CHROM. 13,041

SORPTION OF COPPER(II) IONS ON THE SODIUM AND THE CALCIUM FORM OF ZEOLITES

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SUMMARY

Studies have been made of the sorption of copper by natural clinoptilolite and zeolite X from 0.003 N CaCl$_2$ and 0.7 N NaCl. The exchange capacities of these zeolites with respect to copper have been determined, along with the equilibrium and kinetic characteristics of the process of sorption from the above solutions.

INTRODUCTION

In recent years an increasing number of studies have been made of the ion-exchange properties of natural and synthetic zeolites exhibiting high selectivity for some elements. The possibilities of application of these substances include the separation of isotopes of alkali metals[1], strontium and calcium[2], and the recovery of copper from process solutions[3].

This paper summarizes the results of studies into the sorption of copper by natural clinoptilolite and zeolite X from solutions of various compositions, and the analysis of these processes by methods developed at the Institute[4]. In order to simulate a dynamic ion-exchange process its equilibrium and kinetic characteristics, which are derived experimentally, must be known. These data permit estimation of the contributions of external and internal diffusion, which may vary according to the experimental parameters, such as flow-rate, sorbent grain size, etc. The literature contains descriptions of solutions to the sorption dynamics problems of various models, which include linear external, internal and mixed diffusion[5-7], non-linear external diffusion of one- and multicomponent mixtures and ions of different charges[8,9] and the case of an S-shaped isotherm[10]. The "layer-by-layer" method looks particularly promising, permitting solution of many complex multicomponent problems in dynamics[11]. The available solutions can be used to simulate specific ion-exchange processes, of which there are numerous examples[2,3,12,13].

On the basis of the available theories of the dynamics of the processes under consideration and the experimental data characterizing their models, we have simulated the dynamic process of sorption of copper ion on natural clinoptilolite and synthetic zeolite X.

EXPERIMENTAL

The object of the study was the sorption of copper (from 2 to 10 mg/l) on natural clinoptilolite and zeolite X from a 0.003 N solution of calcium chloride and a 0.7 N solution of sodium chloride (pH 3–5). Known techniques[14] were used for determining the exchange capacities of the calcium and sodium forms of these zeolites with respect to copper, and to establish the equivalence of exchange. To determine the equilibrium characteristics of the sorption process (exchange constants and distribution coefficients) we measured the sorption isotherms of copper on clinoptilolite (Ca^{2+}, Na^+) and zeolite X from 0.01 N mixtures of the respective ion pairs, as well as from a 0.003 N solution of calcium chloride and a 0.7 N solution of sodium chloride. The rate of copper sorption on the zeolites was studied by the "thin-layer" method[15]. To derive kinetic curves we used the same solutions as in the equilibrium tests. The copper concentrations in the solutions were 2 mg/l, pH 5, and 10 mg/l, pH 3, due to the necessity of maintaining the copper in an ionic state.

RESULTS AND DISCUSSION

Table I gives the exchange capacities of various forms of zeolites with respect to copper. The exchange capacity in the case of clinoptilolite varies, depending on the cationic form, from 1.10 to 1.25 mequiv./g and in the case of zeolite X, from 3.25 to 3.40 mequiv./g.

TABLE I

EXCHANGE CAPACITIES (mequiv./g) OF ZEOLITES TOWARDS COPPER ION

Zeolite		Initial cationic form of zeolite	
		Calcium	Sodium
Clinoptilolite {	static	1.25	1.20
	dynamic	1.25	1.10
Zeolite	static	3.40	3.25

