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Preparation and characterization of functionalized poly(vinyl chloride) membranes for selective separation of perchlorate from water

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ABSTRACT

Perchlorate permselective membranes were synthesized and characterized in this study. The membrane with a thickness of ~300 μm was prepared with polyvinyl chloride (PVC) and quaternary ammonium salts in solvent under room temperature. Among the 12 different quaternary ammonium salts, methyltributylammonium chloride (MTBA) showed superior perchlorate permselectivity due to in part to the favorable steric effect of the alkyl chain length. In addition, results from contact angle measurements indicated that modification with quaternary ammonium salts rendered the membranes hydrophobic. Results from Fourier transform infrared (FTIR) spectrum analysis showed that the functional groups responsible for ion exchange were incorporated in the membrane matrix successfully. The surface roughness, averaged pore radius and ion exchange capacity of the MTBA membrane were 3.23 ± 2.58 (nm), 83.6 (Å) and 0.12 (meq/g), respectively. The rate constants of anions transport across the membranes were calculated. In the presence of an electric field, about 60% of perchlorate was separated from the solution while only less than 9% of other anions, specifically, nitrate, sulfate and bicarbonate passed through the membrane under otherwise identical operation conditions simultaneously.

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1. Introduction

Perchlorate is an emerging inorganic contaminant in the United States [1]. It has been reported that perchlorate is present at detectable concentrations in public drinking water supplies affecting more than 11 millions people in the United States [2]. Both natural and anthropogenic origins are contributing sources of perchlorate in the environment. Naturally occurring perchlorate in terrestrial soils has also been observed at a few locations in Texas [3]. Anthropogenic source comes mainly from production and use of rocket fuel, fireworks, and explosives, of which ammonium perchlorate is a major component. According to U.S. Environmental Protection Agency (US EPA), the minimum detection level of perchlorate for data collected under the Unregulated Contaminant Monitoring Rule (UCMR) was 4 ppb. In Japan and United States, perchlorate contaminated milk, forage crops, and lettuce have been reported due to bioaccumulation mechanisms [4–6]. Through the intake of perchlorate containing foods or waters, perchlorate ions can be transported to the thyroid gland and cause adverse effects on the metabolism and production of thyroid hormones [7,8]. The National Academy of Science has recommended a perchlorate reference dose (RfD) of 0.7 μg/kg-day [9]. Perchlorate is already regulated in California and Massachusetts drinking water with the maximum contaminant level (MCL) of 6 and 2 μg/L, respectively [10,11]. In February 2011, the U.S. EPA expressed government's intend to establish a national primary drinking water regulation (NPDWR) for perchlorate [12]. EPA expects to issue a proposal in the end of 2014 and a final rule in September 2015 [13]. Therefore, methods that are effective in eliminating perchlorate from water are needed.

Due to the highly soluble, non-volatile and kinetically inert nature of perchlorate ion in water, [14,15] the elimination of perchlorate from contaminated water is a challenging task. Many efforts have been made to develop efficient techniques for the removal of perchlorate from water. Among the various chemical and physical processes, granular activated carbon (GAC) [16–20] and ion exchange resins [21,22] have received considerable attention as methods for perchlorate removal. Proper functionalization of GAC or ion exchange resins can improve the perchlorate adsorption capacity and selectivity of these materials. It has been reported that GAC modified with cationic quaternary ammonium surfactants [20] and ammonium [16] can increase its perchlorate adsorption capacity by 8 and 4 folds, respectively. Gu et al. [22] reported the removal of perchlorate using bifunctional anion resins (WBR109 and Purolite A530E,), and

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significant perchlorate selectivity and improved reaction rate in the presence of 0.1–10 mM of sulfate. Xiong et al. [23] studied perchlorate adsorption and regenerability of five different ion exchange materials, including strong-base anion (SBA), weak-base anion (WBA), bifunctional resin, polymeric ligand exchangers (PLEs), and an ion-exchange fiber (IXF) and reported that IXF resins exhibited rapid removal of perchlorate in 90 min with efficient regeneration (about 85% of exchange capacity can be recovered). Kim et al. [24] studied the removal of perchlorate using ammonium mono- or bifunctionalized mesoporous molecular sieve (MMS) and reported that the quaternary ammonium bifunctionalized MMS exhibited 1.14–1.88 times greater adsorption capacity and faster removal of perchlorate than other mono-functionalized MMS. Granular ferric hydroxide (GFH) was reported to be effect for perchlorate removal from aqueous solutions at room temperature; the maximum chlorate adsorption capacity of GFH was about 20 mg/g at pH 6.0–6.5 [25]. Fang and Chen [26] compared the performance of raw and oxidized carbon nanotubes (CNTs) on perchlorate adsorption. The oxidized CNTs showed better perchlorate adsorption capacity (3.55 mg/g) than raw CNTs (1.50 mg/g) due to the presence of oxygen-containing functional groups, which provide additional perchlorate adsorption sites. Recently, Lakshmi and Vasudevan studied the adsorption of perchlorate on graphene and reported that graphene achieved 99.2% perchlorate removal in the pH range between 6.0 and 8.0 [27]. Although adsorption process most effective for the removal of perchlorate at trace concentration in water, the process requires regeneration of the adsorbents or ultimate disposal of perchlorate laden spent adsorbent materials. Furthermore competitive and inhibitory adsorption of other anions against perchlorate can be technology barrier for adsorption process.

