



# Influence of organic load on the defluoridation efficiency of nano-magnesium oxide in groundwater



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## ABSTRACT

The study aimed at the determination of the influence of organic load, simulated by the dissolution of appropriate humic acid (HA) concentrations in water, on the defluoridation efficiency of nano magnesium oxide (NMgO), a nascent reactive material for groundwater (GW) defluoridation. The kinetic analysis of the process of sorption of HA and fluoride ( $F^-$ ) by the NMgO showed that the rate of sorbate removal is a function of the sorption capacity of the sorbent and not the solution concentrations of the sorbate. The Frumkin isotherm equation gave the best description of HA sorption while Freundlich isotherm equation gave a better description of the  $F^-$  sorption. The determination of the efficiency of interfering ions on the removal of HA and  $F^-$ , from both synthetic feed water and natural GW systems, showed that the removal of HA was not affected, when  $F^-$  was the interfering ionic specie, but the negative impact of the presence of HA, as the interfering ion, on the defluoridation efficiency of the NMgO was felt only at the initial  $F^-$  concentration that is  $<5$  mg/L. The determination of the effects of simultaneous removal of  $F^-$  and HA on the quality characteristics of the treated GW showed that significant reduction in the ionic activities and the concentrations of the total inorganic carbon and carbonate of the treated GW samples were observed.

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## 1. Introduction

Dissolved natural organic matters (NOM) are components of groundwater (GW) that vitiate the quality characteristics. It is a complex heterogeneous mixture, derived from the breakdown of animal and plant remains, encompassing organic constituents such as humic acids (HA) and fulvic acids that are colored, aromatic and hydrophobic in nature. It also comprises low molecular weight organics that are hydrophilic, including aliphatic and nitrogenous compounds such as amino acids, carbohydrates and proteins [1]. In the treatment of potable water, NOM react and lower residual chlorine levels and serve as a precursor in the formation of disinfection by-products (i.e. trihalomethanes, haloacetic acids and chlorophenols) [2]. The presence of NOM impedes the effectiveness of water treatment operations, by interfering with flocculation and oxidation processes and fouling of membranes and adsorbents [3]. NOM, in aqua matrix, also serve as food source for bacteria, thereby increasing the regrowth of bacteria in the water distribution network [4].

Consequent upon the fact that NOM is always present in GW, its coexistence with fluoride ( $F^-$ ) in this system is inevitable. For

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example, the occurrence of NOM in GW of Bangladesh and West Bengal, in the concentrations that range between 1 and 12 mg/L have been reported [5]. Therefore, it is considered imperative for any sustainable technology for GW defluoridation to recognize the influence of NOM on the process. Adsorption based defluoridation process, using nano-magnesium oxide (NMgO) as the adsorbent, is a nascent technology for GW defluoridation. The efficacy of NMgO, as a reactive material, in aqua defluoridation has been attested to in our earlier treatise [6] and reported by other researchers [7–10]. Premised on the hydrochemistry of NOM, it has been postulated that the high propensity of NOM to get adsorbed onto an adsorbent surface might alter the surficial properties of the adsorbent and possibly block the adsorption sites on the adsorbent [11–13]. Furthermore, it has been affirmed [14] that the carboxylic and phenolic groups on NOM get deprotonated in weakly acidic to basic milieu (this pH range has been confirmed [6] to be the operating pH of the NMgO), thereby transforming the NOM to an anionic entity. The resulting negatively charged NOM now competes with the aqueous phase  $F^-$  for the available adsorption sites on the NMgO.

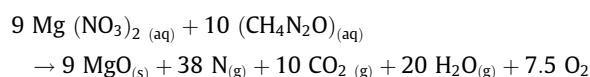
It has been hypothesized [15] that in adsorption process, the mode of adsorbate-adsorbent interaction is greatly influenced by the presence of other ionic species, which can produce three possible types of behavior: synergism, antagonism and non-interaction.

In the adsorption of some oxyanions from aqueous system, the synergistic and antagonistic behavior of co-existing ionic species have been reported [16–19]. At present, the theoretical basis for this study hinged on the hypothesis that the presence of NOM in GW system can modify the process of defluoridation, which ultimately influenced the overall defluoridation efficiency of the NMgO. Premised on this hypothesis, it is apposite to specifically determine the mode of influence of NOM on the defluoridation efficiency of the NMgO in the GW system. Consequently, the defluoridation efficiency of the NMgO shall be studied in the presence of NOM, simulated by the dissolution of HA of varying concentrations (mg/L), in synthetic and real GW systems. The ability of the NMgO to remove F<sup>-</sup> and HA, separately, in single sorbate solution, and simultaneously, in binary sorbate solution, shall be evaluated and the effects of the presence of HA on the fluoride sorption profiles and the presence of fluoride on the HA sorption profiles of the NMgO shall be studied. The effects of the simultaneous removal of F<sup>-</sup> and HA on the overall quality characteristics of real GW shall be evaluated.

