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 Q1 **Exfoliated Mg–Al–Fe layered double**  
 3 **hydroxides/polyether sulfone mixed matrix**  
 4 **membranes for adsorption of phosphate and**  
 5 **fluoride from aqueous solutions**

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**ABSTRACT**

Mg–Al–Fe layered double hydroxides (LDHs) were exfoliated and incorporated in polyether 17  
 sulfone membranes for the removal of phosphate and fluoride for the first time. The exfoliation 18  
 methods, coagulation bath, LDH amount, interfering ions, adsorption isotherm, desorption and 19  
 reuse of the membranes were investigated. It was found that LDHs could be quickly exfoliated 20  
 in formamide/N,N-dimethylformamide (DMF) solvent mixtures with sodium carboxymethyl 21  
 cellulose as a stabilizer. The membranes displayed much higher adsorption capacity for 22  
 phosphate (5.61 mg/g) and faster adsorption rate than the un-exfoliated materials. With 23  
 increased DMF content in the coagulation bath, the static and dynamic adsorption capacity 24  
 rose. Interference from  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  (50 mg/L) on adsorption of phosphates was not apparent. 25  
 The membranes displayed excellent reusability in dynamic adsorption/desorption. The 26  
 membranes also showed high adsorption capacity for fluorides (1.61 mg/g). 27

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42 **Introduction**

44 Water pollution has become a serious threat to human health  
 45 and the eco-environment (Jia et al., 2006). Anionic contaminants,  
 46 such as phosphate, fluoride, arsenic, cyanide, bromate, Cr(VI)  
 47 oxyanions, nitrite, etc., may cause serious environmental and  
 48 health problems. For example, excessive phosphorus in water  
 49 causes eutrophication, which leads to abundant development of  
 50 aquatic plants including algae, threatening aquatic life and  
 51 disturbing the ecological balance in water (Nordqvist et al., 2016).  
 52 In water bodies with poor circulation, 1 mg/L of phosphate is  
 53 sufficient to stimulate algal blooms. The United States Environ-  
 54 mental Protection Agency (EPA) has recommended a level of  
 55 phosphorus in water of less than 50 ng/L, while the Florida

Everglades Forever Act recommends less than 10 ng/L for 56  
 preventing water eutrophication (Mao et al., 2017). Fluoride 57  
 concentrations in drinking water above 1.5 mg/L are detrimental 58  
 to human health, leading to dental or skeletal fluorosis (Miretzky 59  
 and Fernandez Cirelli, 2011). The World Health Organization 60  
 (WHO) has set a desirable and permissible limit range of 61  
 between 0.5 and 1.0 mg/L fluoride in drinking water (Bhatnagar 62  
 et al., 2011). 63

For the removal of dissolved phosphate in water and 64  
 wastewaters, biological, chemical and physical processes 65  
 have been investigated. Biological processes are cost-effective 66  
 and environmentally sound, and are now widely used at the 67  
 industrial level. However, their effectiveness could be affected by 68  
 volatile fatty acids, cations, temperature, pH, sludge quality and 69

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70 settlement. Therefore, biological processes are usually supple-  
 71 mented by an additional treatment to meet the discharge  
 72 requirements. Chemical precipitation is generally not able to  
 73 remove phosphate to levels that can satisfy stringent effluent  
 74 standards. Adsorption is associated with simple operating  
 75 conditions, less sludge production, and stable removal effects,  
 76 especially for trace phosphate. The adsorbents used can be  
 77 classified into several categories. (i) Alunite minerals (Ozacar,  
 78 2003); (ii) metal oxides, e.g., magnetic iron oxide (Yoon et al.,  
 79 2014), zirconium oxide (Su et al., 2013), metal oxide impregnated  
 80 anion exchange resin (Nur et al., 2014), iron-doped activated  
 81 carbons (Wang et al., 2012) and carboxymethylated bagasse  
 82 fibers (Carvalho et al., 2011), lanthanum-modified bentonite  
 83 clay (Phoslock) (Zhang et al., 2012b) and activated carbon fiber  
 84 (Zhang et al., 2012a), and La(III)-chelex resin (Wu et al., 2007);  
 85 (iii) metal hydroxides, e.g., hydrated Fe(III) oxide immobilized  
 86 anion exchange resin, La(OH)<sub>3</sub>-modified exfoliated vermiculites  
 87 (Huang et al., 2014) and activated carbon fiber (Zhang et al.,  
 88 2012b); (iv) mesoporous materials, e.g., Al-MCM-41 (Z. Li et al.,  
 89 2013) and post-synthetic grafted SBA-15 (Choi et al., 2012);  
 90 (v) Layered double hydroxides (LDHs), e.g., LDH nanosheets  
 91 (Koilaraj et al., 2013), and calcined Zn-Al LDHs (Cheng et al.,  
 92 2010); (vi) biomass, e.g., waterworks sludge (D. Li et al., 2013)  
 93 and calcined waste eggshell, etc. To remove fluoride from water,  
 94 precipitation, coagulation, ion exchange (Viswanathan and  
 95 Meenakshi, 2009), reverse osmosis (Sehn, 2008) and electrodi-  
 96 alysis have been studied. However, the shortcomings of most of  
 97 these methods are high operational and maintenance costs,  
 98 secondary pollution and complicated procedures. Adsorption is  
 99 a more attractive method (Gao et al., 2009), and alumina (Nazari  
 100 and Halladj, 2014), mixed oxides (Ghosh, 2015), clay-like mate-  
 101 rials (Thakre et al., 2010), ion-exchange resins (Viswanathan and  
 102 Meenakshi, 2009), and metal-organic frameworks (He et al., 2016)  
 103 etc., have been employed for fluoride adsorption.

