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Research paper

Novel adsorptive mixed matrix membranes by embedding modified montmorillonite with arginine amino acid into polysulfones for As(V) removal

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ABSTRACT

Neat and arginine modified montmorillonite, Mt and Mt-Arg, were embedded into polysulfone (PSf) to prepare adsorptive mixed matrix membranes (AMMMs) for arsenate removal from contaminated water. Prepared membranes were characterized by FE-SEM, XRD, AFM, pure water flux and contact angle measurement. Equilibrium adsorption capacity and adsorption kinetic of AMMMs were determined using batch adsorption experiments. In addition, dynamic adsorption and regeneration studies were also investigated in dead-end filtration setup. Adsorption kinetic of arsenate was found to follow pseudo-second-order kinetic model and equilibrium data showed good correlation with the Langmuir model for AMMMs. The obtained results revealed that the arsenate adsorption was favorable for PSf/Mt-Arg. Regeneration capability of the Mt-Arg embedded PSf membranes was assessed by conducting ten cycles of adsorption-desorption experiments. Arg modified Mt provides interesting properties to adsorb As(V) from water in neutral pH and desorb in alkaline condition; pH = 9, due to negative side group. The obtained results confirmed the applicability of the prepared PSf/Mt-Arg in As(V) removal for multiple cycles.

1. Introduction

Arsenic contamination of drinking water is one of the most serious concerns mainly in developing countries. The most common species of arsenic exist as inorganic oxyanions of arsenite, As(III), or arsenate, As(V). Arsenate is the dominant species in surface water due to the high redox potential while arsenite is usually found in anaerobic groundwater conditions (Ren et al., 2014). The major health concern of arsenic exposure through drinking water is the risk of skin, lung, liver and lymphatic cancer. Due to these health hazards associated with arsenic contaminated water, the World Health Organization (WHO) has changed the maximum contaminant level (MCL) of arsenic from 50 ppb to 10 ppb (Sogaard, 2014). Various treatment technologies including precipitation (Harper and Kingham, 1992), coagulation (Balasubramanian and Madhavan, 2001; Baskan and Pala, 2010; Parga et al., 2005), ion exchange (Pakzadeh and Batista, 2011), adsorption (Mohapatra et al., 2007; Pena et al., 2006; Yua et al., 2013) and membrane filtration (Banerjee et al., 2008; Chutia et al., 2009; Guan et al., 2009; Mandal et al., 2011; Manna and Ghosh, 2007) have been extensively studied for arsenic removal. All these methods have drawbacks, especially regarding efficiencies, costs, lifetime and regeneration capability. For example, separation of adsorbents from filtrate increases the overall cost of treatment. Severe pressure drop and long diffusional path length are the main problems in column adsorption process (Chatterjee and De, 2014; Ladhe et al., 2009; Lin et al., 2013; Sogaard, 2014; Zheng et al., 2011). Nanofiltration (NF) membranes require high operational pressure and costly membranes in comparison with low pressure processes such as microfiltration (MF) and ultrafiltration (UF) membranes. However, MF and UF membranes could not remove arsenic, mainly due to their larger pore sizes. Therefore, researchers have focused on the development of effective and low-cost technologies for arsenic removal from water resources. The adsorptive membrane can be as an attractive alternative technique for removal of small pollutants from water. Adsorptive membranes are a kind of MF/UF membranes developed by chemically coupling of functional groups to the internal surface of membranes or by embedding the inorganic adsorptive materials into porous polymeric matrix (Niedergall et al., 2013; Yin and Deng, 2015). The membranes

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fabricated by second route, which are known as adsorptive mixed matrix membranes (AMMMs), combine the selectivity of inorganic adsorptive materials with the manufacturing ease and the flow behavior of MF/UF membranes. The important issue associated with AMMMs is embedding proper inorganic materials as adsorbent with high adsorption capacity, high selectivity, low cost and easy regeneration (Ladhea et al., 2009). To prepare highly efficient AMMMs for arsenic removal, investigators have used several adsorbents such as iron-manganese binary oxide (Gohari et al., 2013), zirconia (Zheng et al., 2011), titanate nanotubes (Gohari et al., 2015), incorporated in polymer matrix. The serious drawbacks of the reported additives are the release of toxic metal oxides in the permeate water along with their high cost. On the other hand, this issue can be well addressed, if a naturally abundant material is used to be incorporated into polymer matrix. In this practice, Chatterjee et al. (Chatterjee and De, 2015) used laterite as a natural additive to fabricate adsorptive mixed matrix membrane for arsenic removal; however, it suffers from low adsorption capacity. As one of widely available and abundant materials, clay minerals can be used as additive due to their low-cost, large surface areas and chemical-mechanical stability (Bae et al., 2000; Bagherifam et al., 2014; Liu and Zhang, 2007; Naseem and Tahir, 2001). Natural clay mineral displays relatively low adsorption capacity on anionic pollutants such as arsenate due to the existence of net negative charge on the surface (Mohapatra et al., 2007; Yassine et al., 2016). However, modified clay minerals have been explored as efficient adsorbents for the removal of As(V) from aqueous solution (Dousová et al., 2009; Li et al., 2012; Ren et al., 2014). Among the modified clay minerals, amino functionalized organoclay is considered as one of the most effective adsorbents that has attracted great attention for the removal of anionic pollutants owing to its net positive surface charge (Lee et al., 2011; Pan et al., 2016). In this regard amino functionalized clay mineral was used for incorporation into polymer matrix.

