

Bifunctionalized mesoporous molecular sieve for perchlorate removal

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Introduction

Perchlorate (ClO_4^-) has a high reduction potential and is widely used as a strong oxidizing agent. Ammonium perchlorate is used as an oxidant in a solid propellant for rockets and missiles, fireworks, an ingredient of matches, or a component of air bag inflators. Despite these useful applications, perchlorate can hinder the synthesis of thyroid hormones and any kind of disruption in thyroid hormone levels can cause an intellectual and mental retardation [1]. Unfortunately, perchlorate ions cannot be effectively removed by conventional technologies such as carbon filtration, sedimentation, coagulation and catalytic reduction, because it is nonvolatile and highly soluble in an aqueous solution [2]. A biological decomposition has been the most widely investigated method for a perchlorate treatment. Chemical oxidation, tailored granular activated carbon (GAC), reverse osmosis (RO) membrane and nanofiltration have also been studied for a perchlorate removal [1–4].

Recently, an anion exchange using highly selective resins has been proven to be one of the most effective technologies for removing highly stable anions including the perchlorate ion, especially at low concentrations [5]. Other competing anions such as chloride, sulfate, or nitrate in groundwater are at 2 orders of a magnitude higher concentrations than perchlorate [1]. Competing anions have the selectivity delta (Δ , relative to chloride) for specific anion exchange resins.

For the strong base anion exchange resin (quaternary) the filtrate was analyzed by an ion chromatography system (DX-600, Dionex, CA) equipped with an IonPac AS-16 analytical column and AG-16 guard column. The sample size was 1.0 mL, the flow rate was 1.0 mL min⁻¹, and the eluent was 35 mM sodium hydroxide. The perchlorate detection limit was 4 µg L⁻¹ with all the calibration curves having $r_2 > 0.99$ based on standards of 5, 10, 20, 50, and 100 µg L⁻¹.

To obtain the initial sorption rates and the sorption capacities at an equilibrium, all the kinetic data was fitted to the pseudo second-order kinetic model [18]. This kinetic model is quite reliable for many chemisorption reactions of heterogeneous materials. The kinetic rate equation can be expressed as follows:

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where, q_{eq} (mmol g⁻¹) is the adsorption capacity at an equilibrium, q_t is the amount adsorbed at time t (min), and k_2 (g mmol⁻¹ min⁻¹) is the equilibrium rate constant of the second-order sorption. And, the initial sorption rates (v_0 , mmol g⁻¹ min⁻¹) were calculated with the following equation:

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In order to evaluate the perchlorate uptake capacity of each medium, the distribution coefficient for an adsorption of perchlorate, K_d (mL g⁻¹) was also calculated as follows [5,9,13]:

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Results and discussion

X-ray diffraction

The XRD patterns of SBA-15 and ammonium functionalized

SBA-15 with different ratios of TSPMC and TSPBC are shown in Fig. 1. For the XRD pattern of SBA-15, the main peak appears at 0.916° of 2θ and two small peaks appear at 1.60° and 1.84° , respectively. These peak positions match well with the patterns of SBA-15 in Jang et al. [14], representing that the SBA-15 silicate was successfully synthesized. The obtained $d(100)$ spacing and unit cell parameter (a_0) from Fig. 1 are summarized in Table 1. Compared to plain SBA-15, the peak intensity of the ammonium functionalized SBA-15 at $d(100)$ decreased. Furthermore, the peak intensities of the bifunctionalized SBA-15 were lower than those of the monofunctionalized SBA-15. The decrease in the intensity of the (100) peak may be attributed to some extent to the heterogeneities in the ordered hexagonal phase, or the flexibility of the silica framework resulting from the strain of the incorporated ammonium functional groups [9,20,21]. However, there was no phenomenon of complete collapses in the pore structures. Similar phenomenon of pore disorders in mesopore structures have been observed in other studies on the functionalization of silica mesoporous materials [13,14,22]. When 4 mmol of TSPMC was impregnated into SBA-15 (MB40), the position of the (10 0) peak shifted from 0.916° to 0.932° , and the $d(100)$ spacing decreased from 9.64 nm to 9.47 nm. This indicates that the presence of TSPMC affected the shrinkages of the cell dimension for the resultant mesoporous media [23]. A decreasing trend of the unit cell parameter (a_0) might be caused by a grafting of the Si-OR groups of TSPMC onto the mesopores of SBA-15 [24]. As the amount of TSPMC decreased and that of TSPBC increased, the positions of the (100) decreased so that the unit cell increased from 10.9 nm (MB40) to 11.3 nm (MB13). Thus, it can be deduced that an expansion of the unit cell might be caused by a partial dissolution of the mesopore frameworks that occurred from the decomposition of Si-OR on the surface of Si-OH.

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