



Insight into the defluoridation efficiency of nano magnesium oxide in groundwater system contaminated with hexavalent chromium and fluoride



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ABSTRACT

In order to broaden the applications of nano magnesium oxide (NMgO), as a sorbent, in potable water defluoridation, it is pertinent to understand the variables that define the defluoridation efficiency. The defluoridation efficiency of NMgO was evaluated in a groundwater (GW) system that is contaminated with chromium (Cr(VI)), one of the naturally occurring oxyanions in GW. NMgO was synthesized, characterized and the parameters of the sorption of Cr(VI) and fluoride (F^-) were obtained in synthetic feed water and GW that contained single sorbate specie. Competitive sorption studies was carried out, using each of the ionic species, either as the sorbate of interest or the interfering ionic specie, in the two aqueous matrixes. The efficiencies (%) of interfering Cr(VI) in F^- sorption by NMgO and the competition coefficient values were far lower than the values obtained for the same parameters, when the role of F^- was studied as an interfering ionic specie in Cr(VI) sorption by NMgO. The magnitudes of the efficiency of competition of the interfering ionic specie were higher in the GW system than in the synthetic feed water system. In contrast, the values of the competition coefficient were lower in the GW system than in the synthetic feed water system. The determination of the effects of the competitive sorption on the quality characteristics of the GW showed that carbonate also exhibited antagonistic effects on the sorption process.

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1. Introduction

Groundwater (GW), a multicomponent resource, contains plethora of inorganic anions and oxy-anions (e.g. chloride (Cl^-), sulfate (SO_4^{2-}), borate (BO_3^{3-}), nitrate (NO_3^-), arsenate (AsO_4^{3-}), chromate (CrO_4^{2-}) and permanganate (MnO_4^-)). The presence of these anionic species are objectionable and often liable for grievous health challenges. In GW matrix, these anionic species are concurrently present with fluoride (F^-). In potable water, high concentration of F^- (i.e. >1.5 m/L) is detrimental to human health, thus, different defluoridation technologies are being developed to reduce the aqueous concentrations to the beneficial and permissible level (i.e. <1.5 mg/L). Amongst the defluoridation technologies that are being developed, adsorption based defluoridation technologies have shown a lot of promise, with the caveat that a highly efficacious sorbent is used.

In adsorption based defluoridation operations, designed for GW system, the adsorbent should be able to function effectively in the

presence of array of naturally occurring anionic species. This is because a large number of these anions exhibit characteristics that are peculiar to F^- in the aqueous system. Therefore, they can compete with F^- for active sites on the adsorbent. Albeit, the extent of the competition between the different anionic species in aqueous matrix were attributed to the relative concentrations of the ions in solution and their affinity for the adsorbent [1].

In most adsorption based water defluoridation research, an ideal system that uses synthetic feed water, which contains only F^- , is often created. This unrealistic system often rendered the results obtained from such studies invalid in real life systems. Moreover, it has been posited [2] that in adsorption process, the mode of sorbate–sorbent interaction is greatly influenced by the presence of other ionic species, which produces three possible types of behavior: synergism, antagonism and non-interaction. In the adsorption of some oxyanions from aqueous system, the synergistic and antagonistic behavior of co-existing ionic species have been reported [3–6]. Therefore, in order to develop an efficacious adsorbent, that would have broad appeal in groundwater defluoridation, it is pertinent to understand the influence of the presence of anionic and oxyanionic components of GW on the defluoridation efficiency. The information obtained from such investigation shall

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provide insight into the variables that define the defluoridation efficiency of such adsorbent in analogous milieu.

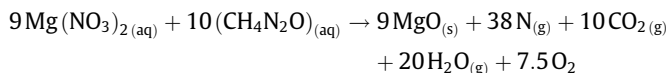
Considering the high defluoridation efficiency, non-toxicity and limited solubility in water, magnesium oxide (MgO) is considered a promising adsorbent, whose use can transit from Laboratory to real life applications. The defluoridation efficiencies of different forms of MgO and MgO rich materials have been reported [7–11]. The high defluoridation efficiency of Mg rich material was ascribed [11] to the fact that MgO possesses high PZC values ($PZC > 10$) which gives it a broad range of pH for F^- ion interaction, via electrostatic mode. Furthermore, on the strength of the hard-soft interaction principle (HSIP) [12], Mg is classified as a hard acid while F^- is considered a hard base. Thus, the affinity of this material for F^- is attributed to the guiding principle regarding the interaction of the electron pair donors and the acceptors; that, the most favorable interactions occur when the acid and base have similar electronic character. Consequently, hard acids preferentially interact with hard bases, and soft acids interact, preferentially, with soft bases.

