Separation and Purification Technology 153 (2015) 108–117

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Assessment of fixed bed of aluminum infused diatomaceous earth as appropriate technology for groundwater defluoridation

N.A. Oladoja *, J.E. Drewes, B. Helmreich

Technische Universität München, Chair of Urban Water Systems Engineering, Am Coulombwall 8, 85748 Garching, Germany

ARTICLE INFO

Article history:
Received 17 February 2015
Received in revised form 29 August 2015
Accepted 1 September 2015
Available online 1 September 2015

Keywords:
Groundwater defluoridation
Aluminum oxide
Diatomaceous earth
Fixed bed operation
Reactive filter

ABSTRACT

Excessive occurrence of fluoride in groundwater supplies is a major issue in many regions of the world. In order to produce a reactive filter (AD) for use as an appropriate groundwater defluoridation technology, the classical co-precipitation method was adopted to enrich diatomaceous earth with aluminum oxide. In a laboratory-scale water system, the breakthrough profile, fixed bed operation parameters and the mass transfer parameters of an AD column reactor were determined to obtain design parameters for real GW defluoridation applications. The defluoridation process variables studied (i.e. AD bed height and initial fluoride (F^-) concentration) had a direct impact on column breakthrough and operating parameters. The mass transfer analysis revealed that external and internal diffusion were not the rate-limiting step of the defluoridation process in the column reactor. Considering the magnitude of the desorbed F^- and the physical integrity of the spent AD using selected regeneration solvents (HCl, HNO_3, H_2SO_4, NaOH and CH_3COOH) at two different concentrations (0.1 and 0.05 M), CH_3COOH was identified as the most suitable solvent to regenerate spent AD. The presence of a substantial amount of total inorganic carbon (68 mg/L), whose dominant species is HCO_3^-, resulted in a decrease in defluoridation efficiency using real groundwater. Based on the physicochemical characteristics of the AD reactor effluents, we proposed a non-specific mode of adsorption as one of the underlying defluoridation mechanism. This was in addition to the specific mode of adsorption that was revealed earlier as the underlying mechanism of fluoride removal using AD.

1. Introduction

In order to prevent the scourges associated with the consumption of water with high fluoride (F^-) concentrations (1.5 mg/L), research efforts are geared towards the development of appropriate technologies for defluoridation. Appropriate technology is generally recognized as an encompassing technological choice and application that is small-scale, decentralized, potentially more labor-intensive, energy-efficient, environmentally sound, and locally controlled [1]. Since operational requirements of adsorption based water treatment operations can fulfill these requirements, efforts are being made to optimize adsorption based water treatment processes for defluoridation.

Most often in adsorption based water treatment research, a batch adsorption protocol is employed to screen and evaluate potential sorbents for pollution control. While batch reactors can be used in a laboratory setting for the treatment of a small volume of water, they are less convenient to use in real life operations, where larger volumes of water are continually needed [2]. Sorbents that have been screened in batch operations for defluoridation include calcite [3], spent spot liner [4], hydrous manganese oxide-coated alumina [5], or manganese-oxide-coated alumina [6]. In order to develop a functional, reactive, permeable material, suitable for use as a filter in groundwater defluoridation, the batch defluoridation ability of aluminum oxide infused diatomaceous earth (AD) was earlier assessed in our laboratory [7]. This investigation addressed defluoridation kinetics, equilibrium parameters, the optimization of process variables and elucidated the underlying defluoridation mechanisms.

In order to obtain the operation parameters for real life applications of this process, it is crucial to study the application of AD in a continuous flow system using a fixed bed reactor. More so, the adsorption capacity from batch studies may not give accurate scale-up information for continuously operated column systems [8]. A fixed bed column is an effective process to establish cyclic sorption/desorption and to study solute breakthrough or the shape of the wave front, which determines the operation life-span of the bed. Such a system makes the best use of the concentration differ-

---

* Corresponding author at: Department of Chemistry, Adekunle Ajasin University, Akungba Akoko, Nigeria.

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

http://dx.doi.org/10.1016/j.seppur.2015.09.001
1383-5866/© 2015 Published by Elsevier B.V.

ence known as the driving force for adsorption and allows more efficient utilization of the sorbent capacity resulting in a better effluent quality. Continuous fixed bed adsorbers also have a number of process-engineering advantages including easy system scale-up and sorbent recovery where a contaminant is concentrated in a small volume of solid material and desorbs into a small volume of eluent for recovery, disposal, or containment [9–11]. Examples of materials that have been investigated for defluoridation from water in a fixed bed operation include activated alumina [12], granular calcite [13], and manganese oxide coated alumina [6].

The aim of this study was the development of an appropriate groundwater (GW) defluoridation technology, using aluminum impregnated diatomaceous earth as a reactive filtration medium. Thus, a fixed bed of AD was prepared and used to treat both the synthetic water contaminated with fluoride and real GW with elevated levels of fluoride. The parameters of both the breakthrough profiles and the fixed bed operations were derived as a function of two process variables (i.e., AD bed height and initial F^- concentrations). Using appropriate mass transfer equations, the mass transfer parameters of the process were derived and the effects of the defluoridation process on other quality characteristics of the GW were assessed.

