



Groundwater fluoride removal using modified mesoporous dung carbon and the impact of hydrogen-carbonate in borehole samples

Hideaki Sano^a, Kiyoshi Omine^b, Mysamy Prabhakaran^c, Andre Darchen^d, Venkataraman Sivasankar^{b,e,*}

^a Division of Chemistry and Materials Science, Department of Civil Engineering, Graduate School of Engineering, Nagasaki University, Nagasaki 852 8521, Japan

^b Geotechnical Laboratory, Department of Civil Engineering, Graduate School of Engineering, Nagasaki University, Nagasaki 852 8521, Japan

^c Post Graduate and Research Department of Botany, Pachaiyappa's College, Chennai 600030, Tamil Nadu, India

^d UMR CNRS no. 6226, Institut des Sciences Chimiques de Rennes, ENSCR, 11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France

^e Post Graduate and Research Department of Chemistry, Pachaiyappa's College, Chennai 600030, Tamil Nadu, India

ARTICLE INFO

Keywords:

Ammonium carbonate modified DDC500

Defluoridation

HCO₃⁻ influence

Groundwater

ABSTRACT

There have been many research reports pertained to the interference of co – ions including hydrogen carbonate against the removal of fluoride from water. In this context, the present research explores the fluoride removal efficiency of ammonium carbonate modified dung derived carbon (DDC500) in the absence and presence of hydrogen carbonate using synthetically made fluoride solutions and groundwater samples. The adsorbent DDC500 was found to achieve the highest removal of 80% of fluoride at pH 6.95 than the washed carbon (DDC500W) and dung ash (DA) of 48% and 23% respectively. In DDC500, the carbon base in concert with inorganic residues actively functioned in the fluoride removal process and chosen for synthetic fluoride solutions (2–5 mg L⁻¹) and 16 groundwater samples (2.1–3.6 mg L⁻¹) from 10 locations of Usilampatti Taluk in Madurai District, South India. After the removal of hydrogen carbonate in groundwater, the percentage of samples was increased in accordance with the safe limits of World Health Organization (WHO) and Bureau of Indian Standard (BIS). Langmuir isotherm model ($R^2 = 0.9379$) was in concordance with the adsorption of fluoride from groundwater free from hydrogen carbonate. The dynamics of other groundwater quality parameters at conditions and the independency between F⁻/HCO₃⁻ ratio and DE were illustrated by scatter plots. Characterization studies for the dried dung (CD110), derived carbons (DDC500 and DDC500W) and ashes (CD110A, DDC500A and DDC500WA) using FE–SEM, XRD, FTIR, Raman and TGA – EGA were done to understand the nature and behavior of materials.

1. Introduction

The anionic form of fluorine (radius: 0.133 nm) is fluoride. Its tendency as ligand to form numerous organic and inorganic compounds in air, water and rock environments. Fluoride is a micronutrient for humans as it reverses the progression of dental decay by remineralization and thus prevents the dental caries (Martinez-Mier, 2012). In adults (60%) and infants (80–90%), the retention and affinity of fluoride should be developed in bones and teeth due to enriched calcium phosphate and the rest is excreted through urine (Barbier et al., 2010). Fluoride in drinking water is nutritious when its concentration is less than 0.5 mg L⁻¹ but becomes hazardous when it is greater than 1.5 mg L⁻¹ according to World Health Organization (WHO, 2011). The Bureau of Indian Standards (BIS, 2012) recommended the acceptable

limit of 1.0 mg L⁻¹, however it can be extended to 1.5 mg L⁻¹ in the absence of other alternate. The potable water quality is deteriorated due to fluoride and it is considered as the major public hazard, conspicuously in Countries such as China (21.5 mg L⁻¹) (Ayoob et al., 2008), India (24.17 mg L⁻¹) (Jha et al., 2013), Iran (10.3 mg L⁻¹) (Yousefi et al., 2018), Pakistan (49.3 mg L⁻¹) (Brahman et al., 2013), Ethiopia (264 mg L⁻¹) (Tekle-Haimanot et al., 2006), Swaziland (18 mg L⁻¹) (Manyatsi and Brown, 2009), South Africa (20 mg L⁻¹) (Ncube and Schutte, 2005), Tanzania (45 mg L⁻¹) (Walker, 2012), Kenya (25 mg L⁻¹) (Cavill, 2007), Ivory Coast (16.78 mg L⁻¹) (Osemwegie et al., 2013) and Thailand (14.12 mg L⁻¹) (Chuah et al., 2016) have been reported to have the highest fluoride in groundwater. The possibility of fluoride in the water and soil through geogenic nature includes several rock forming minerals such as cryolite, fluorite, topaz and

* Corresponding author.

