



# Calcium aluminate–diatomaceous earth composite as a reactive filter material for aqua defluoridation



N.A. Oladoja\*, B. Helmreich

Technische Universität München, Chair of Urban Water Systems Engineering, Am Coulombwall, 85748 Garching, Germany

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## ABSTRACT

Calcium aluminate (CA) was prepared through a self-propagation combustion method and got incorporated, in-situ, into the framework of diatomaceous earth (DE) to produce a composite material (CA–DE) that is capable of serving as a reactive filter material for groundwater defluoridation. Aqua defluoridation potential of the CA–DE was evaluated and optimized in a batch process. The XRD analysis of the CA–DE showed that amorphous CA was incorporated into the DE. The results of the kinetic analysis of the defluoridation process showed that the time–concentration profiles, at different initial  $F^-$  concentrations, were best described by the pseudo-second order kinetic equation. The appraisal of the performance efficiency of the CA–DE, via equilibrium isotherm analysis showed that the monolayer sorption capacity of the CA–DE was 18.22 mg/g and Freundlich isotherm equation gave better description of the defluoridation process. Variation in ionic strength, pH, anionic interference, organic load had minimal effects on the extent of aqua defluoridation by the CA–DE.

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## 1. Introduction

Based on the aqua fluoride ( $F^-$ ) concentration, fluoridation or defluoridation is carried out to ensure safe delivery of potable water to consumers. Fluoridation is required, for prevention of dental caries, when the aqua fluoride concentration is less than 1.5 mg/L, whereas defluoridation is vital, to prevent mottling of teeth, skeletal fluorosis, and crippling fluorosis, when the aqua  $F^-$  concentration is above 1.5 mg/L.

Consequent upon the affinities of calcium ( $Ca^{2+}$ ) and aluminum ( $Al^{3+}$ ) for fluoride ( $F^-$ ) in aqua systems, the performance efficiency of these two metal ions is continually being appraised, as adsorbent, in adsorption based aqua defluoridation processes. For instance, calcium hydroxide ( $Ca(OH)_2$ ) is used for the separation of  $F^-$  from drinking water while calcium chloride ( $CaCl_2$ ) and calcium sulphate ( $CaSO_4$ ) are used in the treatment of industrial wastewater containing  $F^-$  [1]. Some other calcium rich materials have also been assessed as adsorbent in aqua defluoridation processes [2,3]. In a similar vein, the use of aluminum oxide, especially the activated form (activated alumina), and other  $Al^{3+}$  rich materials have been widely reported as adsorbent for aqua  $F^-$  removal [1,4,5]. The Nal-

gonda process, a non-adsorption based defluoridation process, is also based on the affinity of  $Ca^{2+}$  and  $Al^{3+}$  for  $F^-$ . The mode of action of this process is hinged on the synergies of lime and alum, which transformed the aqua  $F^-$  into insoluble  $CaF_2$  specie and got flocculated. Premised on the hard–soft interaction principle (HSIP), developed by Pearson [6],  $Ca^{2+}$  and  $Al^{3+}$  are classified as hard acid while  $F^-$  is a hard base. Thus, the affinity of the metals for the aqua  $F^-$  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 [7]. Consequently, hard acids preferentially interact with hard bases, and soft acids interact preferentially with soft bases.

Recently, mixed metal oxides are being studied because of their potential as advanced materials in the optical industry, ceramics, catalysts and adsorbents for environmental remediation [8–11]. In natural environment, single oxide minerals are very scarce than binary oxide, thus it is assumed that the interaction of particles in binary oxide systems possibly influences the adsorption mechanism of adsorbents produced from such systems [12,13]. On the caveat that low-cost adsorbents, which can effectively remove  $F^-$  around the neutral pH of drinking water is used, adsorption based defluoridation process has been considered attractive because the operation is simple, convenient and economical [14].

As part of the on-going strategies to harness the operational recompenses of adsorption, as a unit process in water treatment,

\* Corresponding author. Permanent address: Department of Chemistry, Adekunle Ajasin University, Akungba Akoko, Nigeria.