2. Materials and methods

2.1. AD synthesis and characterization

The AD was prepared via the co-precipitation procedure, as presented in detail in our earlier publication [7] and is briefly summarized here: an appropriate amount of aluminum sulfate salts [$Al_2(SO_4)_3 \cdot 12H_2O$ (Merck KGaA, Germany)], whose aluminum 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 for 30 min to obtain an even mix. 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 thoroughly with deionized water (electrical conductivity = 0.08 µS/cm). Subsequently, the washed solid portion was dried in the oven (Thermo Scientific, Germany) at 105 °C and then calcined in the furnace (Carbolite, England) at 250 °C. The choice of this calcination temperature was based on our findings [7] that AD calcined at 250 °C resulted in the highest defluoridation capacity.

The AD sample was characterized with respect to mineralogical assemblage, crystallinity and elemental composition using X-ray diffraction (XRD) (Seifert XRD 3003 TT, Germany) and X-ray fluorescence (XRF) (Philips Model-PW2400, Germany), respectively. 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, Germany). The surface area was determined by the Brunauer–Emmett–Teller (BET) method (Beckman Coulter SA 3100 plus, Germany) and surface functional groups were identified using Fourier Transform Infra-red spectrophotometer (FTIR) (Perkin Elmer Spectrum 100 with ATR unit, Germany).

2.2. Defluoridation set-up and operational conditions

The method of Fornwalt and Hutchins [13] was adapted in the preparation of the continuous flow defluoridation set up. In order to avoid air entrainment in the fixed bed column, the AD was weighed into a beaker and made into slurry with deionized water and fed slowly into a glass column (1 cm × 30 cm) displacing a heel of water. Prior to the AD addition into the column, silica sand (5 g) slurry was fed into the column to serve as a base. The sand base was chosen to provide an even distribution of the water within the AD matrix. The column was loaded with feed solutions of known concentrations. The adsorber column was operated in an upflow mode with the aid of a peristaltic pump at a flow rate of 4 mL/min. The fluoride concentration was monitored at the exit of the column and the operation of the column was terminated when the effluent fluoride concentration was equal to 90% of the influent fluoride concentrations. The effects of AD bed height (6.25, 12.5, 25 cm) and influent fluoride concentrations (5, 20 and 40 mg/L) on the continuous flow defluoridation process were studied. All experiments were performed in duplicate.

2.3. Spent sorbent regeneration study

The regeneration of the spent sorbent for reuse was assessed first in a batch process using different solvents (i.e., NaOH, HCl, H_2SO_4, HNO_3, CH_3COOH) at two different concentrations (0.1 and 0.05 M) to determine the most efficient eluting solvent for the spent sorbent. The batch regeneration procedure was performed by contacting 0.1 g of the spent AD, which had been previously washed in deionized water to remove any loosely adhered fluoride species and dried, with 50 mL of the respective regenerating solutions and agitated for a period of 2 h. Subsequently, a sample was withdrawn, filtered through 0.45 µm polypropylene membrane and fluoride concentrations were determined in the filtrate using a fluoride selective electrode (F500) connected to an ion meter (WTW, Germany). The effects of each regenerating solvent on the stability of the spent AD were also assessed.

2.4. Defluoridation of groundwater samples

Samples of GW were collected on the university campus in Garching, Germany and spiked with fluoride to obtain the desired concentrations of GW contaminated with F^-. The following water quality characteristics of the real GW were determined: pH value (using potentiometric method), electrical conductivity (using conductivity cell potentiometric), total hardness (using EDTA titrimetric), fluoride (using ion selective electrode), calcium (Ca) (using AAS), manganese (Mn) (using AAS), magnesium (Mg) (using AAS), aluminum (Al) (using AAS), nitrate (NO_3^-) (using ion chromatography), chloride (Cl^-) (using Mohr method), phosphate (PO_4^{3-}) (using molybdenum–ascorbic acid – UV–VIS spectrophotometer method), total inorganic carbon (TIC) (using ASTM D4129 method) and sulfate (SO_3^{2-}) (ion chromatography). All the samples were analyzed in triplicate. On the basis of the results obtained from the batch defluoridation study, using synthetic feed water [7], the equilibrium isotherm parameters for the GW defluoridation using AD were obtained. The breakthrough profile and the operation parameters of the GW defluoridation process using the fixed bed column reactor were obtained. In addition to the determination of the defluoridation potential of the column reactor, the effects of the defluoridation process on other chemical parameters were also evaluated.

2.5. Definitions of features of primary adsorption zone of column reactor

The portion of the breakthrough curve between the effluent concentration at the exhaustion point (C_e) and breakthrough point (C_b) is defined as the primary adsorption zone (PAZ) and is assumed to have a constant length or depth, δ. The parameters of the PAZ (i.e. t_x, t_δ, t_f, δ and f) were derived from the values of the operating parameters obtained from the breakthrough profiles.