E-mail address: sivshri.20@gmail.com (V. Sivasankar).

<https://doi.org/10.1016/j.ecoenv.2018.09.001>

Received 6 July 2018; Received in revised form 9 August 2018; Accepted 1 September 2018

0147-6513/ © 2018 Elsevier Inc. All rights reserved.

fluorapatite (Garcia and Borgnino, 2015). Fuhong and Shuquin (1988) investigated the geochemical processes such as high pH and soil salinity have control over fluoride concentrations in arid sedimentary aquifers of China, in agreement with the findings of Handa (1975) and Dissanayake (1991). In water, the dual nature of sodium hydrogen carbonate to either donate or accept a proton (H^+) decides its amphoteric behavior. Alkaline carbonate solutions have the tendency to absorb CO_2 from the atmosphere till the solubility limits of cationic salts are reached. However, in a closed system like a borehole source, the transport of CO_2 with the atmosphere would be slow or non-existent. Thus, the pCO_2 changes with respect to the alteration in the distribution of various carbonate species unlike in open systems such as streams, lakes and rivers.

Hydrogen carbonate in groundwater functions as a buffering agent and it raises the pH of solution by lessening the uptake of fluoride (Sivasankar et al., 2012a). In alkaline groundwater with high HCO_3^- and Na^+ concentrations, an effective transfer of F from the solid phase minerals into solution takes place due to the production of OH^- (Sivasankar et al., 2016). At constant pH, the fluoride solubility could be enhanced with an increase in hydrogen carbonate concentration whereas the increase in Ca^{2+} decreases the hydrogen carbonate in water and hence the fluoride (Sreedevi et al., 2006). It can otherwise be understood that weakly alkaline pH with low Ca^{2+} and high Na^+ governs the characteristics of groundwater with high fluoride concentration (Su et al., 2013; Hossain et al., 2016). Decarbonation by boiling reduces the alkalinity and calcium hardness in water containing high temporary hardness. This is due to the driven off CO_2 that helps in the solubility of $CaCO_3$ in water. The expulsion of CO_2 causes the precipitation of $CaCO_3$ in water (Martin, 2011).

Adsorption based removal studies using abundant biomass derived carbons are exclusively preferred for their economic advantage in developing and under-developed countries rather than the other advanced wastewater treatment technologies (Zheng et al., 2018; Zhang et al., 2018). Recently the demand for defluoridation including cost-effective adsorption methods was reviewed by Yadav et al. (2018). In order to validate the practicability of adsorbents, defluoridation studies are focused in real groundwater systems. On consideration of the fluoride removal studies using groundwater, literature revealed the utilization and the fluoride removal efficiency of activated carbons prepared from various biomass materials. Although the activated carbons made from banana peel and coffee husk were identified to achieve the fluoride removal of more than 80% (Getachew et al., 2015), bael fruit shell derived carbon was able to scavenge 49% of fluoride from groundwater at Maharashtra (Singh et al., 2017). The ability of bagasse, raw saw dust and raw wheat straw derived carbons in removing fluoride from groundwater at Haryana was restricted to about 58.3%, 52.2% and 45.5% respectively (Yadav et al., 2013). The hindrance caused by hardness and alkalinity to fluoride removal was rather evident from the reported groundwater quality parameters in Maharashtra and Haryana States of India. The fluoride removal performance of *azospirillum* bio-fertilizer (79.1%) excelled than lignite (57.6%) on treating the groundwater with 9.62 mg L^{-1} of fluoride (Kulkarni et al., 2017). In addition to fluoride adsorption, the sorption of hydrogen carbonate was ascertained by calcium modified pecan nut shell carbon and become witnessed for an unspecific sorption of ionic species in drinking water at Aguascalientes, Mexico (Hernandez-Montoya et al., 2012). Similarly, lanthanum modified bone composite (LBW) was explored to be a good adsorbent with 93.8%, 96.1% and 100% of fluoride removal from spring, bore well and dug well sources. Besides, it removes the other anions in the following order: $HCO_3^- > PO_4^{3-} > SO_4^{2-} > NO_3^-$ (Wang et al., 2017).