The amino acids with amine and carboxylic groups contain both positively and negatively charged chemical groups. Arginine; Arg with two positive amine groups in $pH < pH_{PI}$, can modify Mt with a simple cation exchange method and adsorb anionic pollutants with other positive amine groups. Di-cationic, cationic, zwitterionic and anionic states are four different forms of Arg in different pH of solution. Due to the strong negatively charged chains in zwitterionic and anionic states, the Mt modified with Arg has good potential to regenerate adsorbed anionic arsenate through electrostatic repulsion over pH_{PI}. Mt modified with Arg was embedded in porous polysulfone (PSf) polymeric matrix due to its low-cost, availability, high mechanical strength, thermal and chemical stabilities, resistance over wide range of pH, as well as easy processability (Anadão et al., 2010; Choi et al., 2006; Fan et al., 2008; Ganesh et al., 2013; Yang et al., 2007). To the best of our knowledge, there is no report about the utilization of modified clay mineral in membrane adsorber for pollutant removal. The main objective of this study is to modify Mt with Arg and prepare adsorptive mixed matrix membrane with Mt and Mt-Arg for As(V) removal from water. Modified Mt with Arg was investigated using XRD, FTIR, zeta potential and TGA analysis. In addition, the structural characterization and performance of neat PSf, PSf/Mt and PSf/Mt-Arg mixed matrix membranes were investigated by using FE-SEM, XRD, AFM, contact angle, porosity, membrane pore size and PWF. Furthermore, the adsorption isotherms and kinetics of all membranes, dynamic adsorption and regeneration of membrane with high adsorption capacity were investigated and discussed.

2. Materials and methods

2.1. Materials

Udel P-1700 polysulfone (M_w: 55,500 g/mol) was purchased from Solvay Advanced Polymer LLC and used as polymer. Natural montmorillonite; Mt (Cloisite Na^+) with cation exchange capacity (CEC) of 92.6 meq/100 g was obtained from Southern Clay Products Inc., USA. *N*-methyl-2-pyrrolidon (NMP) (ρ: 1030 kg/m^3) as solvent and polyethylene glycol (PEG) (M_w: 20,000 g/mol) as pore former were provided from Merck and used to prepare membrane. L-arginine monohydrochloride ($C_6H_{14}N_4O_2$, 174.20 g/mol, 99%, Merck) as modifier, isobutanol, NaOH and HCl were purchased from Merck. Arsenate stock solutions were prepared by dissolving $Na_2HAsO_4.7H_2O$ (Sigma-Aldrich) in deionized water. All chemicals and reagents were analytical grade. Mt was dried using atmospheric oven at 110 °C for 24 h before utilization and modification.

2.2. Synthesis and characterization of Mt-Arg

Cation exchange (Jones, 1983) was used to modify pristine Mt by replacement of the sodium cations of Mt with protonated Arg. Typically, neat Mt was dried at 110 °C for 24 h using an atmospheric oven and then, 0.2 g of Mt was added into distilled water (25 mL) and mixed by using a magnetic stirrer for 12 h at 30 °C. Measured amount of Arg was dissolved in 25 mL distilled water while pH of solution was adjusted at 3 by adding 0.1 M HCl. The amount of Arg was equivalent to 3 times the CEC of Mt. It was added to the Mt solution and stirred for 4 h at 70 °C. After precipitation, the modified Mt was centrifuged and washed several times with DI water. Finally, the modified Mt was dried at 60 °C for 12 h.

In order to determine the distance of Mt layers, X-ray diffraction (XRD) patterns of the resulting clay minerals were obtained by (D500 Siemens, Germany) diffractometer using Cu-Kα radiation ($\lambda = 0.154$ nm) under a voltage of 35 kV and a current of 30 mA. All samples were analyzed in continuous scan mode with the 2θ ranging from 2° to 50°. Basal spacing was determined from the position of d (001) reflection which is calculated by Bragg's equation ($n\lambda = 2d \sin \theta$).

The Fourier transform infrared (FT-IR) spectra VERTEX 70 FTIR spectrometer (Bruker, Germany) in the range of 4000–400 cm^{-1}, between KBr pellets used to study the chemical structure of samples. The zeta potentials of unmodified and modified Mt were measured on a Nano ZS (red badge) ZEN 3600. The pH dependences of zeta potentials for samples were measured in the aqueous solutions at different pH values, adjusted by 0.1 N NaOH and HCl. Thermal gravimetric analysis (TGA) was performed by using a Perkin Elmer Pyris Diamond TGA system. Samples were heated up to 800 °C under the nitrogen-flow and a heating rate of 10 °C/min.

2.3. Preparation of membranes

Neat and mixed matrix membranes were prepared by using non solvent induced phase separation (NIPS). Composition and weight percentage of the casting solution (NMP/PSf/PEG/Mt) was constant at (75/14.775/10/0.225) for all sets of experiments. According to previous works in our research center, the weight percentage of polymer, solvent and additives has been finalized to obtain maximum pure water flux (PWF) which is important parameter in AMMMs (Amirabedi et al., 2013; Shokri et al., 2016). The desired amount of pristine and modified Mts were dispersed into 40 g NMP using prob. sonicator (Sonopuls HD 3200, Bandelin) for 30 min. Then 7.8 g PSf and 2.6 g PEG were added to the particles dispersion and mixed at 60 °C for 8 h. Then the resulted homogenous solution was sonicated for 15 min. After completely releasing the bubbles, a portion of homogenous solution was poured onto the flat plate glass and spread out using an automatic casting knife at the speed of 10 mm/s. The thickness of all membranes was kept constant at 150 μm. Immediately after casting, the film was immersed in a water bath to initiate phase inversion. The obtained membranes were thoroughly rinsed with deionized water and dried at 70 °C to remove the residual water.