



Batch defluoridation appraisal of aluminium oxide infused diatomaceous earth



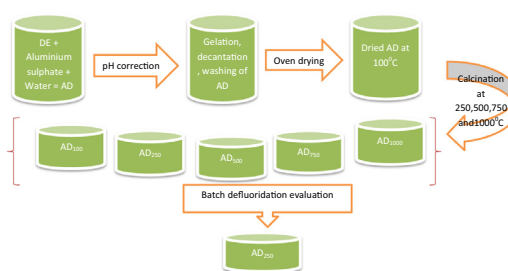
N.A. Oladoja*, B. Helmreich

Technische Universitaet Muenchen, Chair of Urban Water Systems Engineering, Am Coulombwall, 85748 Garching, Germany

HIGHLIGHTS

- DE could be enriched with amorphous Al_2O_3 for aqua defluoridation.
- Surface area had no influence on the magnitude of F^- sorption.
- Defluoridation, using AD was described by the pseudo second order equation.
- Defluoridation process occurred via ligand exchange specific to F^- in this regard.

GRAPHICAL ABSTRACT



Material Synthesis and Screening for Batch Defluoridation Process

ARTICLE INFO

Article history:

Received 12 June 2014

Received in revised form 14 July 2014

Accepted 15 July 2014

Available online 24 July 2014

Keywords:

Batch defluoridation
Diatomaceous earth
Aluminium oxide
Fluoride
Groundwater
Co-precipitation

ABSTRACT

Diatomaceous earth (DE) was enriched with aluminium oxide, via the co-precipitation method, to produce a permeable, reactive material (AD) for groundwater defluoridation. The AD was characterized, using appropriate instrumental methods, and the defluoridation potential was evaluated in a batch process. The infusion of amorphous aluminium oxide on the DE was confirmed by X-ray diffraction analysis and the optimum calcination temperature for AD synthesis was attained at a temperature of 250 °C. The kinetic analysis of the time–concentration profile of the defluoridation process showed that the pseudo second order gave better description and the value of the approaching equilibrium factor ($R_W < 0.01$) obtained showed that the process drastically approached equilibrium, at the longest operating time of 300 min. The value of the Langmuir monolayer sorption capacity ($q_e = 13.1$ mg/g) obtained for AD was comparable with what has been reported for other aluminium rich materials, used as sorbents in batch defluoridation processes. Evidences from the results of kinetic analysis and the results obtained from the process variables (i.e. F^- solution pH, ionic strength, and anionic interference) optimization procedures showed that the mechanism of the defluoridation process occurred via inner sphere association, a chemical process that is specific to F^- on the AD surface.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Fluoride (F^-) is a common constituent of groundwater but the presence, at certain concentration (<1.5 mg/L) is desirable (prevention of dental caries) and above certain concentrations (>1.5 mg/L)

is undesirable (causes mottling of teeth, skeletal fluorosis, and crippling fluorosis). Consequent upon over dependence on groundwater resource, in the developing world and remote areas of the developed world, and the negative impact of F^- , efforts are now focused on the development of simple and low cost functional reactive materials that can scavenge F^- from the aqua stream

In recent time, the abilities of oxides and hydroxides of trivalent and tetravalent metal ions are continually being studied for aqua defluoridation because of their strong affinities for F^- . Majority of

* Corresponding author. Permanent address: Department of Chemistry, Adekunle Ajasin University, Akungba Akoko, Nigeria. Tel.: +49 1521749097.

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

these metal oxides and hydroxides have their point zero charge (PZC) above the natural water pH of 7 (e.g. granulated ferric hydroxide pH 7.5–8.0 [1], activated alumina pH 8.25 [2], γ -alumina pH 8.0 [3]). Thus, at the pH of natural water, the surfaces of these materials are predominated by positive charges, which favour the adsorption of the negatively charged aqua F^- species.

Amongst the oxides and hydroxides of metal ions that have been widely used for aqua defluoridation, the oxides of aluminium, especially the activated form, has been the most commonly used [4–8]. Activated alumina is produced by thermal degradation of aluminium hydroxide to obtain materials with high specific surface area and a distribution of micro- and macro-pores [8]. The high affinity and selectivity of activated alumina for F^- have made defluoridation processes, based on activated alumina, attractive at both domestic and community level. In order to optimize the defluoridation potential of aluminium oxide species, different modification procedures have been studied. The enhanced defluoridation abilities of alumina impregnated Lanthanum and Ytterbium have been reported [9]. The faster defluoridation kinetics of alumina, coated with manganese oxide, and the enhanced ability to bring F^- concentrations below the statutory limit for drinking water (<1.5 mg/L), when compared with activated alumina has also been confirmed [2]. It has also been reported that magnesia-amended activated alumina adsorbed F^- from drinking water more effectively than activated alumina [10].

