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Exchange of heavy metal ions in titanosilicate Na-ETS-10 membrane from molecular dynamics simulations

A. Nalaparaju, Z.Q. Hu, X.S. Zhao, J.W. Jiang*

Department of Chemical & Biomolecular Engineering, National University of Singapore, 4 Eng. Drive 4, Singapore 117576, Singapore

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ABSTRACT

The exchange of heavy metal ions Pb^{2+}, Cd^{2+} and Cu^{2+} in a titanosilicate Na-ETS-10 membrane is investigated using molecular dynamics simulations. The simulation system consists of Na-ETS-10 membrane and ionic solution in a dielectric continuum. Ion exchange is observed from the temporal variation of ion density profiles. The residence time distributions, mean square displacements and radial distribution functions are determined to characterize the dynamic and structural properties of exchanged ions in the membrane. Pb^{2+} ions are highly coordinated with Ti atoms and strongly bound with the membrane. Consequently, Pb^{2+} ions reside in the membrane exclusively and have smallest mobility, while Cd^{2+} and Cu^{2+} ions exchange with their counterparts outside the membrane and exhibit relatively larger mobility. With increasing concentration of Pb^{2+} ions, the favorable binding sites in the membrane tend to be saturated and exchange occurs for the excess Pb^{2+} ions. The presence of competitive ions has negligible effect on the residence of Pb^{2+} ions in the membrane. The exchange efficacy of Na-ETS-10 for the three heavy metal ions follows the order $Pb^{2+} > Cd^{2+} > Cu^{2+}$, consistent with experimental observation.

1. Introduction

Over years a substantial amount of contaminants have been introduced into water, such as heavy metal ions Cu^{2+}, Cd^{2+} and Pb^{2+}. These ions are hazardous to environment, toxic and carcinogenic to human being. As a consequence, it is of central importance to remove them from wastewater. A technologically feasible and cost-effective treatment is through ion exchange in inorganic materials. Due to the high thermal stability and resistance to radiation, inorganic ion exchangers are superior to organic resins. In addition, they possess uniform pore structures and offer pronounced characteristics as a combination of ion exchange and molecular sieving. In the past, natural and synthetic zeolites have been used as exchangers for the removal of heavy metal ions [1]. With increasing aluminum content in a zeolite, the number of non-framework cations increases and the capability for ion exchange is thus enhanced. However, the trade-off between structural instability and exchange capability restricts the performance of zeolite, furthermore, the small pore sizes in zeolite only allow slow ion exchange [2].

Recently, titanosilicates have attracted considerable attention, particularly, for their distinct ability in highly selective removal of ions [3,4]. Formed by Ti octahedra and Si tetrahedra, titanosilicates consist of non-traditional primary building units. Compared to the traditional aluminosilicate zeolites, titanosilicates open new avenue for the development of novel porous structures with unique active sites. As a typical titanosilicate material with a wide channel of approximately 8 Å, ETS-10 (Engelhard TitanoSilicate No. 10) has been the subject of interest because of its fast and high sorption capacity towards heavy metal ions [5]. A number of experimental studies have been reported on the removal of heavy metal ions by ETS-10. The major objective of these studies was to determine equilibrium adsorption capacity or to examine adsorption kinetics [2,3,5,6]. Kuznicki and Thrust reported that ETS-10 and ETAS-10 (aluminum-substituted ETS-10) have an extraordinarily rapid adsorption rate toward Pb^{2+}. The concentration of Pb^{2+} was observed to reduce to a negligible amount from 2000 ppm in a very short contact time at a liquid-to-solid ratio of 100:2.4 (g/g) [7]. Lv et al. extensively investigated the adsorption properties of ETS-10 and modified ETS-10 toward heavy metals under various conditions [8–10]. From batch adsorption experiments at pH≈5, the uptake of heavy metal in ETS-10 was found to occur from both ion exchange and chemisorption, similar to the mechanism prevalent in zeolites. The maximum adsorption capacities of different divalent ions were analyzed based on ionic hydration energies [8]. The competitive adsorption ability for Pb^{2+}, Cd^{2+} and Cu^{2+} binary and ternary systems was identified to be $Pb^{2+} > Cd^{2+} > Cu^{2+}$ and a high selectivity of Pb^{2+} was observed [9]. From column regeneration study, it was reported that 93% of sorbed Pb^{2+} ions can be regenerated, which reveals that the dominant contribution to ion removal is through ion exchange [10].