104 LDHs have received widespread attention in adsorption,  
 105 catalysis, polymer nano-composites, pharmaceuticals, and  
 106 sensors (Mallakpour et al., 2016). The general formula of LDHs  
 107 can be expressed as  $M^{2+}_{1-x}M^{3+}_x(OH)_2A^{n-}_{x/n}yH_2O$ , where  $M^{2+}$   
 108 and  $M^{3+}$  represent di- and tri-valent metal cations,  $A^{n-}$  is the  
 109 intercalated anion, and  $x$  normally ranges from 0.17 to 0.33  
 110 (Hamouda et al., 2014). The high charge density of LDH sheets  
 111 originates from the isomorphic substitution of  $M^{2+}$  by  $M^{3+}$ .  
 112 The exchangeability of interlayer anions makes LDHs excel-  
 113 lent and cheap adsorbents for removing anionic pollutants  
 114 from aqueous environments (Yu et al., 2015). Considering the  
 115 potential risk of Al to human beings, Fe-based LDHs with  
 116 partial Fe substitution for Al such as Mg-Al-Fe have been  
 117 reported as promising candidates for waste treatment (Zhang  
 118 et al., 2014). However, LDHs are usually ultrafine powders,  
 119 resulting in high resistance in adsorption fixed beds (Ho Nguyen  
 120 Nhat et al., 2016). To solve this problem, immobilizing LDHs on a  
 121 porous support or matrix has been reported (Hernadi et al., 2002).

122 Membrane adsorption has emerged as a novel adsorption  
 123 technology in recent years (Guo and Jia, 2016; Jia et al., 2016). By  
 124 incorporating nanosized adsorbents in a membrane matrix, the  
 125 as-obtained mixed matrix membranes (MMMs) can be employed  
 126 for the removal of trace solutes from aqueous solution (He et al.,  
 127 2014; Mukherjee and De, 2014), exhibiting low internal diffusion  
 128 resistance, high filtration rate, and good reusability (Salazar et al.,  
 129 2016). To prepare LDH MMMs with high adsorption efficiency,

LDHs should be exfoliated and dispersed in the membrane 130  
 matrix, which has not been reported. Herein, Mg-Al-Fe LDHs 131  
 were prepared, exfoliated, and incorporated in polyether sulfone 132  
 (PES), and the as-obtained well-exfoliated LDHs/PES MMMs were 133  
 employed for removal of phosphate and fluoride from aqueous 134  
 solution for the first time. The exfoliation methods, coagulation 135  
 bath, LDH amounts, effects of interfering ions, adsorption 136  
 isotherm, desorption, and reuse of the membranes were 137  
 investigated. 138

## 1. Experimental 189

### 1.1. Materials 141

Fe(NO<sub>3</sub>)<sub>3</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, Al(NO<sub>3</sub>)<sub>3</sub>, KH<sub>2</sub>PO<sub>4</sub>, NaF, ammonium molybdate 142  
 solution, ascorbic acid, formamide, N,N'-dimethylformamide 143  
 (DMF), sodium carboxymethyl cellulose (CMC), and hydrochloric 144  
 acid were analytical grade and purchased from Beijing Chemical 145  
 Factory. Polyether sulfone (PES, E2010) was purchased from BASF 146  
 Company (German). 147

### 1.2. Preparation of LDHs 148

Nitrate-containing Mg-Al-Fe LDHs were synthesized by a 149  
 co-precipitation method. A mixed solution (200 mL) containing 150  
 0.05 mol/L Fe(NO<sub>3</sub>)<sub>3</sub>, 0.5 mol/L Mg(NO<sub>3</sub>)<sub>2</sub>, 0.25 mol/L Al(NO<sub>3</sub>)<sub>3</sub> and 151  
 0.01 mol/L hydrochloric acid was prepared with degassed deion- 152  
 ized water. Then the solution was added to 200 mL of 1 mol/L 153  
 NaOH solution drop by drop under magnetic stirring at room 154  
 temperature. After reaction at 80°C for 24 hr, the resulting slurry 155  
 was centrifuged, washed with deionized water, and dried. For 156  
 comparison, Mg-Al LDHs were also prepared with 0.2 mol/L 157  
 Mg(NO<sub>3</sub>)<sub>2</sub> and 0.1 mol/L Al(NO<sub>3</sub>)<sub>3</sub>. 158

### 1.3. Synthesis of LDHs/PES membranes 159

To exfoliate the LDHs, LDH powder was ultrasonically dispersed 160  
 in mixed formamide/DMF solutions (volume ratio of 1:10) with 161  
 CMC (2 wt.% of LDHs' mass) as stabilizer. Then, polyether 162  
 sulfone (PES) was added, dissolved under stirring, and degassed. 163  
 The as-obtained casting solution was cast on non-woven 164  
 fabrics using a knife, immersed in a coagulation bath for phase 165  
 inversion, and washed with deionized water 3 times to remove 166  
 the organic solvents. 167

### 1.4. Adsorption 168

Static adsorption was conducted in 50 mL of phosphate 169  
 (KH<sub>2</sub>PO<sub>4</sub>) or fluoride (NaF) solution under stirring for 24 hr. 170  
 The adsorption capacity ( $Q_e$ , mg/g) was calculated as, 171

$$Q_e = \frac{(C_0 - C_e)v_0}{w_0} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentration 172  
 (PO<sub>4</sub><sup>3-</sup>, mg/L) respectively,  $v_0$  (L) the solution volume, and  $w_0$  (g) 174  
 the adsorbent mass. The desorption rate (DR, %) was calculated 175  
 as, 176

$$DR = \frac{C_1 v_1}{w_1} \times 100\% \quad (2)$$

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