Characterization of granular matrix supported nano magnesium oxide as an adsorbent for defluoridation of groundwater

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HIGHLIGHTS

- The magnesia particle size had profound influence on the defluoridation efficiency.
- Defluoridation process was limited by pore diffusion.
- Defluoridation mechanism occurred via specific and non-specific interactions.
- Mg^{2+} that leached from the GSN increased the total hardness of the treated GW.

GRAPHICAL ABSTRACT
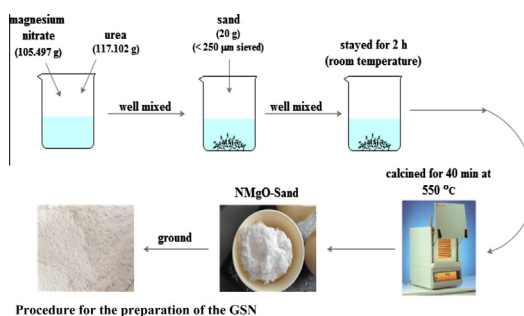
Procedure for the preparation of the GSN

ABSTRACT

Different magnesium (Mg) containing nanoparticles, magnesium hydroxide, $(Mg(OH)_2)$, magnesium oxide (NMgO) and activated magnesium oxide (AcMgO) were tested, in a first step, to identify a highly efficient adsorbent for groundwater (GW) defluoridation. Consequently, the NMgO, which was the most suitable material, was impregnated on a granular matrix (sand) to produce a reactive filtration material (GSN). Amongst the different features (surface area, total pore volume, pH_{pzc} mineralogical assemblage and particle size) of the investigated magnesia species, only the particle size had profound influence on defluoridation efficiency. Kinetic analysis showed that the defluoridation process was limited by pore diffusion while experimental evidences showed that both specific and non-specific mode of interaction were the underlying mechanism of the process. In the defluoridation system, the thermodynamic parameters (ΔG) of precipitation of magnesium fluoride (MgF_2) was negative but no MgF_2 peak was observed in the XRD pattern of the spent GSN. The defluoridation efficiency of the GSN in a real groundwater system at different initial F^- concentrations was comparable with that of simulated water. The evaluation of the quality characteristics of the treated water showed that Mg^{2+} that leached from the GSN enhanced the total hardness while the concentrations of Ca^{2+} was greatly reduced. Reduction in the magnitude of the total inorganic carbon content of the GW was observed.

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1. Introduction

The human health repercussions of the presence of fluoride (F^-) in drinking water sources are concentration dependent. At concentrations <1.5 mg/L, fluoride is beneficial in the prevention of dental caries while at concentrations >1.5 mg/L it becomes detrimental to human health. The severity of these implications escalates with increasing F^- concentrations, thus above concentrations of 1.5 mg/L, mottling of teeth occurs to an objectionable degree; at concentration that range between 3 and 6 mg/L skeletal fluorosis occurs, while at concentration level in excess of 10 mg/L, crippling fluorosis ensues. Consequently, the need to reduce

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aqueous F^- to beneficial concentration levels has been of interest to public health officials and water providers alike.

In view of the desired operational requirements of adsorption based water treatment operations (e.g. simplicity and low cost), a number of promising adsorbents (e.g. calcium chloride modified zeolite [1], Fe(III) modified natural stilbite zeolite [2], chitosan based microporous alumina [3] and magnesia-loaded fly ash ceno-spheres [4] aluminum infused diatomaceous earth [5]) have been previously investigated for defluoridation of contaminated water. Among the list of sorbents studied, metal (oxides and hydroxides) rich materials have exhibited high potential in defluoridation. The effectiveness of metallic materials for defluoridation was predicated on the amphoteric nature of metal surfaces. A commonly applied parameter to express the propensity of a surface to become either positively or negatively charged is the value of the pH required to give zero net surface charge [6]. In order for F^- to interact with a metal ion surface, a source of protons is required to protonate the surface to create a potential between the metal ion surface and the F^- specie in water. The surface reactions that favor F^- interactions occur mainly at pH range below the point zero charge (PZC) of the surface which caused the predominance of the surface with positive charges and promotion of electrostatic interactions between the surface and the anionic species. Magnesium (Mg) possesses high PZC values (PZC > 10) which gives it a broad range of pH for F^- ion interaction. Furthermore, on the strength of the hard–soft interaction principle (HSIP) developed by Pearson [7], Mg is classified as a hard acid while F^- is considered a hard base. Thus, the affinity of the metals for the aqueous F^- could be attributed to the guiding principle regarding the interaction of electron pair donors and acceptors; that the most favorable interactions occur when the acid and base have similar electronic character [8]. Consequently, hard acids preferentially interact with hard bases, and soft acids interact preferentially with soft bases.

