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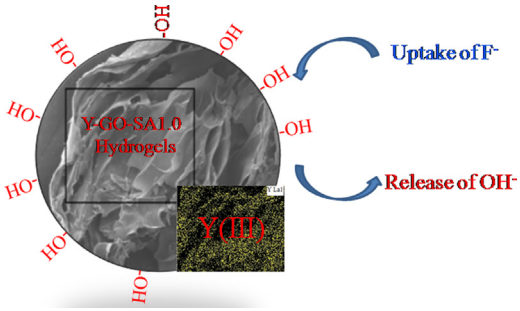
Regular Article

A novel 3D yttrium based-graphene oxide-sodium alginate hydrogel for remarkable adsorption of fluoride from water

Jinsong He [a,*], Anan Cui [a], Fan Ni [b], Shihuai Deng [a], Fei Shen [a], Gang Yang [a]

[a] Institute of Ecological and Environmental Sciences, Sichuan Agricultural University, Chengdu, Sichuan 611130, China
[b] Department of Chemical Engineering, Northwest University for Nationalities, Lanzhou, Gansu 730030, China

GRAPHICAL ABSTRACT



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ABSTRACT

3D macrostructure adsorbents have attracted great attention in water treatment recently. A series of novel 3D yttrium-based graphene oxide-sodium alginate hydrogels were prepared by sol-gel process for removal of fluoride. The hydrogels displayed a 3D network porous and amorphous structure composed of 2D sheets, with the uniform dispersion of Y(III) onto the gels. The hydrogel Y-GO-SA1.0 was selected as the optimized adsorbent for the fluoride removal due to its best adsorption performance. The adsorption experiments revealed that the maximum adsorption of fluoride occurred at pH 4. The adsorption equilibrium could be achieved within 24 h at both pH 6.5 and optimal pH 4. Based on Langmuir isotherm model, the maximum adsorption capacity of fluoride was 288.96 mg/g at pH 4.0, much higher than many other reported adsorbents. The adsorption was retarded obviously by the presence of phosphate anions. The regenerated hydrogels maintained high adsorption level for fluoride, which could be easily recycled in operation. Furthermore, the column study exhibited that the hydrogel could be used as column packing for effective removal of fluoride via continuous filtration. The column adsorption data was well described by the Thomas model, with the value of q_0 much lower than that for batch adsorption experiment under the same initial F^- concentration. Finally, the uptake of F^- was associated with the release of –OH groups bonded to Y(III) on the gels. These results imply that the present 3D hydrogels can be potentially applied for the treatment of fluoride-containing water.

1. Introduction

Fluoride contamination of drinking water is a worldwide issue of great concern, since excessive intake of fluoride can cause a severe threat to human beings such as dental and skeletal fluorosis,

* Corresponding author.
E-mail addresses: hejinsong@sicau.edu.cn, hejinsong@nus.edu.sg (J. He).

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infertility, brain damage and fetal cerebral function [1]. It has been estimated that higher than 250 million globally consume drinking water with a fluoride concentration higher than 1.5 ppm, which is the maximum allowable fluoride concentration level (MCL) for drinking water regulated by the World Health Organization (WHO). Therefore, a series of technologies have been employed to remove fluoride from water, such as precipitation, coagulation, ion-exchange, adsorption, and membrane filtration [1–3].

Among these technologies, adsorption is considered to be one of the most powerful technologies owing to its ease in operation, comparably low cost, and good industrial track record [4]. A variety of available adsorbents have been used for treatment of fluoride including alumina-based sorbents [4,5], iron-based sorbents [6,7], zirconium-based sorbents [8,9], manganese-based sorbents [10], magnesium-based sorbents [11,12], etc. Recently, it has been reported that the rare-earth metal based adsorbents have shown high affinity towards fluoride [13–15]. Among these, yttrium-based adsorbents also displayed potential adsorption of fluoride [16]. However, these adsorbents usually suffer from difficult dispersion due to the aggregation, poor separation as well as secondary environmental pollution mainly caused by the release of fine-structure powder, hindering their practical application in water treatment.

The 3D assembled macrostructure adsorbents have been recognized as one of the most promising strategies to overcome the above issues [17]. It has been documented that 3D network structure prevents aggregation and guarantees mass transport to the internal structure. Besides, the morphology of 3D structure adsorbents offers convenient recycling after water treatment, minimizing the potential environmental pollution [17,18].

Graphene oxide (GO) nanosheets as a two-dimensional material possess large specific surface and abundant functional groups, such as carboxyl hydroxyl and epoxy groups, which have been reported to be a promising material for the assembled 3D architectures [17]. Many efforts have been devoted into the development of 3D GO-based materials for the water treatment, such as alginate-graphene oxide gels for copper removal [19], graphene oxide-chitosan hydrogels for water purification [20], graphene oxide-encapsulating alginate beads for removal of acridine orange [21], etc. Our preliminary study had shown that the GO sheet could be easily crosslinked by the yttrium ion, forming the complex. Thus, it would be interesting to find out whether such a Y-GO composite with 3D structure can be developed for fluoride removal.

