}_4^{2-}] \\
 &= [\text{Zn}^{2+}] \left( 1 + \sum_{i=1}^4 \beta_i [\text{Cl}^-]^i \right) = [\text{Zn}^{2+}] \alpha \quad (7)
 \end{aligned}$$

where

$$\beta_i = \frac{[\text{ZnCl}_i^{2-i}]}{[\text{Zn}^{2+}][\text{Cl}^-]^i} \quad (8)$$

$$\alpha = 1 + \sum_{i=1}^4 \beta_i [\text{Cl}^-]^i \quad (9)$$

Equations (3), (4) and (7) are combined to give the following expression:

$$\begin{aligned}
 D &= K_{\text{ex}} [\overline{\text{R}_3\text{NHCl}}]^2 \beta_2 [\text{Cl}^-]^2 / \alpha \\
 &= Y \beta_2 [\text{Cl}^-]^2 / \alpha \quad (10)
 \end{aligned}$$

where

$$Y = K_{\text{ex}} [\overline{\text{R}_3\text{NHCl}}]^2 \quad (11)$$

In the determination of the distribution ratio, we used:

$$\begin{aligned}
 [\overline{\text{Zn}}] &= [\overline{(\text{R}_3\text{NH}^+)_2\text{ZnCl}_4^{2-}}] \\
 &= ([\text{Zn}]_0 - [\text{Zn}]_{\text{total}}) V / W \quad (12)
 \end{aligned}$$

$$[\overline{\text{R}_3\text{NHCl}}] = [\overline{\text{R}_3\text{N}}]_0 - 2[\overline{\text{Zn}}] \quad (13)$$

$$[\text{Cl}^-] = [\text{HCl}]_0 - [\overline{\text{R}_3\text{N}}]_0 W / V \quad (14)$$

where  $V$  is the volume of the aqueous solution and  $W$  is the weight of the sorbent.

To make sure of the above relationships, the effects of the initial concentration of hydrochloric acid and the TOA content in the sorbent on the sorption equilibria were examined. The results obtained for the sorption of zinc in the batch operation are plotted according to Eq. (10) in Fig. 2. The data points are on straight lines with a slope of 1 as expected from Eq. (10). In this calculation, we used the following values<sup>1)</sup> as the overall stability constants of the chloro complexes of Zn(II):

$$\begin{aligned}
 \beta_1 &= 0.316 \quad \beta_2 = 0.100 \quad \beta_3 = 1.00 \\
 \text{and} \quad \beta_4 &= 0.100
 \end{aligned}$$

Values of  $Y$  defined by Eq. (11) were evaluated from the intercepts of the straight lines in Fig. 2. The results are plotted against  $\log[\overline{\text{R}_3\text{NHCl}}]$  in Fig. 3, giving a straight line with a slope of 2 as expected from Eq. (11).

The solid lines in Figs. 2 and 3 are calculated ones, and hence the sorption equilibrium of Zn(II) between the two phases could be expressed satisfactorily by Eq. (2). The value of  $K_{\text{ex}}$  was found to be  $3.59 \times 10^5$  from the intercept in Fig. 3.

When hydrochloric acid in the aqueous phase was

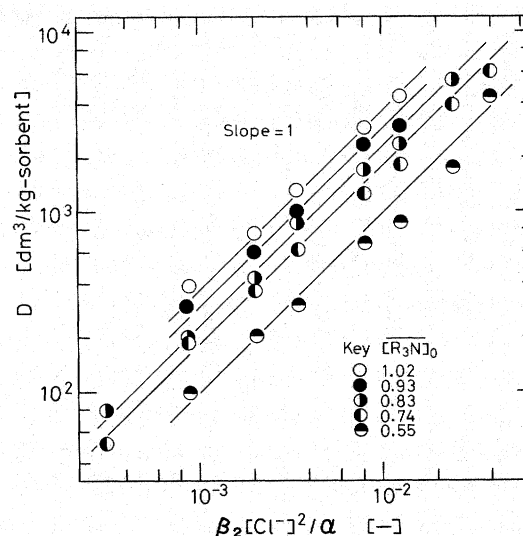


Fig. 2. Effects of chloride ion concentration and TOA content in sorbent on distribution ratio of Zn(II).  $[\text{Zn}]_0 = 1 \times 10^{-4} \text{ mol/dm}^3$