Membrane technology such as ultrafiltration (UF) and nanofiltration (NF) has been used to remove perchlorate from water. Yoon et al. [28,29] reported that increase in pH and conductivity can render NF and UF membrane surface negatively charged, which led to greater perchlorate rejection. The UF membrane modified with cationic surfactants also showed enhancement in perchlorate rejection from synthetic water due to the decrease in pore size of the membrane [30]. Roach et al. [31,32] studied the removal of perchlorate from aqueous solution by a colloid-enhanced ultrafiltration (CEUF) method in the presence of poly(4-vinylpyridine) and poly(diallyldimethylammonium) chloride and reported greater than 95% of perchlorate (initial concentration of 10.3 ppm) removal in the presence of competition anions. Xie et al. [33] studied the effect of chitosan on the separation of perchlorate using UF process and reported 92% perchlorate removal at pH 4.3 and initial perchlorate concentration of 10 mg/L. However, lack of selectivity and use of chemicals (polymers) make the method unattractive.

Electrodialysis (ED) technique is a promising alternative for ion separation from water since the technology requires no or low addition of chemical reagents while maintaining high degree of robustness toward mass loading rate and other operational conditions. ED has been used for brackish and sea water desalination and the production of table salts, acids and bases in the chemical and food industry [34]. Sata and Wang studied the removal of perchlorate at high silica concentrations using a pilot electrodialysis reversal (EDR) process and reported percent removal of 70–97% depending on the initial perchlorate concentration and system configuration, i.e., number of treatment stage [35]. However, competition against perchlorate by other majoranions in water is inevitable using conventional ED process. Therefore, there is need to improve the selectivity and effectiveness of the membranes during conventional ED applications.

There have studies on improving the membrane selectivity toward cations [36] or anions [37]. Eyal and Kedem attempted to improve the nitrate permselectivity of membranes by incorporating polyfunctional groups such as tertiary and quaternary ammonium groups [35]. Sata et al. [38] developed ion exchange membranes with anion exchange groups of different hydrophobicities for nitrate ion removal from groundwater by electrodialysis. The permselectivity of membrane for nitrate increases with increasing chain length of the alkyl groups of the anion exchange groups. Kesore et al. [39] used carboxylic group modified anion exchange membrane for enhancement of nitrate selectivity. To the best of our knowledge, no study has been done on developing perchlorate permselective ion exchange membrane.

In order to selectively separate perchlorate from water, it is necessary to prepare membranes that are permeselective to perchlorate. It is hypothesized that by modifying the ion exchange characteristics of membrane with different types of functional groups, specifically quaternary ammonium salts, and by manipulating the chemical composition and the physical properties such as thickness and hydrophobicity, it is possible to enhance the permselectivity of perchlorate over that of other major anions in water such as nitrate, bicarbonate, and sulfate. The objective of this study was to synthesize and test plastic membranes modified with quaternary ammonium salts in terms of perchlorate permselectivity.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals were either of analytical or reagent grade, or the highest purity available from suppliers. All aqueous solutions were prepared with de-ionized, distilled water. Tetrahydrofuran (THF, HPLC grade, Fisher Scientific, Fair Lawn, NJ, USA), Polyvinyl chloride (PVC, molecular weight is around 60,000–150,000 g/mol, MP Biomedicals, Solon, OH, USA) and Tributyl *O*-acetylcitrate (TBOAC, 98%, Aldrich, St. Louis, MO, USA) were used for the synthesis of the membrane. Tetramethylammonium chloride (TMA, 98+%) tetraethylammonium chloride (TEA, 99%), tetrapropylammonium chloride (TPA, 94%), benzyldimethylhexadecylammonium chloride (BDMHA, 97%), benzyltributylammonium chloride (BTBA, 98+%), methyltributylammonium chloride (MTBA, 98%) and methyltrioctylammonium chloride (MTOA) were purchased from Acros organics (NJ, USA). (n-Octyl)trimethylammonium bromide (OTMA, 97%), (1-hexyl)trimethylammonium bromide (HTMA, 98%) and (1-Dodecyl)trimethylammonium bromide (DDTMA, 97%) were purchased from Alfa Aesar (Ward Hill, MA, USA). Cetyltrimethylammonium bromide (CTMA, 98–101%) and benzyltrimethylammonium bromide (BTMA) were obtained from Avocado Research Chemicals (Heysham, UK).

The certified standard anions solution (1000 mg/L) of nitrate (NO_3^-), perchlorate (ClO_4^-) and sulfate (SO_4^{2-}) were purchased from SPEX CertiPrep (Metuchen, NJ, USA). Sodium perchlorate (ACS reagent, >98%, Sigma-Aldrich, St. Louis, MO, USA), sodium bicarbonate (analytical grade ACS, 99.7%), sodium chloride (reagent grade ACS, >99%), and sodium nitrate (analytical grade ACS, >99%) from Acros Organics, sodium carbonate (HPLC grade), and sodium sulfate (certified ACS) from Fisher Scientific were individually dissolved into deionized water to prepare stock solutions. NaOH (50% w/w, Fisher Scientific, Fair Lawn, NJ, USA) was used as mobile phase solution in ion chromatography analysis.

2.2. Preparation of membranes

Membranes were prepared by dissolving a given amount of polyvinyl chloride (PVC), TBOAC, and quaternary ammonium salts in 10 mL of tetrahydrofuran (THF) solvent under room temperature at weight percentage of 34.5% – 59.8% and 5.7%, respectively. TBOAC is regarded as a relatively nontoxic material than phthalate plasticizer

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