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Towards the development of a reactive filter from green resource for groundwater defluoridation

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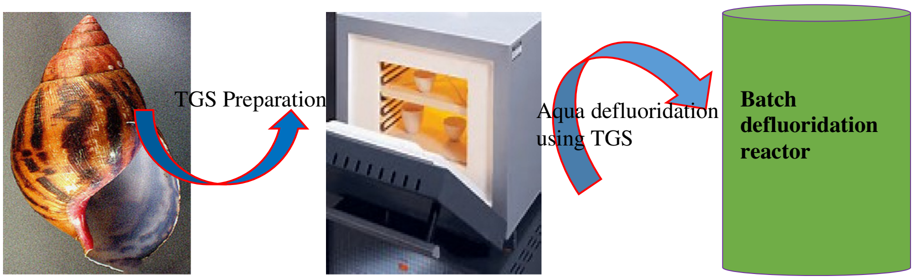
HIGHLIGHTS

- Transformations of $CaCO_3$ to CaO enhanced the defluoridation efficiency of TGS.
- pH, organic load and ionic strength had no influence on the defluoridation efficiency.
- Only carbonate impacted negative on the defluoridation efficiency.
- The underlying defluoridation mechanisms were diverse and not straitlaced.
- GW defluoridation altered some physicochemical characteristics of the product water.

GRAPHICAL ABSTRACT

Preparation of a reactive filter from green resource for groundwater defluoridation.



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ABSTRACT

In order to develop a low cost reactive filter from a green biogenic resource, the shell of a Gastropod (GS) was calcined at different temperatures and the defluoridation efficiencies of the raw and calcined GS were evaluated in a batch process. The highest defluoridation efficiency was obtained with the GS calcined at 1000 °C (i.e. TGS_{1000}). The time–concentration profiles of the defluoridation process were described by the pseudo-second order kinetic equation and the Temkin equilibrium isotherm equation gave the best description of the defluoridation process in synthetic feed water and groundwater (GW) system. The determination of the effects of hydrochemistry on the defluoridation efficiency of the TGS_{1000} showed that variations in pH value, organic load and ionic strength had no visible influence on the magnitude and trend. Amongst the array of interfering ionic species studied, only carbonate exhibited negative impact on the defluoridation efficiency. Experimental evidences revealed that the underlying mechanisms of the defluoridation process were diverse (ionic bond formation, electrostatic attraction, ion exchange and occlusion into $Ca(OH)_2$ framework) and not straitlaced. Groundwater (GW) defluoridation, using TGS_{1000}, showed that the residual F^- in the defluoridated water increased with initial F^- concentration. The value of the monolayer Langmuir sorption capacity was lower in the GW system ($q_m = 6.17$ mg/g) than in the synthetic feed water system ($q_m = 19.84$ mg/g). The values of pH, electrical conductivity, Ca^{2+} concentrations, total hardness values were higher in the defluoridated water relative to the raw GW samples. The Mg^{2+} concentrations were below the detection limit and nitrate concentrations were appreciably attenuated in the treated water samples.

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1. Introduction

The presence of fluoride (F^-) in potable water could be likened to a double edge sword. At concentration below 1.5 mg/L, it is desirable while at concentration above 1.5 mg/L, it is undesirable. The presence of F^- in potable water at low concentration helps in the prevention of dental caries but above this concentration, it causes mottling of teeth, skeletal fluorosis, and crippling fluorosis [1]. Higher level of F^- in groundwater is a global problem that includes various countries in Africa, Asia and the USA [2–4].

In terms of process economy, operational simplicity, adsorbate removal capacity, adsorbent regeneration and reuse potential, adsorption based water treatment technologies are promising protocols for potable water defluoridation. Premised on the high affinity of calcium for F^-, array of calcium rich materials has been studied as adsorbent in aqua defluoridation systems [5–7]. The propensity of calcium rich materials in sequestrating F^- in aqua matrix is asserted by the fact that water with high F^- composition is usually found in calcium deficient groundwater system in many basement aquifers, such as granite and gneiss, geothermal waters and some sedimentary basins [8]. Calcium hydroxide [$Ca(OH)_2$], Calcium chloride [$CaCl_2$] and calcium sulfate [$CaSO_4$] have been used in the treatment of drinking water [9] and industrial wastewater containing F^- [10]. Calcite has also been used for the precipitation of F^- from industrial wastewater and for purification of groundwater [5].

F^- is highly electronegative, possesses small ionic size, classified as a hard base and exhibits strong affinity towards multivalent metal ions [11]. Pearson [12] opined that the guiding principle regarding the interaction of electron pair donors and acceptors is that the most favorable interactions occur when the acid and base have similar electronic character. Thus, hard acids preferentially interact with hard bases, and soft acids interact preferentially with soft bases. Premised on Pearson's classification, Ca^{2+} and F^- are classified as hard acid and base, respectively, thus, the interaction between the two species is favored.