In this study, we attempted to develop a series of 3D yttrium based-graphene oxide hydrogels for the first time via sol-gel process for the removal of fluoride. Sodium alginate was selected as supporter due to its highly water dispersion, biocompatibility, relatively low-cost and porous structure of its hydrogels. The physical-chemical properties of the hydrogels were characterized. The adsorption experiments were studied under batch and column modes to obtain the key parameters in the treatment of fluoride-contaminated water. Finally, the adsorption mechanism was studied for better understanding of the uptake of fluoride.

2. Materials and method

2.1. Materials

Yttrium(III) chloride hexahydrate was purchased from Kaima Biochemistry Compony. Graphene oxide (GO) (purity > 99.5%) was purchased from Suzhou Tanfeng Tech. Inc. Sodium alginate (SA) was purchased from Chengdu Kelong Chemical Industry. Sodium fluoride, nitrate acid and the other chemicals used in this study were purchased from Sichuan Xilong Chemical Industry.

2.2. Synthesis of 3D hydrogels

3D hydrogels were prepared by the sol-gel process. Specifically, GO was dissolved into DI water (1 mg/mL) homogeneously under ultrasonic. 2% SA solution was prepared. 25 g of 2% SA solution was mixed with 20 mL of 1 mg/mL GO solution and stirred to get a homogeneous solution. The obtained mixed solution was then added dropwise into 100 mL of yttrium chloride hexahydrate solution with different concentration, i.e. 0.25 M, 0.5 M, 0.75 M and 1.0 M, under constantly magnetic gentle stirring to prevent agglomeration of the formed hydrogels. After the hydrogels were aged for 4 h, the hydrogels were reacted with 200 mL of NaOH solution with the corresponding concentration (0.25 M, 0.5 M, 0.75 M and 1.0 M) for 4 h. Finally, the obtained 3D hydrogels were washed with DI water to reach neutral pH, and used in the hydrated form in the subsequent adsorption experiments. The final products were denoted as Y-GO-SA0.25, Y-GO-SA0.5, Y-GO-SA0.75, and Y-GO-SA1.0, respectively, according to their different yttrium concentrations.

2.3. Characterizations of 3D hydrogels

The morphology of the dried hydrogels was investigated by a field emission scanning electron microscopy (FESEM) (JEOL JMS-7500F, Japan) and the elemental distribution was detected by Energy Dispersive X-ray Spectroscopy (EDS). The Brunauer-Emmett-Teller (BET) surface area and pore size were measured by a surface area analyzer (Quantachrome ASIQ, USA). The crystalline of dried hydrogels was characterized by X-ray diffraction (XRD) instrument (Bruker D8 Advance, Germany). The surface chemistry was studied by Fourier Transform Infrared spectroscopy using a FTIR spectrometer (PerkinElmer Spectrum Two, US). The elemental status was analyzed by an X-ray photoelectron spectroscopy (XPS) (Kratos XSAM800, Shimadzu, Japan). The surface charge density was measured as described in other studies [22,23].

2.4. Adsorption in batch reactor

A stock fluoride solution with concentration of 1000 F mg/L was prepared by dissolving sodium fluoride in the DI water. The stock solution was diluted with the DI water to prepare fluoride solution with the expected concentrations for the subsequent batch adsorption experiments.

To find out the optimal 3D hydrogels for the fluoride removal, the comparison experiment of adsorption performance was conducted between different 3D hydrogels. 10 mg different 3D hydrogels (the weight obtained after the hydrogels were dried) were added into 50 mL fluoride solution at pH 4.0 and neutral pH, respectively, and shaken for 48 h. The pH value was controlled as constant value during the adsorption process. The fluoride concentrations were determined by a fluoride electrode (PF-1-01, Leici, China). The measurement of fluoride was following the method described in reported study [24]. The details were provided in Supplementary data.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2018.07.017.

The pH effect experiments were performed by using Y-GO-SA1.0 hydrogels into fluoride solution with initial concentration of 22.42 mg/L under the initial pH in the range of 3–12. The other procedures were the same as the above comparison experiment.

Adsorption kinetics experiments were conducted by shaking 0.2 g Y-GO-SA1.0 hydrogels into 1 L fluoride solution on a stirrer with a high speed of 220 rpm to eliminate the resistance to the boundary layer. The solution pH was controlled as constant at pH 4.0 ± 0.1 and 6.5 ± 0.1, respectively. The samples were collected at different time intervals and measured.