



Adsorptive removal of fluoride ions from aqueous solution by using sonochemically synthesized nanomagnesia/alumina adsorbents: An experimental and modeling study



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ABSTRACT

Wet impregnation followed by sonochemical approach was applied to dope γ - Al_2O_3 with MgO nanocrystals in order to synthesize a new and more efficient fluoride nanosorbent (4–30 nm). The effects of operating conditions such as pH, fluoride concentration, contact time and dosage were studied. The adsorbents were characterized by using the pH_{ZPC} measurement and FTIR, HR-SEM, XRD, EDAX, and BET analyses. The optimum fluoride removal (>85%), adsorption capacity of ~ 5.6 mg/g, was obtained at 140 min, neutral pH range of 6.3–7.3, and adsorbent dosage of 0.5 g/L. The isomorphic substitution of OH^- of brucite in the nanosorbent with fluoride ions could be herein the dominant sorption mechanism. Furthermore, other ions (Cl^- , SO_4^{2-} , HCO_3^- , PO_4^{3-}) in the solution had very little interference in the fluoride adsorption. However, PO_4^{3-} was the greatest competitor for fluoride adsorption. Finally, the experimental adsorption equilibrium and kinetic data were closely followed the Langmuir adsorption isotherm and pseudo second order kinetic model respectively.

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1. Introduction

In general, finding a solution to treat water and wastewater containing excess fluoride concentrations (<1 mg/L, World Health Organization (WHO) standard) is very important. Among various treatment processes, adsorption is the most promising one for defluoridation of water due to the ease of operation and maintenance, lower cost and being a relatively more environment friendly process [1,2].

Alumina-based adsorbents are one of the most popular defluoridating materials. This is due to the availability, high surface area, acceptable mechanical strength and strong affinity of alumina for fluoride ions [3,4]. Nevertheless, the main disadvantages of alumina are its slow rate of adsorption, residual aluminium and soluble aluminium fluoride complexes, and narrow available pH range which is typically below 7.0 [5]. Recently, a considerable amount of work has been devoted to conquer these limitations by incorporating various types of alkaline and alkaline earth metal oxides into the different adsorptive materials in order to improve their removal efficiency. Magnesia is one of these promoters [6]. However, magnesia is only available as fine powder

that leads to such limitations as difficulty of solid–liquid separation, low hydraulic conductivity, excessive pressure drop during filtration process and leaching of the metal or metal oxide by the treated water [7]. Thus, it has been suggested that chemical modification of various accessible adsorbents to form different composite materials such as magnesia-amended activated alumina granules [6], magnesium-doped nano-ferrihydrite [4], magnesium incorporated bentonite clay [8], magnesia-amended silicon dioxide [7], magnesia/chitosan biocomposite [9] and magnesia-loaded fly ash cenospheres [10]. Nevertheless, the main drawbacks of these wet chemistry-based approaches are high cost demands, being time consuming and their difficulties to control the morphology of synthesized particles especially when the scale of formed crystals goes down to nano-meters. Thus, it is thought desirable to find a new ultrasound driven synthetic route to modify surface structure of γ - Al_2O_3 through deposition of sonochemically prepared magnesia nanoparticles [11]. This is a very simple and fast method that does not need any complicated facilities. The sonochemical method involves radical reactions and/or thermal reactions, which originate from the extremely high temperature and pressures generated in the cavitation bubbles [12]. Recently, Song et al. [13] have successfully synthesized magnesium hydroxide (MH) nanoparticles, in the range of 10–17 nm, in a one step precipitation reaction and in the presence of ultrasonic irradiation. In another work by Alavi and Morsali [14], nanostruc-

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Nomenclature

C_0	initial concentration of fluoride (mg/L)
C_e	equilibrium concentration of fluoride in the solution (mg/L)
CNT_s	carbon nanotubes
E	mean sorption energy (kJ/mol)
K_1	pseudo-first-order rate constant of adsorption (min^{-1})
k_2	pseudo-second-order rate constant of adsorption (min^{-1})
K_{diff}	the intra-particle diffusion rate constant (mg/g/ $\text{min}^{1/2}$)
K_F	the Freundlich constant which indicates relative adsorption capacity of the sorbent
K_L	the Langmuir adsorption constant (L/mg)
m	sorbent mass (g)
n	the Freundlich constant which indicates adsorption intensity
q_1	equilibrium amount of the adsorbed fluoride ions (mg/g) for pseudo-first-order adsorption
q_2	equilibrium amount of the adsorbed fluoride ions (mg/g) for pseudo-second-order adsorption
q_e	equilibrium amount of the adsorbed fluoride ions (mg/g)
q_{max}	maximum sorption capacity (mg/g) upon the Langmuir isotherm model (mg/g)
q_t	amount of fluoride uptake at any time (mg/g)
R_L	separation factor or equilibrium parameter
V	sorbent free solution volume (L)

ured MH was ultrasonically synthesized from magnesium acetate and sodium hydroxide in ethanol. Magnesia nanoparticles were also obtained by calcining the so-called nanostructured MH powders. Ultrasound assisted one pot method was also used by Gandhi et al. [15] to get magnesia coated polyvinyl alcohol (MgO/PVA) nanocomposites.