E-mail addresses: [bioladoja@yahoo.com](mailto:bioladoja@yahoo.com), [n.oladoja@tum.de](mailto:n.oladoja@tum.de) (N.A. Oladoja).

calcium aluminate (CA), was recently synthesized and employed in an adsorption based defluoridation process [15]. The theoretical basis for the choice of CA as an adsorbent in the defluoridation process hinged on the synergistic effects of  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  and the basicity, provided by  $\text{Ca}^{2+}$  in the alumina phase. CA exists as fine particles and this might pose a challenge to use in the conventional procedure for large scale operations (i.e., the continuous flow system). Thus, it is assumed that incorporating the particulate CA into diatomaceous earth (DE), a porous lightweight sedimentary rock, would combine the excellent stable and porous characteristics of DE with the specific affinity of the CA for  $\text{F}^-$  in the aqua matrix. DE has been approved as a food-grade material by the U.S. Food and Drug Administration (FDA) and it is stable in aqueous medium, given that it originates and produced from seas or lakes.

The aim of the present study is the preparation of permeable, reactive filter material, via the incorporation of CA into the framework of DE. The capability of this new filter material shall be studied in groundwater defluoridation. In order to produce the CA–DE composite, the self-propagating combustion synthesis method was employed to synthesize the CA, in the DE matrix. The basis of the combustion synthesis technique comes from the thermochemical concepts used in propellant chemistry. The technique [16] consists of bringing a saturated aqueous solution of the desired metal salts and a suitable organic fuel to boil, until the mixture ignites and a self-sustaining and fast combustion reaction takes off, resulting in a dry, usually crystalline, fine oxide powder. Since the reactions that produced CA was carried out in the DE matrix, in-situ hybridization of the CA into the DE matrix occurred, to produce the permeable, reactive material, CA–DE. The defluoridation potential of the CA–DE was evaluated in a batch process and the defluoridation rate and equilibrium isotherm parameters were derived. The defluoridation process variables were optimized, by method of continuous variations, and the mechanism of the defluoridation process by the CA–DE was also elucidated.

## 2. Materials and methods

### 2.1. Material synthesis and characterization

The CA–DE was prepared via the self-propagating combustion synthesis method [15], and in-situ hybridization of CA into the DE framework, as shown in the reaction scheme (Fig. 1). All the reagents used were obtained from Merck KGaA, Germany. Aqueous solution mixture of 5.91 g calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) and 10 g aluminum nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) was prepared in 20 mL of deionized water (electrical conductivity of  $0.08 \mu\text{S}/\text{cm}$ ). 5 g of DE was added to the aqueous solution mixture and mixed, thoroughly, to obtain an even mix. 6.51 g of Urea ( $\text{CH}_4\text{N}_2\text{O}$ ) solution was also prepared in 20 mL of water and added to the DE-metal salts solution and mixed thoroughly. The evenly mixed solution was kept in a muffle furnace, at  $600^\circ\text{C}$  for 30 min, for the simultaneous self-propagating combustion reaction and the in-situ hybridization of the CA into the DE framework. The product obtained was ground and homogenized, before transferring it into a muffle furnace for calcination, at  $550^\circ\text{C}$  for 3 h. The calcined material was washed with copious amount of deionized water and dried at  $110^\circ\text{C}$  for 4 h in the drying oven. The material produced was labeled CA–DE and subsequently used as adsorbent in the batch defluoridation process to evaluate the potential as a reactive, permeable material for aqua defluoridation.

The CA–DE was characterized thus: mineralogical assemblage, crystallinity and elemental composition were determined using X-ray diffractometer (XRD) (Seifert XRD 3003 TT) and X-ray fluorescence (XRF) (Philips Model-PW2400), respectively; surface microstructure and elemental composition were determined using

scanning electron microscope (SEM) equipped with energy dispersive analysis of X-ray equipment (EDAX) (XL 30 FEG ESEM); the surface area was determined by Brunauer–Emmett–Teller (BET) method (Beckman Coulter SA 3100 plus); and the surface functional groups were determined using Fourier Transform Infra-red spectrophotometer (FTIR) (Perkin Elmer Spectrum 100 with ATR unit).

