



# The kinetics of fluoride sorption by zeolite: Effects of cadmium, barium and manganese

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## ABSTRACT

Industrial wastewaters often consist of a complex chemical cocktail with treatment of target contaminants complicated by adverse chemical reactions. The impact of metal ions ( $\text{Cd}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Mn}^{2+}$ ) on the kinetics of fluoride removal from solution by natural zeolite was investigated. In order to better understand the kinetics, the pseudo-second order (PSO), Hill (Hill 4 and Hill 5) and intra-particle diffusion (IPD) models were applied. Model fitting was compared using the Akaike Information Criterion (AIC) and the Schwarz Bayesian Information Criterion (BIC). The Hill models (Hill 4 and Hill 5) were found to be superior in describing the fluoride removal processes due to the sigmoidal nature of the kinetics. Results indicate that the presence of Mn ( $100 \text{ mg L}^{-1}$ ) and Cd ( $100 \text{ mg L}^{-1}$ ) respectively increases the rate of fluoride sorption by a factor of  $\sim 28.3$  and  $\sim 10.9$ , the maximum sorption capacity is increased by  $\sim 2.2$  and  $\sim 1.7$ . The presence of Ba ( $100 \text{ mg L}^{-1}$ ) initially inhibited fluoride removal and very poor fits were obtained for all models. Fitting was best described with a biphasic sigmoidal model with the degree of inhibition decreasing with increasing temperature suggesting that at least two processes are involved with fluoride sorption onto natural zeolite in the presence of Ba.

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## 1. Introduction

The aluminum smelter at Kurri Kurri, NSW Australia has been utilizing the Hall–Héroult method to produce aluminum for about 43 years. Historical disposal of Spent Pot Lining (SPL), a hazardous waste by-product of the aluminum smelting process, has rendered the nearby groundwater with as much as  $1500 \text{ mg L}^{-1}$  fluoride, far beyond the recommended concentration of  $1.5 \text{ mg L}^{-1}$  (WHO, 2011) for potable water or  $20 \text{ mg L}^{-1}$  for discharge to sewer. Many other regions

around the world also experience groundwater fluoride toxicity. For instance, in China, the wastewater from aluminum industry usually contains about  $80\text{--}90 \text{ mg L}^{-1}$  fluoride (Zhang et al., 2011), while about  $33 \text{ mg L}^{-1}$  and  $5 \text{ mg L}^{-1}$  fluoride has been detected, respectively in the drinking water in Ethiopia (Nigusse et al., 2007), and southern California (Fan, 2003). An excessive intake of fluoride can lead to fluorosis, a chronic disease manifested by mottling of teeth, softening of bones, liver and thyroid lesions, and neurological damage (Tor, 2006; Wang and Reardon, 2001).

Several methods have been utilized to remove fluoride from water, namely adsorption (Chaturvedi et al., 1988), precipitation (Saha, 1993), electro dialysis (Adhikary et al., 1989), ion exchange (Haron et al., 1995), reverse osmosis (Joshi et al., 1992), nanofiltration (Simons, 1993), Donnan dialysis (a membrane separation process) (Hichour et al., 1999), and the Nalgonda technique (Droste, 1997). Most of these techniques have high material and operational costs. For example, ion

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exchange and electro dialysis are effective methods for reducing the fluoride concentration, however the resins and membranes are expensive and may need frequent regeneration (Fan, 2003). Therefore low-cost sorbents such as calcite (Fan, 2003; Turner et al., 2005), diatomaceous earth (Janta et al., 2008), clays and soil (Bower and Hatcher, 1967), activated alumina (Beneberu, 2005) and zeolite (Díaz-Nava et al., 2002) have been studied. Natural zeolite is cheap, abundant and with the properties of ion-exchange, adsorption, and molecular sieving, it is of particular interest for the remediation of both cationic and anionic contaminants.

More than 40 kinds of natural zeolite have been found (Wang, 2012) among which clinoptilolite is commonly used and has been investigated by several authors (Díaz-Nava et al., 2002; Nyembe et al., 2010; Zhao et al., 2008). Clinoptilolite is a microporous, aluminosilicate mineral with a cage-like structure and regular channels and cavities. It has a negatively charged framework and is counter-balanced by exchangeable cations ( $K^+$ ,  $Na^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$ ). When adsorption occurs, metal ions will not only replace hydrogen ions through an inner-sphere complexation mechanism, but will also exchange with these counterbalanced ions at external sites (Eqs. (1) – (3)) (Doula, 2009): outer-sphere complex



inner-sphere complex



where C is the counterbalanced ion with charge n + (n = +1 or +2) (e.g.  $K^+$ ,  $Na^+$ ,  $Mg^{2+}$ , or  $Ca^{2+}$ ), M stands for metal ions with charge z + (z = +2 or +3), and S corresponds to surface Si or Al.

