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Determination of kinetics and equilibrium of Pb/Na exchange on clinoptilolite

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Abstract

Ion exchange kinetics and equilibria of lead on Na-pretreated clynoptilolite have been studied using batch method by means of electrometric and polarographic techniques. Equivalent fraction of lead ions exchanged with sodium has been determined by measuring time dependent Na^+ ion concentration with sodium ion selective electrode (SISE). Electrode readings could be taken for a time interval of 15 s at early time of exchange. Time dependence of pH during exchange process has been followed simultaneously. Time dependent exchange curves showed a sharp increase at the beginning followed by a slower one for longer times until reaching equilibrium. The McKay equation for isotopic exchange kinetics has been applied to describe experimental results both in terms of out- and in-going ions. The film and particle diffusion coefficients evaluated from the McKay constants are not significantly affected by initial solution concentrations studied in the range of 1×10^{-4} to 1×10^{-4} M. Kinetic curves have been successfully modeled using the diffusion coefficients. An increase in the pH values at low concentrations below 10^{-3} M Pb can be attributed to contribution of H^+/Na^+ exchange whereas the decrease of pH is indicative of the uptake of hydroxyl ions to form lead hydroxide clusters into clinoptilolite at higher concentrations. Total amount of Pb adsorbed and exchanged at equilibrium condition has been determined from polarographic measurements and compared with those found for exchanged Pb. Equilibrium data have been analyzed and modeled in terms of Freundlich and Langmuir adsorption isotherms. Thermodynamic parameters for transition state have been evaluated from temperature dependent kinetic results.
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1. Introduction

Industrial wastewater is contaminated with a wide variety of potentially toxic chemicals, heavy metals and organics being the most significant. These contaminants can have serious effects on human and animal health. The heavy metals of particular concern are lead, cadmium, mercury, zinc, copper, chromium and nickel, because of the risk of their entry into the food chain or into the water supply. Lead, the focus of this work, is the cumulative poison and concentrates primarily in the bones. There are numerous industrial activities involving this metal and, as a result, there are many sources of industrial effluents discharging this metal into the environment, such as tanneries, metal plating facilities and mining operations [1,2].

Many concentration and separation processes including precipitation, ion exchange, membrane separation, solvent extrac-

tion, foam flotation and biosorption are applicable to removal metal undesirable heavy metal ions from industrial wastewater. Ion exchange is the most preferential method among water treatment processes point of view applicability and economical when cheap and commercially available materials are used as exchanger. The natural and synthetic zeolites for heavy metal removals have been extensively studied [1–12]. Zeolites are microporous crystalline solids with well defined structures, which have great potential for a number applications in various fields, such as adsorption, separation ion exchange and catalysis [13,14]. It is characterized by a framework structure that encloses interconnected cavities occupied by ion-exchangeable large metal cations and water molecules permitting reversible dehydration. Among the most frequently studied natural zeolites is clinoptilolite because of its abundance [1–10]. Despite the interest on the ion exchange of heavy metals on clinoptilolite, in general, researches have been focused on determining ion-exchange equilibria between aqueous solution and clinoptilolites from different origins [2–6] and selectivity sequences of heavy metal ions [7,9]. Limited data are available for this

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material based on kinetics of Pb removal [8–10,15]. In these studies, amount of exchanging ions have been determined by measuring remaining concentration of Pb^{2+} ions at various time intervals after separation solid and liquid phases by centrifuging and filtering. These procedures suffer from disadvantages of being time consuming. The reported time intervals are minimum 5 min or longer while ion exchange reactions are very rapid and complete in a few minutes. The use of ion selective electrode is simple, rapid and can be used to measure quite accurately ion exchange rate without any separation procedures, such as centrifugation or filtration [16].

The aim of this study is to investigate the kinetics of lead–sodium exchange on a clinoptilolite converted to Na-form by using electrochemical techniques.

2. Experimental

A clinoptilolite type zeolite used as an exchanger in this study was obtained from the Gördes deposit in Aegean Sea region of Turkey. Batch kinetic studies were performed in order to determine the rate-limiting step of lead–sodium ion exchange process.

2.1. Exchanger specifications

2.1.1. Characterization of exchanger
XRD results show that zeolite sample consists of mainly clinoptilolite (80%). The impurities include volcanic glass (10%), clay + quartz + biotite (10%). The chemical composition of clinoptilolite by weight determined by X-ray fluorescence (XRF) measurements is as follows: SiO_2, 74.7%; Al_2O_3, 13.7%; Fe_2O_3, 1.45%; TiO_2, 0.15%; CaO, 2.76%; MgO, 0.69%; Na_2O, 1.07%; K_2O, 5.25%.