Fig. 1 shows the sorption isotherms of copper on clinoptilolite and zeolite X in their sodium and calcium forms, from which the exchange constants of copper were calculated (for each of the above ions). The calculated exchange constants are listed in Table II. From Table II it can be seen that the dimensionless constants of copper–sodium exchange are almost 4.5 times greater than those of copper–calcium exchange, which suggests that in extracting copper from the mixture sodium inhibits sorption to a much lesser extent than Ca^{2+}. Comparative analysis of the sorption of copper on clinoptilolite from 0.003 N $CaCl_2$ and 0.7 N NaCl has shown that the more dilute $CaCl_2$ solution inhibits the sorption to a greater extent than the 0.7 N solution of NaCl. From Fig. 2, the sorption isotherms of copper from solutions of the above compositions are linear in the given concentration range and characterized by distribution coefficients of $1 \cdot 10^3$ and $2 \cdot 10^3$, respectively. The distribution coefficient of
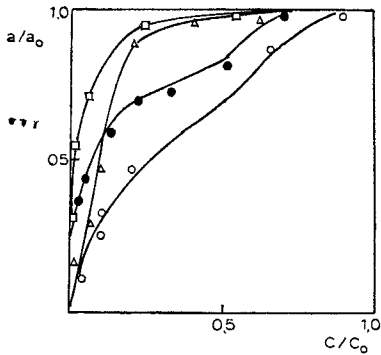
Fig. 1. Sorption isotherms of copper ions in 0.01 N solution on clinoptilolite (Na⁺, Ca²⁺) and zeolite X: a/a_0 and c/c_0 are the equivalent cation fractions in the zeolite and the solution, respectively. □, NaX; ●, clinoptilolite (Na⁺); △, CaX; ○, clinoptilolite (Ca²⁺).

TABLE II

EQUILIBRIUM COEFFICIENTS OF COPPER ION ON ZEOLITES

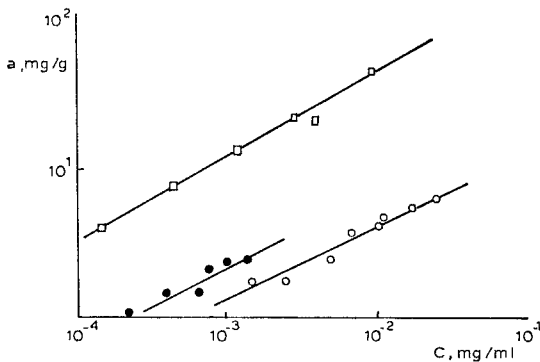| Sorbent	$K_{Cu}{}^{\ominus}{}_{Na}$		$K_{Cu}{}^{\ominus}{}_{Ca}$ (dimensionless)
	(g/ml)^{1/2}	dimensionless	
Clinoptilolite	0.26	18.2	4.1
Zeolite X	1.10	142.5	—

Fig. 2. Sorption isotherms of copper ions on the clinoptilolite and NaX: a, c are the concentrations of copper ions in the zeolite and the solution, respectively. □, NaX; ○, natural clinoptilolite, 0.003 N CaCl₂; ●, natural clinoptilolite, 0.7 N NaCl.

copper on zeolite X is 10^4 (from a 0.003 N solution of CaCl₂), which is indicative of high selectivity of this zeolite to copper.

The results of the kinetic study of copper sorption on clinoptilolite and zeolite X are given in Fig. 3. It can be seen that the rate of sorption from 0.003 N CaCl₂ is somewhat greater than from 0.7 N NaCl. The copper diffusion coefficients were calculated in each case, and the results are summarized in Table III. The use of these diffusion coefficients, and of external-diffusion coefficients β calculated from a known
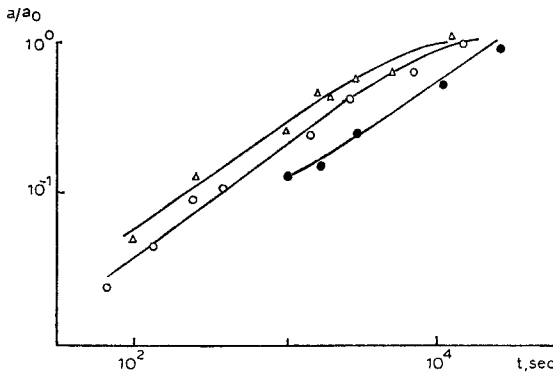
Fig. 3. Experimental exchange kinetics: fractional attainment of equilibrium (a/a_0) of copper ions against time. Particle radius, 0.02 cm; $\triangle$, natural clinoptilolite; $\bigcirc$, NaX, 0.003 N CaCl$_2$, pH 5; $\bullet$, natural clinoptilolite, 0.7 N NaCl, pH 5.