Chromium is a common GW contaminant at hazardous waste sites, while subsurface contamination stems from industrial processes such as metal plating, leather tanning, and pigment production [13]. It has also been proven that Cr(VI) exists naturally in groundwater that has been unaffected by local industrial activity, and it can exist as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) in GW [14]. The speciation of chromium in groundwater is governed by the activity of hydrogen ions (pH) and activity of electrons (Eh) [14]. Concerning the speciation of chromium in GW system, an hypothesis was postulated that naturally occurring F^- forms a soluble complex with Cr(III)-bearing minerals, after which the dissolved Cr(III) contacts with MnO_2 -containing aquifer material, causing oxidation to Cr(VI). In the present study, it is hereby postulated that, in some regions of the world, chromium is one of the constituents of GW and Cr(VI), the prevailing species in the GW system is a hard base, its presence might vitiate the defluoridation efficiency of MgO in the GW system. Consequently, we aimed at elucidating the defluoridation profiles of nano magnesium oxide (NMgO), in the presence of Cr(VI). In order to achieve this, NMgO shall be synthesised, characterised and the defluoridation efficiency shall be studied in the presence of Cr(VI). This study shall be carried out separately in synthetic feed water and real life GW as the aqua matrix. The efficiency of competition and competitive coefficients of the interfering ionic specie (Cr(VI) or F^-) on the sorbate of interest (F^- or Cr(VI)) shall be determined in a binary system of F^- and Cr(VI). The effect of the competitive sorption on the overall physico-chemical characteristics of the GW shall also be evaluated.

2. Materials and methods

2.1. Synthesis and characterization of NMgO

The nano magnesium oxide (NMgO) (see [supplementary information \(SIF. Fig. 1\)](#)) was prepared by adapting the self-propagating combustion reaction procedure [15–18]. In order to prepare the NMgO, an aqueous solution containing magnesium nitrate ($Mg(NO_3)_2 \cdot 6 H_2O$) 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.



The characterization of the NMgO materials was carried out using X-ray diffraction (XRD) (Seifert XRD 3003 TT) determine the mineralogical assemblage and crystallinity. Surface

microstructure and elemental composition were determined using scanning electron microscopy (SEM) equipped with X-ray energy dispersive analysis (EDAX) (XL 30 FEG ESEM). A transmission electron microscope (TEM) (JEM-2010, JEOL GmbH) was used for particle size and morphological studies. The surface area was determined by the Brunauer–Emmett–Teller (BET) method (Beckman Coulter SA 3100 plus) and the pH_{PZC} was determined via solid addition method described by Oladoja and Aliu [19].

2.2. Sorption studies in synthetic feed water

2.2.1. Determination of time-concentration profiles and equilibrium isotherm parameters

The time-concentration profiles of the sorbate uptake in a single solution system were determined at different initial sorbate (i.e. F^- or Cr(VI)) concentrations (mg/L) that ranged between 2.5 and 30 mg/L. The NMgO (1.0 g) was added into 500 mL of the sorbate solution of known concentration (mg/L) and agitated. Samples were withdrawn from the agitating mixture at fixed time intervals, filtered using 0.45 μm polypropylene membrane and the filtrate was analyzed for residual sorbate concentration using a F^- selective electrode (F500) connected to an ion meter (WTW, Germany). The Cr(VI) concentration was determined spectrophotometrically, at 540 nm (λ_{max}), using a UV/visible spectrophotometer (UV-1601, Shimadzu), following the 1,5-diphenylcarbazide (Merck, Germany) protocol [20]. The amount of sorbate uptake was determined using the mass balance procedure.

The sorption equilibrium isotherm parameters in a single sorbate system were obtained via the addition of 0.1 g of the NMgO into 50 mL of the sorbate solution of varying initial concentrations that ranged between 2.5 and 30 mg/L. The mixture was agitated until the attainment of the equilibrium time, subsequently filtered using 0.45 μm polypropylene membrane and the filtrate was analyzed for the residual sorbate concentration.

2.2.2. Competitive sorption in a multicomponent system

The experiment was conducted in synthetic feed water (containing only two solutes i.e. the F^- and Cr(VI)), at varying initial concentrations that ranged between 2.5 and 30 mg/L, for each of the sorbate of interest. The concentrations of the sorbate of interest were varied between 2.5 and 30 mg/L while the concentrations of the interfering ionic species were kept constant.

The equilibrium isotherm parameters of the competitive sorption process were determined by contacting 50 mL solutions of known concentration of sorbate of interest in binary solutions containing both the sorbate of interest and the interfering ionic specie. The details of the variations in the concentrations of the sorbate of interest and the interfering ionic specie employed in the competitive sorption are presented in [SIF. Table 1](#). Samples were withdrawn at the end of the sorption process, centrifuged and the supernatant concentrations of both the sorbate of interest and interfering ionic specie were determined.

2.3. Sorption studies in real GW system

Groundwater was collected from the Garching Campus of the Technical University of Munich, Germany, and the physicochemical characteristics (pH value, electrical conductivity, total hardness (TH), total inorganic carbon (TIC), F, Al, Mn, Mg, Fe, Ca, NO_3^- , Cl^- , PO_4^{3-} , CO_3^{2-} and SO_4^{2-}) were determined. Since the concentrations of F^- and Cr(VI) in the GW sample were very low and under the detection limit, respectively, it was spiked with different concentrations of F^- and Cr(VI) to give the desired initial concentrations of the respective sorbate that ranged between 2.5 and 30 mg/L. The sorption equilibrium isotherm parameters of the sorbate in single and

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