The stability of the CA–DE in acidic, basic and neutral medium was assessed by agitating a 100 mL sample of  $\text{F}^-$  solution dosed with 0.1 g CA–DE for 1 h at a pH that ranged between 5 and 9. After the agitation, samples were taken and filtered through a  $0.45 \mu\text{m}$  polypropylene membrane and the filtrate was analyzed for leached  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  metal ion concentrations, using Atomic Absorption Spectrophotometer (Varian Spectr. AA-240FS) according to the standard methods 3111 and 3113. Prior to analysis, the samples were acidified to a pH value below 2. The detection limit was  $2 \mu\text{g}/\text{L}$ .

### 2.2. Batch defluoridation process

The kinetic parameters of the process were obtained at different initial  $\text{F}^-$  concentrations that ranged between 4.3 and  $38.4 \text{ mg}/\text{L}$ . The choice of the concentration range of the synthetic  $\text{F}^-$  solution was based on the commonly reported concentration range of  $\text{F}^-$  in real contaminated groundwater. The CA–DE (1.0 g) was added into 500 mL of  $\text{F}^-$  solution of different initial  $\text{F}^-$  concentrations ( $\text{mg}/\text{L}$ ) and stirred at fixed stirring speed. Samples were withdrawn from the agitating mixture at fixed time intervals, subsequently filtered using  $0.45 \mu\text{m}$  polypropylene membrane and the filtrate was analysed for residual  $\text{F}^-$  concentration. The amount of  $\text{F}^-$  sorbed per unit mass of the CA–DE (in  $\text{mg}/\text{g}$ ) for each sample collected was calculated using the mass balance procedure.

The sorption equilibrium isotherm parameters of the process were obtained via the addition of 0.1 g of the CA–DE into 50 mL of  $\text{F}^-$  solution of varying initial  $\text{F}^-$  concentrations that ranged between 5.32 and  $38.12 \text{ mg}/\text{L}$ . The mixture was agitated until the attainment of the equilibrium time, subsequently filtered using  $0.45 \mu\text{m}$  polypropylene membrane and the filtrate was analyzed for residual  $\text{F}^-$  concentration.

The effects of process variables (i.e., initial  $\text{F}^-$  solution pH, ionic strength, inorganic and organic interferences), similitude of what obtains in the groundwater matrix, was simulated as presented herein. The effects of initial solution pH were studied between pH 4.6–8.7. The effects of anionic interference were simulated by the addition of different concentrations ( $\text{mg}/\text{L}$ ) (10, 50 and 100) of different anions (i.e.,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$ ). The effects of organic interference were simulated by the addition of humic acid (HA) of concentrations ( $\text{mg}/\text{L}$ ) (5, 10 and 20). The ionic strength was tested in NaCl solutions (%): 0, 0.05, 0.1, 0.2, 0.5 and 1, equivalent to ionic strengths ( $\text{mol}/\text{L}$ ) of 0, 0.0085, 0.017, 0.0342, 0.085 and 0.17.

## 3. Results and discussion

### 3.1. Material synthesis and characterization

The synthesis of CA, through the self-propagating combustions methods, has been advanced and optimized to produce very fine crystalline un-agglomerated multi-component oxides, without the intermediate decomposition and/or calcination steps. In the reacting mixture, placed in the furnace, the formation of CA involves the decomposition of nitrate solutions at temperatures below  $700^\circ\text{C}$ , with the evolution of the gases of nitrous oxides, such as  $\text{NO}_2$ ,  $\text{NO}$ , and  $\text{N}_2\text{O}_5$  [17]. Urea also decomposes into biuret ( $\text{H}_2\text{N}-\text{CO}-\text{NH}-\text{CO}-\text{NH}_2$ , i.e.,  $\text{C}_2\text{H}_5\text{N}_3\text{O}_2$ ), Cyanuric acid ( $\text{H}_3\text{C}_3\text{N}_3\text{O}_3$ ), and ammonia ( $\text{NH}_3$ ) at  $\sim 200^\circ\text{C}$ . Biuret further decom-

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