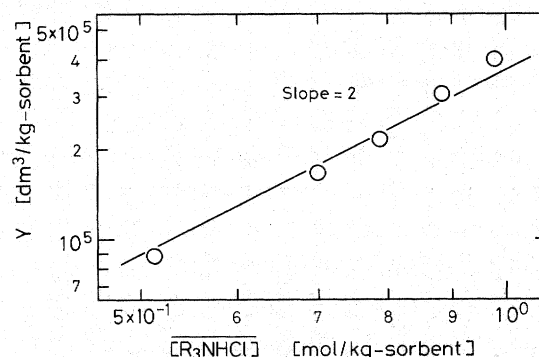


Fig. 3. Relation between TOA content in sorbent and the value of  $Y$  defined by Eq. (11)

replaced by potassium chloride except for the amount required to chlorinate the impregnated TOA, no change in the distribution ratio was found. This suggests that hydrogen ion does not participate in the sorption of zinc with the exception of the chlorination of TOA in the same way as the solvent extraction.

According to the equilibrium relation, the retention of zinc in the sorbent should be half the TOA content. Figure 4 shows the effect of the initial concentration of zinc in the aqueous phase on the sorption with various TOA contents, indicating that the zinc retained in the sorbent did not amount to half the impregnated TOA even for solutions of higher concentration. This suggests that in the resin the molecule of TOA might have a negative effect such as a steric hindrance or an occlusion.

Typical results for the desorption of zinc from the preloaded sorbent are given in Table 1. The zinc retained in the sorbent could be easily eluted by basic solutions such as a sodium hydroxide solution. In addition, 99% recovery of the zinc was attained by

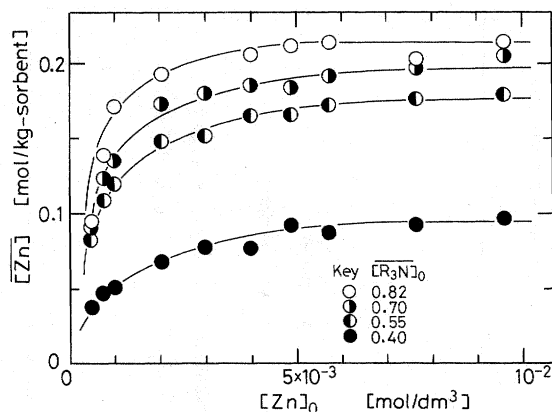


Fig. 4. Effects of initial concentration of Zn(II) and TOA content in sorbent on retention of Zn(II).  $[\text{HCl}] = 1.0 \text{ mol/dm}^3$

Table 1. Desorption of Zn(II) from preloaded sorbent

Strip Solution	0.01 M HCl	H <sub>2</sub> O	0.01 M NaOH	1.00 M NaOH
Initial Zn(II) content [mol/kg-sorbent]	0.132	0.131	0.131	0.129
Residual Zn(II) content [mol/kg-sorbent]	0.007	0.001	0.001	0.00
% Stripping	95	99	99	100

using deionized water as an eluant.

Figure 5 shows typical results for the separation of zinc and copper from hydrochloric acid media by two TOA-impregnated sorbents in the batch operation. The sorption of zinc takes place even at lower concentrations of hydrochloric acid and gives a maximum value of retention at about 2 M, whereas copper cannot be sorbed from a solution of HCl below 1 M. Such sorption behavior is in accordance with the result for the solvent extraction with TOA by Sato *et al.*<sup>6)</sup> Thus the present TOA-impregnated sorbent has a viability of continuous separation of zinc and copper from their dilute solution. This will be demonstrated in column operation in the following section.