With tremendous growth of computational power, molecular simulations have increasingly become robust tool in material

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* Corresponding author. Tel.: +65 65165083; fax: +65 67791936.
E-mail address: chejj@nus.edu.sg (J.W. Jiang).

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science and engineering. Microscopic pictures from simulations can provide the underlying physics and subsequently guide the rational design of materials. A wealth of simulation studies have been reported to exploit many practically important issues in aluminosilicate zeolites [11]. These include the distribution of cations [12], the interplay with water molecules in hydrated systems [13], and the role of water in ion exchange and mobility [14]. Handful of simulation studies have been carried out in ETS-10, primarily focused on the information of non-framework cations. Knowing cation siting and energetics in porous materials is critical to adsorption, diffusion and catalytic properties. Using Monte Carlo (MC) simulation, Anderson et al. examined the interaction of guest molecules in ETS-10 [15]. In their study, knowledge of the cation distribution was incomplete; consequently, the influence of cation on interaction was evaluated qualitatively. Using MC packing algorithm implemented with CVFF force field, Grillo et al. identified cation locations in both K-ETS-10 and Na-ETS-10 [16]. Identical cation sites were observed for Na^+ and K^+, but with different electrostatic energies. It was also shown that the electrostatic interaction of K^+ with ETS-10 is more favored than Na^+. Ching et al. performed the first-principles density-functional theory calculations to determine the electronic structure of ETS-10 and cation location sites [17]. Based on the interatomic separation and total energy, they concluded that the cations are unlikely to sit in either 12-ring pore (due to the long distance from Ti–O chain) or 3-ring pore (due to the spatial restriction). All four possible cation sites from their work are in the 7-ring channel at varying distances from Ti atoms, in which the intermediate distance is the most favorable. Their study also demonstrated the mechanical stability and rigid nature of ETS-10 from the bond-order calculations, which supports the rigid framework model used in the present work. From ^{23}Na 3Q MAS NMR and lattice energy minimization, Anderson et al. proposed that five types of cation sites exist in ETS-10, with the fifth type located in the 12-ring (main) channel [18]. Recently we investigated the interplay of cations and non-polar/polar sorbates in Na-ETS-10. The predicted adsorption isotherms of methane and water in Na-ETS-10 were in good agreement with the literature data. Water has a substantially stronger interaction than methane with the cations, which leads to cation rearrangement and change of dynamic behavior upon increasing water loading [19].

To our best knowledge, no molecular-level information is currently available on ion exchange in ETS-10. Nevertheless, this information is essential to exploit the suitability of ETS-10 for large-scale ion exchange process and for the rational design of high-performance adsorbents for water treatment. The present study is aimed to use molecular dynamics (MD) simulations to explore the time evolution of ion exchange process in a Na-ETS-10 membrane for heavy metal ions Pb^{2+}, Cd^{2+} and Cu^{2+}. In Section 2, the models and interaction potentials used for Na-ETS-10 and metal ions are described briefly. The simulation methodology is introduced in Section 3. This includes the setup of simulation system, the choice of ion concentration, and the simulation detail. In Section 4, first we present the density profiles of ions in the membrane, which informs the spatial distribution of ions. Then, we consider the exchange rates of ions inside and outside the membrane by estimating the residence times of ions in the membrane. In addition, the diffusion of ions in the membrane and the radial distribution functions of ions are examined. The key remarks are concluded in Section 5.