The ability of a thermally treated Gastropod shell (GS), African land snail (*Achatina achatina*), for phosphorus (P) recovery from aquaculture wastewater has been ascertained [13]. The GS has got the same basic construction as other Mollusk shells and it contains mainly $CaCO_3$ as well as various organic compounds [14,15]. Oladoja et al., [13] hinged the adoption of the thermal treatment protocol on the report [16] that the common way to enhance the P removal efficiency of calcium-rich materials is via high temperature heating. It was advanced that during heating, CaO, which has a more reactive Ca^{2+} phase than commonly existing $CaCO_3$ will be formed. Contrary to the claim that the conversion of the carbonate to the oxide form was totally responsible for the superior P-recovery of thermally treated calcium rich materials, Oladoja et al., [13] established that the enhanced defects in the surficial physiognomies, imparted by the thermal treatment process, also contributed to the higher P-recovery efficiency and not just the formation of the active CaO phase. Premised on the guiding principle regarding the interaction of electron pair donors and acceptors and the fact that phosphate and F^- are both hard bases, it is hereby postulated that the thermal treatment of GS can enhance the defluoridation efficiency in aqua matrix.

The present study aimed at the development of a low cost reactive filer material from the shell of GS, a waste biogenic resource, for groundwater (GW) defluoridation. Raw GS and thermally treated GS were screened for aqua defluoridation, to determine the optimum calcination temperature. The time–concentration profiles, kinetics and equilibrium isotherm parameters and the effects of hydrochemistry on the defluoridation efficiency of the reactive material were determined. The defluoridation efficiency of the reactive material in real GW system was evaluated and the effects of the defluoridation process on the physicochemical characteristics of the GW were examined.

2. Materials and methods

2.1. Material preparation, screening and characterization

The GS was prepared as previously described [14,15,17–19] and subjected to thermal treatment, in the furnace, at varying temperatures (100, 250, 500, 750 and 1000 °C) for 2 h. The products were labeled TGS_{100}, TGS_{250}, TGS_{500}, TGS_{750} and TGS_{1000}; the subscripts indicate the temperature of thermal treatment.

The optimum calcination temperature for the TGS was determined via batch defluoridation process viz: 50 mL of F^- solution of fixed concentration (20 mg/L), derived from sodium fluoride (NaF) salt (Merck KGaA, Germany), was contacted with 0.1 g of each reactive material (i.e., raw GS and TGS_{100}–TGS_{1000}). 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 thermal treatment temperatures on the elemental composition and the mineralogical assemblage of the samples were determined using X-ray fluorescence (XRF) and X-ray diffractometer (XRD), respectively. The BET surface areas were determined using an ASAP 2010 Micromeritics instrument (Bru nauer–Emmett–Teller (BET) method). The surface functional groups were determined using an FTIR spectrophotometer (Thermo Scientific, USA).

2.2. Batch defluoridation process

The kinetic parameters of the defluoridation process were obtained at different initial F^- concentrations that ranged between 2.5 and 30 mg/L. The choice of the concentration range of the synthetic F^- solution was based on the commonly reported concentration range of F^- in groundwater system. The TGS (1.0 g) was added into a 1 L of F^- solution of different initial F^- concentrations (mg/L) and stirred at fixed stirring speed. Samples were withdrawn from the agitating mixture at fixed time intervals, subsequently filtered using 0.45 μm polypropylene membrane and the filtrate was analyzed for residual F^- concentration. The amount of F^- adsorbed per unit mass of the TGS (in mg/g) for each sample collected was calculated using the mass balance procedure.

The adsorption equilibrium isotherm parameters of the efluoridation process were obtained via the addition of 0.l g of the TGS into 50 mL of F^- solution of varying initial F^- concentrations that ranged between 2.5 and 30 mg/L. The mixture was agitated until the attainment of equilibrium time, subsequently filtered using 0.45 μm polypropylene membrane and the filtrate was analyzed for residual F^- concentration.

The effects of hydrochemistry (i.e., F^- solution pH, anionic interference, organic load and ionic strength) on the defluoridation process were determined to simulate conditions in typical groundwater matrix. These conditions are summarized as follows: initial solution pH that ranged between pH 5.0 and 9.0; anionic interference by the addition of different concentrations (10, 50 and 100 mg/L) of different anions (NO_3^-, Cl^-, PO_4^{3-}, CO_3^{2-} and SO_4^{2-}) derived from potassium salts (Merck KGaA, Germany); ionic strength (tested in NaCl solutions of 0%, 0.05%, 0.1%, 0.2%, 0.5% and 1%, equivalent to ionic strengths of 0, 0.0085, 0.017, 0.0342, 0.085 and 0.17 mol/L). All experiment was conducted in duplicate.