Colloids and Surfaces A: Physicochem. Eng. Aspects 468 (2015) 114–121

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Adsorption of perchlorate from aqueous solutions by anion exchange resins: Effects of resin properties and solution chemistry

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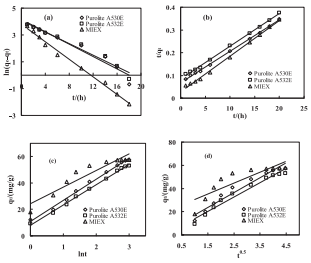
HIGHLIGHTS

- The comparison of perchlorate sorption rate and sorption capacity among the three resins has investigated.
- Both Purolite A530E and Purolite A532E resin showed superior perchlorate selectivity than MIEX.
- Equilibrium isotherms of perchlorate adsorption by the three resins were investigated.
- Thermodynamics of perchlorate adsorption by the three resins were calculated.
- The impacts of independent variables on perchlorate sorption by the three resins were analysed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 September 2014
Received in revised form
24 November 2014
Accepted 30 November 2014
Available online 12 December 2014

Keywords:
Perchlorate (ClO_4^-)
Perchlorate selective resin
Magnetic ion exchange resin (MIEX)
Sorption kinetics
Sorption isotherm

ABSTRACT

In this study, the perchlorate sorption behaviors of three various representative anion resins were systematically investigated with respect to sorption kinetics, equilibrium capacity, perchlorate selectivity, thermodynamics and isotherms. Results showed that the equilibrium capacity of the three investigated resins followed the order of Purolite A530E≈magnetic ion exchange resin > Purolite A532E due to the effect of structure type, while magnetic ion exchange resin (MIEX) reached the equilibrium much faster than Purolite A530E and Purolite A532E, which can be attributed to its smaller particle size and larger surface area. Furthermore, the two Purolite resins showed superior perchlorate selectivity than MIEX resin because of matrix and functional groups. The adsorption kinetics for each of three selected resins fitted best with the pseudo-second-order model, indicating the adsorption process was controlled by chemical sorption. While the fitting of intra-particle model implied that intra-particle diffusion was not the only rate-limiting step of the whole process. The isotherm data can be best described by the Freundlich isotherm and the value of intensity of adsorption was larger than 1, suggesting the process was heterogenous and favorable adsorption. The negative ΔG° manifested that the adsorption of perchlorate by each of the three resins was a spontaneous process, and the positive indicated it was also an endothermic and entropy driven process. Besides, the effects of independent variables on the perchlorate sorption of the three resins were also evaluated completely. Results suggested that the removal of perchlorate increased with the increase of resin dosage and temperature for each of the three resins, and the sorption process was nearly independent of solution pH in a wide range of 4–10 for each of the resins.

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http://dx.doi.org/10.1016/j.colsurfa.2014.11.062
0927-7757/

1. Introduction

In recent years, perchlorate has been recognized as a major inorganic contaminate interfering with the uptake of iodine into the thyroid and even inhibiting the development of the skeletal system and the central nervous system of infants [1]. Studies have proved that perchlorate can be generated naturally in fertilizers and produced atmospherically [1,2]. Also, it has been widely used as an oxidizer in explosives and solid propellants for rockets and missiles, and its improper disposal has resulted in the release of perchlorate into the environment [3,4]. By far, it has been detected in various water bodies, including sewage, surface water, groundwater and even bottled water [5–8]. Because of its global distribution and potential harm to human beings, perchlorate has received a current worldwide concern and also been categorized in the drinking water contaminant candidate list by the U.S. EPA [9]. In 2008, the US EPA has set an Interim Drinking Water Health Advisory level of 15 μg/L [10].