According to the chemical analysis, the total (or maximum) exchange capacity of Gordes clynoptilolite is 2.78 meq/g, calculated as the sum of Mg, Ca, K and Na cations. This value is well consistent with those found for other two clinoptilolite samples around Aegean Sea, a Greek clinoptiloite of 2.62 meq/g and a Bigadic clinoptilolite of Turkey of 2.57 meq/g [7,8,10]. Particle density is 2.27 g/cm^3.

2.1.2. Determination of point of zero charge (pH_{pzc})
In a previous study, electrokinetic properties of Gordes clinoptilolite in some mono- and multivalent salts have been reported [17]. The results of zeta potential measurements show that clinoptilolite exhibits a negative surface charge and has no an isoelectric point (iep) in the pH range of 2–12. The pH_{pzc} is defined as the pH at which the surface charge equals zero. In the present study, the pH_{pzc} of the clinoptilolite was determined as 3.35 by using potentiometric titration method. A portion of 0.1 ml NaOH of 0.1 M was added to a clinoptilolite suspension of 2 g/dm^3 in electrolyte medium of 0.1 M NaCl of 25 cm^3. After equilibration for 24 h the pH of the suspension was measured as 10.15. It was back titrated with 0.1 M HCl up to pH 2.74 using a Metrohm E 485 titrator. The pH measurements were carried out with a Jenway pH meter equipped with a combined glass electrode. The basic supernatant was utilized as the system blank and titrated with HCl in a manner identical to that of the sample suspension. Surface charge density (σ) on hydrous oxides is defined by the net uptake of protons, i.e.

$$\sigma = F(\Gamma_{H^+} - \Gamma_{OH^-}) \tag{1}$$

where Γ_{H^+} and Γ_{OH^-} are the moles of H^+ and OH^- ions adsorbed per unit surface area and F is the Faraday constant. The value of pH_{pzc} was determined from the σ–pH curve to be the pH at zero net adsorption of protons and hydroxide ions, i.e. $\Gamma_{H^+} - \Gamma_{OH^-} = 0$

2.2. Preparation of the exchanger

Previous experiments performed with NaCl solutions in the concentration range of 1.0×10^{-5} to 1.0 M showed that clinoptilolite could be converted to near homo ionic Na form by treating NaCl solution of 1×10^{-1} M at a solution/solid ratio of 0.5 dm^3/g. In order to prepare Na-modified clinoptilolite samples, a size fraction of 140–180 μm were agitated at 25 °C for a period of 60 min and kept over night. Then, solid phase was washed with deionized water until all traces of Cl^- ions were removed and dried at 105 °C to constant weight. Amount of Na ions in homo ionic form of clinoptilolite is found to be 2.5 meq/g.

2.3. Ion exchange experiments

2.3.1. Time dependent Na^+ ion and pH measurements
A sodium ion selective electrode combined with Ag/AgCl electrode (Orion 8611BN) and a pH electrode were immersed in a Pyrex polarographic cell with water jacketed containing 25 cm^3 lead nitrate solution a known concentration in the range of 1×10^{-4} to 1×10^{-2} M. For the kinetic measurements, a weighing amount of 0.050 g sample of clinoptilolite powders in Na-homo ionic form was added to the solution which is continuously stirred at a constant level with a Teflon-covered stirring bar and a timer was started. Electrode readings were taken at 1/4 min intervals until the first min and longer time intervals were sufficient from 1/2 to 5 min until reaching equilibrium conditions.

The readings were made by using Jenway Model 3040 ion analyzer. Accuracy of ion analyzer instrument for ion activity measurements in the range from 10^{-8} to 1 is ±0.5%. Calibration of sodium electrode was performed in a series of standards from 10^{-5} to 10^{-1} M. The Na^+ ion concentration of the samples was determined by using this calibration curve. The potential developed under standard conditions is reproducible ±2%.

The equivalent amount of Pb^{2+} exchanged with Na^+, q, was calculated by measuring Na concentration in the solution at any time t:

$$q = C\frac{V}{m} \tag{2}$$

where C is the Na^+ concentration (in equiv./dm^3) and V/m is the solid/solution ratio (in dm^3/g). The values of C are calculated from the difference in the presence and absence of lead ions because Na^+ cations are also released from zeolitic material in aqueous medium [14].