To the best of our knowledge, only a few works have been reported on assessment of performance of nanocomposites for fluoride removal from water. Mg/ferrhydrite [4], $\gamma\text{-Al}_2\text{O}_3/\text{CNTs}$ [16], hydroxyapatite/chitin [17], and polypyrrole/magnetic Fe_3O_4 [18] nanocomposites are some of them. In the present study, sonochemical assisted synthesis method was applied to prepare a new nanocomposite adsorbent. The as-synthesized nanomagnesia coated γ -alumina has been thoroughly characterized using XRD, SEM, EDAX, FTIR and BET surface area analyses. This nanosorbent was applied to defluoridation of water through a batch adsorption process with the variation of solution pH, adsorbent dose, temperature and initial fluoride concentration in order to determine various equilibrium and kinetic parameters and to understand the probable mechanisms of adsorption. Moreover, the effects of different anions which commonly exist in drinking water were investigated on the fluoride removal efficiency of the sorbent.

2. Experimental

2.1. Materials and methods

All chemicals used in the present study were of analytical reagent grade. Millipore de-ionized (Milli-Q 18.2 M Ω cm at 25 °C) water was used in all the experiments. A stock solution of

1000 mg/L fluoride was prepared by dissolving appropriate amounts of sodium fluoride (Merck, Germany) in double distilled water and the entire standard and fluoride spiked solutions for removal experiments and analyses were prepared by appropriate dilution from the freshly prepared stock solution.

Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Merck, Germany), ethanol (Merck, Germany), ammonia (24 wt.% aqueous solution) were used in all the experiments. The dried $\gamma\text{-Al}_2\text{O}_3$ powder was sieved and fine powder (mesh < 100 μm) of $\gamma\text{-Al}_2\text{O}_3$ was used as a host for the experiments.

2.2. Sonochemical preparation of magnesium oxide/alumina nanocomposites

The applied recipe for obtaining pristine nano-MgO and nano-MgO/ $\gamma\text{-Al}_2\text{O}_3$ particles is briefly explained below.

The preformed fine powder of $\gamma\text{-Al}_2\text{O}_3$ and an aqueous solution of magnesium nitrate and isopropanol were added in a 250 mL round glass bottom flask for 24 h with continuous stirring by a magnetic stirrer at 150 rpm and room temperature. The argon gas was allowed to bubble through the prepared slurry at a rate of 80 mL/min, before and during irradiation, by an immersed sparger in order to expel dissolved oxygen and to decrease cavitations threshold.

The applied recipe for ultrasound irradiation of as prepared mixture has been reported elsewhere [15,19]. Finally, the resulted fine precipitate was centrifugally separated from the solution, washed thoroughly with plenty of water and ethanol and aged in vacuum oven at 120 °C overnight and calcined under helium atmosphere at 650 °C for 6 h to get magnesia nanoparticles from thus synthesized magnesium hydroxide nanostructures. Nanometer size virgin MgO particles were also obtained with the same above mentioned recipe, except that the annealed alumina was not present in the reaction vessel during sonication.

2.3. Characterization of materials

The X-ray diffraction (XRD) patterns of the samples were recorded by Philips diffractometer with a copper anode and step sizes of 0.04° and 0.08° in order to identify the crystalline phases of the samples. The Brunauer–Emmett–Teller (BET) surface area, pore volume and average pore radius of the samples were determined by multipoint N_2 adsorption–desorption isotherm at liquid nitrogen temperature (77 K) using NOVA 2000 series instrument (Quantachrome, USA). Examination of surface morphologies and elemental ingredients of samples with high resolution scanning electron microscope (HR-SEM) with Philips-CM120 model operating at 200 kV and fitted with an energy dispersive X-ray analyser (EDAX) were accomplished. Fourier transform infrared spectroscopy (FTIR) spectra of the samples were collected using a PerkinElmer, Spectrume GX FTIR spectrometer (USA, 2005) in the wavelength range of 4000–400 cm^{-1} to confirm the formation of expected functional groups. The pH measurements were done by a Metrohm pH meter (model no. E-632). The pH value of zero point charge (pH_{ZPC}) of adsorbent particles was determined through a pH drift method.

2.4. Evaluation of adsorbent performance

A series of 250 mL Erlenmeyer flasks containing a predetermined dose of sorbent (0.5 g/L) in 100 mL of NaF spiked solution with a known initial concentration (5 mg/L) were kept in a Heidolph magnetic shaker with continuous stirring at 150 rpm, a constant pH at room temperature (25 °C) for specified adsorption time intervals, upon which samples were withdrawn to determine the concentration of remained F^- ions. After equilibration, the

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