Since perchlorate has non-volatility, high solubility and chemical stability, the removal of perchlorate from water is very difficult [11,12]. Of all the technologies available for perchlorate removal, ion-exchange has been identified as the most effective and attractive technology for light-polluted drinking water of perchlorate due to its effective and convenient operating conditions and high capacity [13,14]. Various kinds of ion exchangers of different matrices and functional groups have been developed and used for perchlorate treatment. Xiong et al. compared perchlorate sorption behaviors of various classes of ion exchangers and observed that styrenic resins can offer much higher perchlorate capacity than polyacrylic resins because the hydrophobic nature of polystyrene matrix and lower hydration energy of perchlorate enhanced Lewis acid–base interaction [15]. Gu et al. developed perchlorate selective strong-base anion exchange resins with two quaternary ammonium groups, one with a long alkyl chain for high selectivity, and the other one with a short alkyl chain for enhanced reaction kinetics [16]. Based on the porosity of the resins, perchlorate selective bifunctional resins can be categorized into gel and macroporous types. The pores of gel resins are formed only when the resins are highly swollen in water and the size of the pore is very small (ranging between 0.0005 and 0.005 μm) [13,17]. Besides, the gel resins are translucent and have a low crosslinking degree (about 4–10% crosslinking) [18]. While the macroporous resins have permanent large pores (the average size of these pores is about 0.6 μm) and have an average crosslinking degree of 20–25% [18–20]. In comparison with the gel type, the macroporous resins are less susceptible to bio-fouling, yet they have lower capacity. Generally, the regeneration of such perchlorate selective resins is a great challenge and most of these resins are disposed by incineration or landfill after one time use [3,14,21,22]. Compared with conventional anion exchange resins, the magnetic ion exchange resin (MIEX) can solve the problem of leaching and realize separation easily due to iron oxide incorporated into the matrix [23]. Besides, the MIEX resin has large external surface area due to its small particle size (150–180 μm, 2–5 times smaller than conventional resins), allowing for a rapid adsorption kinetic and a high recover rate (>99.9%) [24]. Tang et al. investigated the perchlorate adsorption characteristics of the magnetic ion exchange resin (MIEX) and found that it can remove perchlorate with a wide pH range of 4.0–9.0 quickly and effectively, but several coexist anions can significantly reduce the removal of perchlorate [25].

Although plenty of research has been dedicated to ion exchange technology for perchlorate removal, the perchlorate sorption behaviors of various ion exchange resins have not been sufficiently and systematically investigated. Accordingly, the overall objective of this research was to systematically compare perchlorate adsorption performance of the two types of perchlorate selective resins Purolite A530E and Purolite A532E and the newly developed ion exchange resin MIEX, discussing the effects of matrix, functional groups and porosity on perchlorate sorption of anion exchange resins. The specific objects were to (1) evaluate the effects of experimental factors including contact time, resin dosage, initial solution pH, co-existing anions and temperature on perchlorate removal, (2) interpret the adsorption kinetic and isotherm patterns of perchlorate on each of the three resins, (3) analyze the thermodynamic process of perchlorate sorption on each of the three resins, and (4) elucidate the effects of resin properties on perchlorate sorption.

2. Experiment

2.1. Experimental materials

2.1.1. Adsorbents

Three strong-base anion-exchange resins were obtained from Purolite Int. Ltd. (A-530E, A-532E) and Orica Watercare of Victoria (MIEX), respectively. And their salient properties are presented in Table 1. Before use, all resins were rinsing with 1 mol/L hydrochloric acid, deionized water, 1 mol/L sodium hydroxide and deionized water by turns, then air-dried at 313 K.

2.1.2. Chemicals and reagents

All chemicals were supplied by Sinopharm Chemical Reagent (Shanghai, China) as analytical grade reagents. Deionized water was used to prepare all solutions throughout the experiments. And solutions of perchlorate, sulfate, carbonate and chloride were prepared with $NaClO_4$, Na_2SO_4, Na_2CO_3 and NaCl, respectively. The 1000 mg/L standard stock solution of perchlorate was prepared by dissolving accurately weighed sample of $NaClO_4$ in deionized water. A series of standard perchlorate solution were prepared by appropriate dilution of the stock solution.

2.2. Experimental methods

2.2.1. Kinetic tests

Batch kinetic tests were carried out in 250 mL capped glass tubes. In each test, 0.03 g anion exchange resin was brought in contact with a 200 mL solution with 10 mg/L ClO_4^- at 120 rpm and 298 K using a thermostat orbital shaker for 20 h, and the pH value of the perchlorate solution was kept original without any adjustment. At predetermined time intervals, ~4 mL samples were taken and filtered by 0.22 μm membrane for analysis.

2.2.2. Batch adsorption isotherm tests

Batch sorption isotherm experiments were conducted at different initial perchlorate concentrations ranging from 2.5 mg/L to 15 mg/L. Fixed dosage (0.03 g) of various resins was exposed to a set of 200 mL perchlorate solution with different initial concentrations at 120 rpm and 298 K in the thermostat orbital shaker. The solution samples were taken after 20 h and filtered by 0.22 μm membrane for analysis.

2.2.3. Independent variable tests

Independent variable experiments were carried out to investigate the impact of resin amount (0.01–0.05 g), initial pH of solution (4–10) and temperature (288–308 K) on perchlorate sorption. Effect of each independent parameter was evaluated by varying this parameter within a certain range and keeping other parameters constant. The initial pH of each solution was adjusted to the desired value with 0.1 mol/L NaOH and HCl. The detailed experimental procedures were similar to the batch isotherm tests.