The ability of MgO for water defluoridation has been reported over seventy years ago, thus, considering the high F^- adsorption capacity, non-toxicity and limited solubility in water, it is considered a promising material for water defluoridation [9–11]. Despite the high potential of MgO in water defluoridation, the transition from laboratory to field-scale application has been challenged by the fact that MgO occurs as a fine powder. The powdery nature of the MgO makes it difficult to use in a continuous flow system because of the difficulty of solid–liquid separation, low hydraulic conductivity and leaching of Mg ions into the treated water. In the present study, the provision of a granular support for MgO, to form a composite system, was based on the assumption that since MgO is a fine particulate, doping it on a traditional granular filter medium of larger particle size, to produce a hybrid adsorbent, would help to obviate the identified challenges. It is assumed that the hybrid adsorbent would combine the excellent handling and flow characteristics of traditional granular media filtration with the specific affinity of MgO toward the targeted pollutants.

The aim of this study was to incorporate Mg that has high affinity for F^- onto a granular matrix (silica sand) to produce a composite material that might serve as a reactive filter medium for groundwater (GW) defluoridation. Thus, different species of Mg (Mg(OH)₂, activated MgO and Nano MgO) were synthesized and the defluoridation potential of each material was evaluated in a batch system. The magnesium species with the highest defluoridation potential were incorporated on the granular matrix (*in situ*) and the defluoridation potential of the composite material was appraised systematically for a batch process. The defluoridation rate and the equilibrium isotherm parameters was derived and the effects of process variables on the defluoridation process were determined. In a batch rector, the performance efficiency of the composite material in real groundwater defluoridation applications was investigated and the efficiency of the defluoridation process on other water quality characteristics of the treated water was determined.

2. Materials and methods

2.1. Effects of synthesis procedure on defluoridation efficiency

2.1.1. Preparation of Mg(OH)₂ nanoparticles

The magnesium hydroxide (Mg(OH)₂) nanoparticles were prepared by adding 2.0 M sodium hydroxide (NaOH) solution into a preheated (50 °C) 1.0 M magnesium chloride (MgCl₂) solution (50 mL) at a discharge rate of 3 ml/min [12]. The suspension was allowed to age for 2 h in the mother liquor, while vigorous stirring was ensured. The precipitate produced was filtered, washed with deionized water and dried at 80 °C to obtain the Mg(OH)₂ nanoparticles (Supplementary Fig. (SIF) 1A).

2.1.2. Preparation of activated MgO (AcMgO) nanoparticle

Activated MgO (AcMgO) nanoparticles (see SIF 1B) were prepared by heating the Mg(OH)₂ nanoparticles solution derived from the process in Section 2.1.1 at 300 °C for 4 h in a furnace [12].

2.1.3. Preparation of Nano MgO (NMgO)

The nano magnesium oxide (NMgO) (SIF 2A) was prepared by adapting the self-propagating combustion reaction procedure [13–16]. In order to prepare the NMgO, an aqueous solution containing magnesium nitrate (Mg(NO₃)₂·6H₂O) as oxidizer (O) and urea as fuel (F), (corresponding F/O ratio, $\phi = 1.11$ as shown in the Equation below) was mixed thoroughly in a beaker for 120 min and then transferred into a ceramic crucible before it was finally introduced into a muffle furnace maintained at 550 °C for 40 min (SIF 2A).

$$9Mg\,(NO_3)_{2(aq)} + 10(CH_4N_2O)_{(aq)} \rightarrow 9MgO_{(s)} + 38N_{(g)} + 10CO_{2(g)} + 20H_2O_{(g)} + 7.5O_2$$
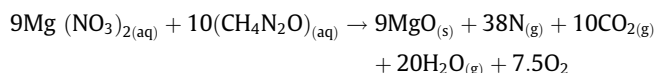
2.1.4. Evaluation of defluoridation potential of synthesized materials

In order to determine the best defluoridation ability, the synthesized materials (i.e. Mg(OH)₂, AcMgO and NMgO) was tested using a batch defluoridation process viz. 50 mL of F^- solution (20 mg/L) derived from sodium fluoride (NaF) salt (Merck KGaA, Germany) was brought in contact with 0.1 g of each material. The mixture was agitated at 200 rpm for 2 h, samples were subsequently removed, filtered using 0.45 μm polypropylene membrane and the filtrate was analyzed for residual F^- concentration using a F^- selective electrode (F500) connected to an ion meter (WTW, Germany). The amount of F^- uptake was determined using the mass balance procedure in each case.

2.1.5. Preparation of granular supported NMgO (GSN)

The granular matrix used (silica sand) was repeatedly washed in copious deionized water, dried, sieved and the fraction whose size was less than 250 μm was chosen as the granular support. The granular supported NMgO (GSN) was prepared via *in situ* hybridization of NMgO onto the sand matrix thus (SIF 3): the granular support, silica sand (10 g), was added into a beaker containing an aqueous solution mixture of magnesium nitrate (Mg(NO₃)₂·6H₂O) (O) and urea (F), (F/O ratio, $\phi = 1.11$). The mixture was agitated thoroughly, for a period of 120 min., before it was transferred into a ceramic crucible and then introduced into a muffle furnace (maintained at 550 °C) for 40 min. An aerogel of the sand/NMgO composite (SIF 2B) produced was ground and designated as the GSN.