The mechanisms of fluoride retention by this material can be described by occlusion and ion-exchange. Fluoride, whose ionic radius is ~1.34 Å, would be easily occluded in the zeolite cavity due to the Donnan effect, which is related to the associated cations in the solution (Barrer and Walker, 1964; Maruthamuthu and Sivasamy, 1994). The Donnan effect is a phenomenon where charged ions fail to distribute evenly in a cavity, resulting in an uneven electrical charge. Fluoride having an ionic radius similar to  $OH^-$  (1.40 Å), can also be removed by exchanging with hydroxylated zeolite surface sites ( $\equiv SiOH$  &  $\equiv AlOH$ ) (Díaz-Nava et al., 2002).

According to previous studies, information about fluoride removal by zeolite in the presence of metal ions is very scarce, with the majority of the literature reporting zeolite-metal or zeolite-fluoride ion interactions (Doula, 2006, 2009; Rajic et al., 2010). Since industrial effluent such as SPL leachate is a complex chemical cocktail (Kumar et al., 1992; Pong et al., 2000) containing metal ions, it is necessary to understand how these chemicals will behave during the defluoridation process. The present study aims to determine the influence of co-existing metal ions (Mn, Cd and Ba) on the kinetics of fluoride removal by natural zeolite. For this purpose, a series of “free-drift” kinetic tests as well as XRD studies, geochemical and kinetic modeling are presented.

## 2. Materials and methods

### 2.1. Materials

Zeolite was obtained from the Castle Mountain Zeolite Company, Quirindi, NSW, Australia, and sieved into a particle size fraction of <150 μm. The Brunauer–Emmett–Teller (BET) surface area analysis was applied by using a Micromeritics ASAP2010 instrument to determine the specific surface area. The nitrogen adsorption isotherms were measured at 77.3 K and the pore size distribution was analyzed via the Barrett–Joyner–Halendar (BJH) method. X-ray diffraction (XRD) analysis was undertaken using a Philips X'Pert X-ray diffractometer ( $CuK\alpha$  radiation conducted at 40 kV and 40 mA,  $2\theta = 5\text{--}70^\circ$ ). Patterns were collected with a step size of  $0.004^\circ$ . The results show that the main crystalline component of the zeolite used in the present study is clinoptilolite, with the main mineral content of 71.81% silicon dioxide, 12.1% aluminum oxide, 2.6% calcium oxide, 2.33% sodium oxide, 1.14% iron oxide and 0.9% potassium oxide. Metals were obtained in the form of spectroscopic standards (Sigma-Aldrich) and diluted to the required concentration using DI (de-ionized) water.

### 2.2. Kinetic tests

“pH-stat” (constant pH) and “free-drift” methods are the most commonly used techniques in kinetic experiments. In the present study, the “free-drift” method was selected due to the fact that this methodology is most useful for studying the systems closer to equilibrium (Plummer et al., 1978). Electronic overhead stirrers (Jeio Tech MSP-3) were used to provide the required rates (200 rpm) which were logged using Lab Companion software. pH and fluoride ion-selective electrodes (Orion instruments) were connected to a datalogger for recording pH and fluoride concentration every 10 s.

A fluoride stock solution ( $2000 \text{ mg L}^{-1}$ ) was prepared using anhydrous potassium fluoride (KF) (Sigma-Aldrich) with de-ionized water (DI) obtained from a Millipore Milli-Q 185 water de-ionizer ( $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ), and the exact concentration of fluoride was determined by ion chromatography (IC). The initial concentration of synthetic fluoride solutions used in the kinetics test was  $200 \text{ mg L}^{-1}$  (the “representative” concentration of fluoride contamination in groundwater at the Hydro Aluminium site), obtained by diluting the stock solution with DI water. Analysis of groundwater samples at the Hydro Aluminium site showed that among many other contaminants, total metal concentrations maximum were  $Ba^{2+} \sim 0.36 \text{ mg L}^{-1}$ ;  $Cd^{2+} \sim 0.7 \mu\text{g L}^{-1}$ ; and  $Mn^{2+} \sim 0.38 \text{ mg L}^{-1}$ . In these experiments consistent metal concentrations of 10 &  $100 \text{ mg L}^{-1}$  were used as a “worst case” test for determining their effect on fluoride removal by zeolite.

At the beginning of each test, the pH and fluoride electrodes were calibrated. pH was measured using Orion 9165BN pH electrodes calibrated using pH 4, 7 and 10 NIST buffers as per the Orion 9165BN pH manual. Fluoride was measured with Orion 9609BN ion-selective electrodes calibrated using 10, 100, 1000 and  $2000 \text{ mg L}^{-1}$  of potassium fluoride until a slope of  $-54 \pm 2 \text{ mV decade}^{-1}$  was achieved. All standards used for calibrating the fluoride ion selective electrodes were then analyzed by ion chromatography (IC) which provides the

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