## 2.2 Column operation

One gram of the sorbent was packed in a glass column (I.D.: 9.6 mm; bed height: 29 mm). A 1 M HCl solution containing  $0.28 \text{ mmol/dm}^3$  of zinc was passed downward at a flow rate of 15.7 bed volume (b.v.) per hour, i.e.,  $33 \text{ cm}^3/\text{hr}$ , at  $25^\circ\text{C}$ . The breakthrough curves obtained are shown in Fig. 6, wherein the concentration of zinc in the effluent gradually increased with elapsed time after 80–120 b.v., but no clear breakpoint appeared. This may be due to a slow sorption rate of zinc and hence a wide sorption zone. The closed symbols in Fig. 6 represent the behavior of the cyclic operation for eluting zinc with deionized water, and the breakthrough curve is in reasonable agreement with that for the first one. This indicates

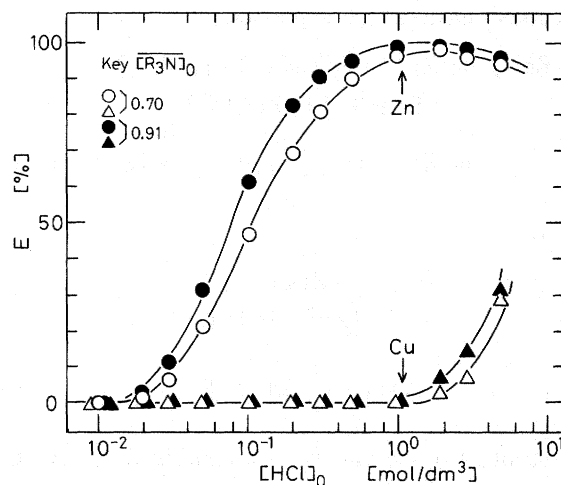


Fig. 5. Effect of hydrochloric acid concentration on separation of Zn(II) and Cu(II) by sorbent in batch operation.  $[\text{Zn}]_0 = 3 \times 10^{-4} \text{ mol/dm}^3$ ,  $[\text{Cu}]_0 = 3 \times 10^{-4} \text{ mol/dm}^3$

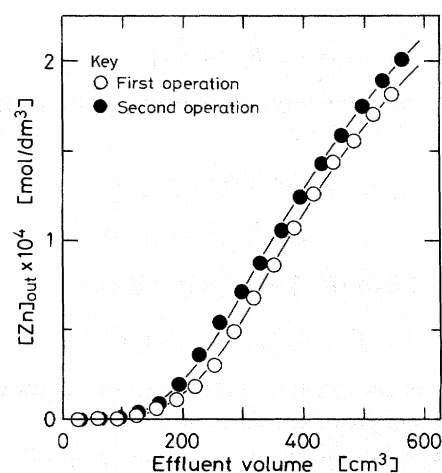


Fig. 6. Breakthrough curves for Zn(II) in cyclic sorption. Flow rate =  $33 \text{ cm}^3/\text{hr}$ ,  $[\text{R}_3\text{N}]_0 = 0.68 \text{ mol/kg-sorbent}$ ,  $[\text{HCl}]_f = 1.0 \text{ mol/dm}^3$ ,  $[\text{Zn}]_f = 2.8 \times 10^{-4} \text{ mol/dm}^3$

that the dissolution of TOA from the sorbent is small enough to be ignored.

Figure 7 shows the desorption curves of the zinc retained in the bed with deionized water as an eluant. The curves obtained in the first and second operations are in good agreement. The total amount of zinc eluted from the bed was  $0.12 \text{ mmol}$ , which is very close to the value obtained from the breakthrough curve in Fig. 6.

Figure 8 illustrates the separation of zinc and copper from their aqueous mixture through the sorbent bed. In this experiment, hydrochloric acid concentration in the aqueous feed was fixed at  $1 \text{ mol/dm}^3$  according to the result in Fig. 5. Copper ion in the feed was completely discharged from the bed without sorption throughout the experiment, while zinc was sorbed in the same way as indicated by the breakthrough curve in Fig. 6. Thus the separation of zinc from copper