Metal oxides exist as fine particles which make it difficult to use in a continuous flow system, especially when it comes to separation after treatment. It is assumed that doping the particulate oxides within the traditional adsorbents of larger particles would combine the excellent handling and flow characteristics of the adsorbent supports with the specific affinity of the metal oxides toward the targeted pollutants. The use of mechanically stable synthetic or natural solid matrices, as support, in separation and purification technology is a common practice. Diatomaceous earth (DE) was chosen as the mechanically stable, solid matrix on which aluminium oxide is to be incorporated because it is a porous, low density material and readily available. It is a sedimentary rock that is made up of, mainly, silica microfossils of aquatic unicellular algae and consists of various pores with up to 80–90% voids [11]. DE has been approved as a food-grade material by the U.S. Food and Drug Administration and it is stable in contact with liquids, given that it originates from seas or lakes.

This study aimed at developing a cheap and easily producible material as a permeable reactive material for groundwater defluoridation. Thus, aluminium oxide was impregnated into DE, to produce a mechanically stable, permeable, reactive material, to be used in groundwater defluoridation process. The defluoridation potential of the material produced was evaluated and optimized in a batch process

2. Materials and methods

2.1. Material synthesis and screening

The permeable reactive material, aluminium oxide infused diatomaceous earth (AD), was prepared via the co-precipitation procedure, as presented in the reactions scheme (Fig. 1), viz: appropriate amount of the aluminium sulphate salts $[Al_2(SO_4)_3 \cdot 12H_2O]$ (Merck KGaA, Germany), whose aluminium concentration (in g) is equivalent to 20% of the DE (Applichem, Germany) to be added, was dissolved in a beaker containing 100 mL of deionized water and stirred thoroughly before 10 g of DE was added and stirred to obtain an even mix for 30 min. The pH of the mixture was corrected to pH 8 ± 0.2 using 4 M NaOH (Merck KGaA, Germany), under vigorous stirring. The mixture was allowed to settle and

then washed severally with deionized water (electrical conductivity = 0.08 $\mu S/cm$) and the washed solid portion was dried in the oven at 105 °C and then calcined in the furnace at different temperatures (250, 500, 750 and 1000 °C) or 3 h. The products were labeled AD₁₀₀, AD₂₅₀, AD₅₀₀, AD₇₅₀ and AD₁₀₀₀; the subscript showing the temperatures at which each material was calcined.

The optimum calcination temperature, for the AD synthesis, was determined via batch defluoridation process viz: 50 mL of F^- solution, derived from sodium fluoride (NaF) salt (Merck KGaA, Germany), of fixed concentration (40 mg/L) was contacted with 0.1 g of each calcined material (i.e., AD₁₀₀–AD₁₀₀₀). The mixture was agitated at 200 rpm for 2 h, samples were 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.

The effects of the calcination temperatures on the surface area, and the mineralogical assemblage of the AD samples were also determined.

2.1.1. Material characterization

The AD sample was characterized thus: mineralogical assemblage, crystallinity and elemental composition were determined using X-ray diffraction (XRD) (Seifert XRD 3003 TT) and X-ray fluorescence (XRF) (Philips Model-PW2400), respectively. Surface microstructure and elemental composition were determined using scanning electron microscopy (SEM) equipped with energy dispersive X-ray (EDX) (XL 30 FEG ESEM). The surface area was determined by the 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 AD in acidic (pH = 4.7), neutral (7.3) and basic (pH = 9.6) medium was assessed by agitating 50 mL sample of F^- solution dosed with 0.1 g AD for 4 h at the different pH values. After agitation, samples were taken and filtered through a 0.45 μm polypropylene membrane and the filtrate was analyzed for the leached Al^{3+} concentration, using atomic absorption spectrophotometer (Varian Spectr AA-240FS) according to the standard methods 3111 and 3113. The samples were acidified prior to analysis to a pH below 2. The detection limit was 2 $\mu g/L$.

2.2. Batch defluoridation process

The time–concentration profiles of the sorption of F^- by AD were studied in a batch reactor to obtain the kinetic parameters viz: 1.0 g of the AD was added into 500 mL of F^- solution of different initial concentrations (mg/L) that ranged between 4.46 and 38.00. Solution samples were withdrawn at intervals between 0 and 5 h, filtered using 0.45 μm polypropylene membrane and the filtrate was analyzed for residual F^- concentration. The amount of F^- sorbed per unit mass of the AD (in mg/g) was calculated using the mass balance procedure.

The sorption equilibrium isotherm parameters of the batch defluoridation process were obtained via the addition of 0.1 g of the AD into 50 mL of F^- solution of varying concentrations (mg/L) that ranged between 5 and 40. The mixture was agitated for 4 h, filtered using 0.45 μm polypropylene membrane and the filtrate was analyzed for residual F^- concentration.

The defluoridation process variables (F^- solution pH, inorganic and organic interference and ionic strength), similitude of what obtains in the groundwater matrix, was simulated viz: initial solution pH that ranged between pH 5.0 and 9.0; anionic interference by the addition of different concentrations (mg/L) (10, 50 and 100) of different anions (NO_3^- , Cl^- , PO_4^{2-} , CO_3^{2-} and SO_3^{2-}) derived

Download English Version:

<https://daneshyari.com/en/article/146939>

Download Persian Version:

<https://daneshyari.com/article/146939>

[Daneshyari.com](https://daneshyari.com)