## 2. Materials and methods

### 2.1. Synthesis and characterization of NMgO

The NMgO (see supplementary information (SIF. Fig. 1)) was prepared by adapting the self-propagating combustion reaction procedure [20–23]. In order to prepare the NMgO, an aqueous solution containing magnesium nitrate (Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), 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 was carried out using X-ray diffraction (XRD) (Seifert XRD 3003 TT), to determine the mineralogical assemblage and crystallinity. Surface microstructure and elemental composition were determined using scanning electron microscopy (SEM) equipped with energy dispersive analysis of X-ray (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<sub>PZC</sub> was determined via solid addition method described by Oladoja and Aliu [24].

### 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<sup>-</sup> or HA) concentrations (mg/L) that ranged between 2.5 and 30 (for F<sup>-</sup>) and 4.0–12.0 (for HA). 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 fluoride selective electrode (F 800, WTW, Germany) connected to an ion meter (pH/Ion340i, WTW, Germany). The HA was quantified through the UV<sub>254</sub> absorbance determination at  $\lambda_{\text{max}} = 254$  nm, with a UV/VIS spectrophotometer. 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 (mg/L) that ranged between 2.5 and 30 (for F<sup>-</sup>) and 4.0 and 12.0 (for HA). 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. F<sup>-</sup> and HA), at varying initial concentrations (mg/L) that ranged between 2.5 and 30 (for F<sup>-</sup>) and 4 and 12.0 (for HA). In each case, the concentration of the sorbate of interest was varied while the concentration of the interfering ionic species was 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 solution, con-

**Table 1a**  
Kinetic parameters for HA sorption in Synthetic Feed Water System.

Initial conc. (mg/L)	1st Order			2nd Order			3rd Order			Pseudo 1st order			Pseudo 2nd order		
	k	[C] <sub>0</sub>	r <sup>2</sup>	k	[C] <sub>0</sub>	r <sup>2</sup>	k	[C] <sub>0</sub>	r <sup>2</sup>	q <sub>e1</sub> (mg/g)	K <sub>1</sub> (g/(mg min))	r <sup>2</sup>	q <sub>e2</sub> (mg/g)	K <sub>2</sub> (g/(mgmin))	r <sup>2</sup>
3.92	0.0045	2.96	0.5004	0.0012	8.54	0.5100	0.0006	4.27	0.5100	2.283	0.164	0.9043	0.75	1.28	0.9989
5.76	0.0031	2.57	0.6377	0.0012	6.63	0.7044	0.0023	0.83	0.7044	4.532	0.009	0.1324	1.82	0.72	0.9968
7.60	0.0027	2.84	0.7528	0.008	8.11	0.7528	0.0004	4.05	0.7528	6.631	0.045	0.6273	2.58	0.95	0.9993
9.44	0.0055	3.15	0.687	0.0014	9.87	0.687	0.0007	4.94	0.687	3.022	0.04	0.8529	3.52	0.75	0.9996
11.25	0.0007	2.52	0.0933	0.0002	6.33	0.0933	0.0001	3.16	0.0933	1.56	0.0021	0.1324	4.42	51.2	1.000

**Table 1b**  
Kinetic parameters for F<sup>-</sup> sorption in Synthetic Feed Water System.

Initial conc. (mg/L)	Pseudo 1st order			Pseudo 2nd order		
	q <sub>e1</sub> (mg/g)	K <sub>1</sub> (g/(mg min))	r <sup>2</sup>	q <sub>e2</sub> (mg/g)	K <sub>2</sub> (g/(mg min))	r <sup>2</sup>
2.4	1.29	0.028	0.9961	1.39	0.031	0.9915
4.4	2.19	0.023	0.9822	2.84	0.030	0.9721
9.8	5.29	0.026	0.9946	5.51	0.033	0.9798
19.7	9.77	0.022	0.9978	10.86	0.029	0.9832
30.1	13.25	0.017	0.9846	16.92	0.019	0.9826

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