TABLE III

DIFFUSION COEFFICIENTS OF COPPER ION ON ZEOLITES

Zeolite	Solution	D (cm^2/sec)
Clinoptilolite	CaCl$_2$	$2.5 \cdot 10^{-9}$
	NaCl	$3.0 \cdot 10^{-10}$
Zeolite X	CaCl$_2$	$3.52 \cdot 10^{-10}$

formula[4], has made it possible to determine the relative contribution of external and internal diffusion to a specific dynamic process ($H = \beta r^2/DI'$). The results are given in Table IV. It is suggested that in the given range of rates and grain sizes the process is represented by a mixed-diffusion model with a predominant contribution of external diffusion; the value of H varies in the range of 0.52–3.62.

TABLE IV

H VALUES FOR DIFFERENT PARAMETERS OF THE DYNAMIC PROCESS

$10^2 \cdot d$ (cm)	V (cm/sec)	
	$2.55 \cdot 10^{-3}$	$1.9 \cdot 10^{-2}$
3.3	0.52	2.20
6.5	1.27	3.12
9.7	1.47	3.62

The literature contains a solution to this dynamic problem (linear isotherm and mixed-diffusion kinetics)[7]. By using this solution and the above experimental equilibrium and kinetic data in accordance with the previously described method[4], we constructed curves representing sorption of copper from 0.003 N CaCl$_2$ per gram of natural clinoptilolite at $v = 0.0058$ cm/sec and $d_g = 0.025$–0.05 cm. The results are given in Fig. 4. It is obvious that in the course of dynamic sorption the pH increased
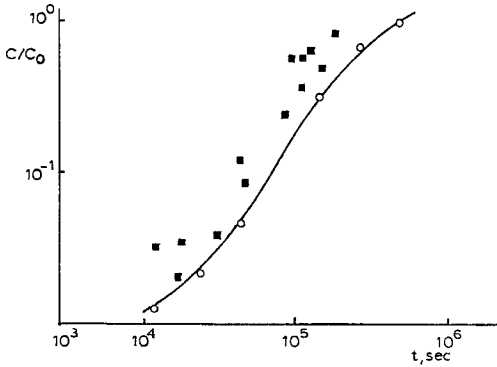
Fig. 4. Theoretical (○) and experimental (■) break-through curves of copper ions from 0.003 N CaCl$_2$ on the clinoptilolite, pH 5. c_{Cu} = 10 mg/l; v = 0.006 cm/sec; particle radius, 0.02 cm.

to 7–7.3. This probably accounts for the irregular increase in the copper concentration beyond the sorbent layer. However, the fit between the experimental and calculated curves is quite good.

In order to eliminate the effect of pH variations on the copper sorption, the solution was acidified to pH 3, and clinoptilolite was converted into an equilibrium form with respect to the macroion and hydrogen of the initial solution. Fig. 5 shows the good agreement between the calculated and experimental break-through curves for copper sorption from 0.7 N NaCl per gram of clinoptilolite (grain size, 0.05–0.025 cm), and sorption rates of 0.02–0.003 cm/sec. The same methods were used in the calculations. A value of 3 was obtained for the copper distribution coefficient.

Thus, the results demonstrate the possibility of using the described methods in simulating dynamic sorption processes on zeolites.
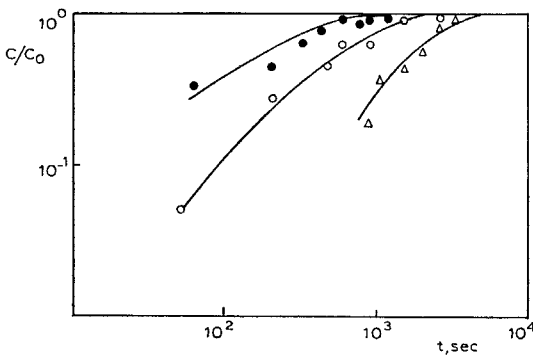

Fig. 5. Theoretical (—) and experimental break-through curves of copper ions from 0.7 N NaCl, pH 3, on the clinoptilolite. v = 0.02) (○), 0.01 (○) and 0.003 cm/sec (△). Particle radius, 0.02cm.

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