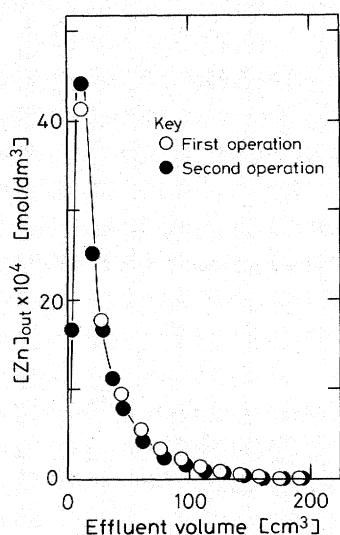


Fig. 7. Elution curves of Zn(II) from sorbent bed loaded with Zn(II) in cyclic desorption. Flow rate = 33 cm<sup>3</sup>/hr

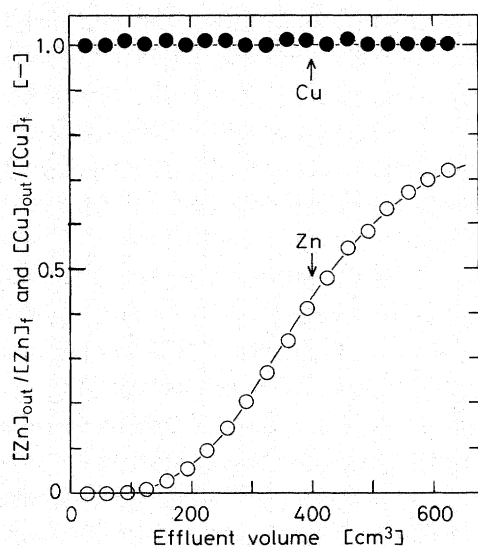


Fig. 8. Breakthrough curves for a mixed solution of Zn(II) and Cu(II). Flow rate = 33 cm<sup>3</sup>/hr,  $[R_3N]_0 = 0.69$  mol/kg-sorbent,  $[HCl]_f = 1.0$  mol/dm<sup>3</sup>,  $[Zn]_f = 2.9 \times 10^{-4}$  mol/dm<sup>3</sup>,  $[Cu]_f = 2.9 \times 10^{-4}$  mol/dm<sup>3</sup>

ions in dilute solution can be attained satisfactorily in column operation for an effluent volume less than 100 cm<sup>3</sup>. Research on the kinetics of the sorption is now being undertaken to analyze the breakthrough curve.

## Conclusion

The sorption of zinc ion in hydrochloric acid media by TOA-impregnated sorbent was studied from the viewpoint of equilibrium distribution and separation from copper ion. The following results were obtained.

1) The impregnation of TOA on Amberlite XAD-2 was achieved to a content below 1.02 mol/kg-sorbent.

2) The mechanism of Zn(II) sorption is expressed by the same equilibrium relation as in solvent extraction, and the equilibrium constant was found to be  $3.59 \times 10^5$ . However, the loading capacity of the metal ion to the impregnated TOA is less than that to the solvent extraction.

3) The desorption of zinc from loaded sorbent is completely achieved, even with deionized water as an eluant.

4) The separation of zinc and copper in aqueous solution by the sorbent can be obtained in either batch or column operation.

## Nomenclature

$D$	= distribution ratio defined by Eq. (4)	[dm <sup>3</sup> /kg-sorbent]
$E$	= percent sorption of metal	[%]
$K_{ex}$	= equilibrium constant defined by Eq. (3)	[kg-sorbent · dm <sup>3</sup> /mol <sup>2</sup> ]
$V$	= volume of aqueous phase	[cm <sup>3</sup> ]
$W$	= weight of TOA-impregnated sorbent	[g]
$Y$	= defined by Eq. (11)	[dm <sup>3</sup> /kg-sorbent]
$\alpha$	= defined by Eq. (9)	[—]
$\beta_i$	= overall stability constant of $i$ -th chloro complex of Zn(II)	[(dm <sup>3</sup> /mol) <sup><math>i</math></sup> ]
[ ]	= concentration or content in the sorbent	[mol/dm <sup>3</sup> ], [mol/kg-sorbent]

## <Subscripts>

$f$	= aqueous feed
$org$	= organic phase
$out$	= effluent
$0$	= initial

## <Superscript>

—	= sorbent phase
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