2. Models and potentials

The membrane consisted of four (2 × 2 × 1) unit cells of Na-ETS-10 and was located at the center of a simulation box. Fig. 1a shows the simulation box along the *x*-direction before simulation (*t* = 0). Each side of the membrane was in contact with ionic solution compartment. The overall dimensions of the simulation box were 59.40 Å × 29.70 Å × 27.08 Å. A trial simulation with a thicker membrane of eight (4 × 2 × 1) unit cells gave qualitatively similar results. As in our recent work, the Na-ETS-10 membrane consisted of polymorph-A structure with lattice parameters $a = b = 14.85$ Å and $c = 27.08$ Å [15]. A unit cell of Na-ETS-10 consists of 16 Ti atoms, 80 Si atoms, 208 O atoms, and 32 Na^+ non-framework cations for electroneutrality. The coordinates of Ti, Si and O atoms were adopted from the experimental crystallographic data of Anderson et al. [15]. The partial charges of the framework atoms were estimated from density-functional theory (DFT) calculations on a fragmental cluster via Dmol^3 [20]. The cluster chosen was half of the ETS-10 unit cell, in which the Si- and O-bonds were saturated separately by hydroxyl group and hydrogen atoms. The DFT calculations was performed with gradient-corrected approximate correlation functional BLYP and the effective core potentials. In the latter, pseudo-potentials were used to represent the potential of nucleus and core electrons experienced by the valence electrons. This allows only the softer valence electron wave-functions to be explicitly treated, which is usually the portion that controls the chemistry and can significantly reduce computational cost. The double-ζ numerical polarization (DNP) basis set was used with a fine convergence threshold (10^{-6}). DNP basis set incorporates *p*-type polarization into hydrogen atoms and *d*-type polarization into heavier atoms, and is comparable to 6-31G(*d*, *p*) Gaussian-type basis

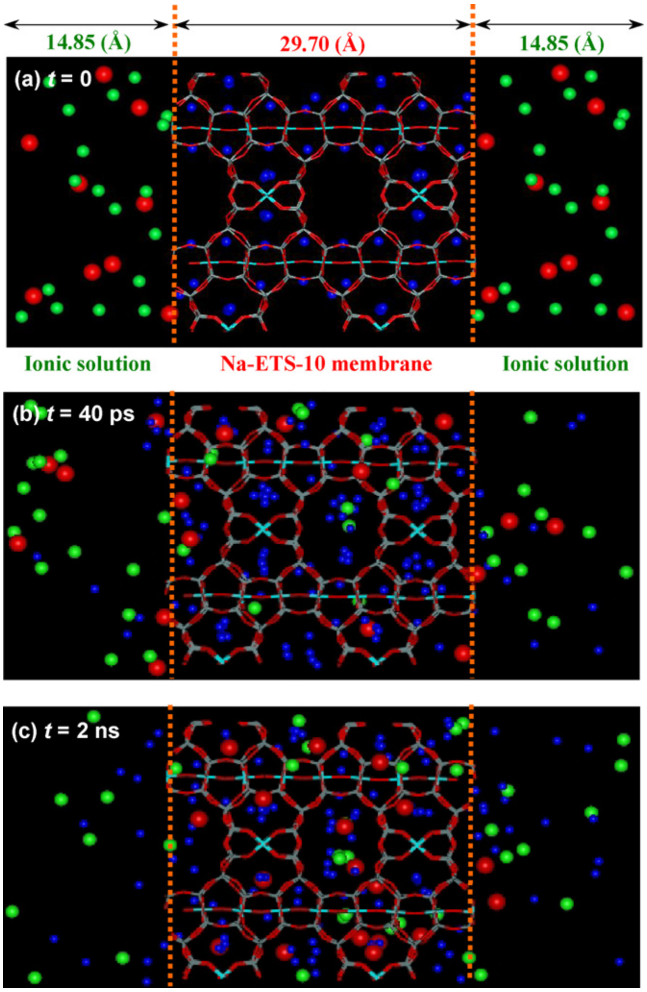

Fig. 1. Simulation system consisting of one Na-ETS-10 membrane and two ionic solution compartments in a single-component system (Cu^{2+}) at different times (a) *t* = 0, (b) *t* = 40 ps and (c) *t* = 2 ns. Ti: cyan; Si: grey; O: red; Na^+: blue balls; Cu^{2+}: red balls; Cl^-: green balls.