The effect of hydrogen carbonate in fluoride removal process is quintessential because of its appreciable solubility and governance of pH system in groundwater. It is reported to be the major inhibiting co-ion against fluoride sorption both in synthetic fluoride solutions and groundwater samples. Taking this view into consideration, the present

work significantly represents the impact of hydrogen carbonate on fluoride removal using dung derived carbons from synthetic solutions and groundwater as well. The present study also explored the defluoridation efficiency of carbons which inherently contain fluorophilic elements especially calcium and magnesium. In addition, a comprehensive discussion is made on the dynamics of other groundwater quality parameters before and after the adsorption process. The compositional dynamics in the ammonium carbonate modified dung derived carbon and ashes through the characterization studies are elaborately detailed in this paper.

2. Materials and methods

All the chemicals used in the study were purchased from Kishida chemical company Limited, Osaka, Japan.

2.1. Synthesis of DDC500

Wet cow dung from the local sources of Usilampatti Taluk of Madurai District, South India was procured and air-dried for two weeks. Later, the dried dung was crushed using steel mixer-grinder for the particle size less than $250\ \mu\text{m}$ and oven-dried (FS-320 Advantec air-oven, Japan) at $110 \pm 5^\circ\text{C}$ for 2 h (CD110). This oven-dried dung of 16 g was taken with 0.05 M $(NH_4)_2CO_3$ solution and stirred for 2 h followed by autoclaving the filtered wet mass at the temperature of 127°C and pressure of 0.18 MPa for 2 h using KT-2322/3022 Model autoclave, Japan. Then the autoclaved mass was hydrothermally treated at the heating rate of 10°C per minute at 200°C for 2 h and 500°C for another 2 h under ambient conditions in the electric furnace (Yamato, FO300, Japan). Finally the obtained carbonized mass of 5.4 g was abbreviated as DDC500. DDC500W was obtained by removing ($\sim 6.5\%$) all the soluble inorganic compounds in solution till the pH of washings reached the neutral condition followed by drying at $110 \pm 5^\circ\text{C}$ for 2 h. The further pulverized carbons of DDC500 and DDC500W are abbreviated as PDDC500 and PDDC500W respectively. The derived ash materials are borne with acronyms such as CDA110, DDC500A and DDC500WA. The dry carbon adsorbents of particle size less than $105\ \mu\text{m}$ was used for the defluoridation experiments.

2.2. Characterization

The morphology of dung derived carbons and ashes were examined using field emission scanning electron microscopy (FE-SEM) with JEOL JSM-7500 FAM and JEOL EDS JSM-7500 equipped with FA View (JEOL) software. The structural characterization of the dung based materials were investigated by powder X-ray Diffractometer (XRD) using Rigaku MiniFlex 600 operated at 40 kV and 15 mA and the phase identification was performed with the PDXL2 (Rigaku) software. The functional group identification was done by Fourier transform infrared spectroscopy (FTIR) using ThermoNicolet Nexus 670 NT FT-IR being equipped with the Attenuated Total Reflectance (ATR) spectrophotometer method. In addition, Raman spectroscopic measurements were done with JASCO NRS-3000 using 532 nm laser in the range of $100\text{--}4000\text{ cm}^{-1}$. The thermo gravimetric (TGA) analyses were carried out using TG-EGA equipment with thermo gravimetric analyzer (TG: Shimadzu: TGA-50 H, resolution - 1 μg), non-dispersive infrared gas analysis apparatus (NDIR; Shimadzu: CGT-7000, ranges CO: $0\text{--}100\text{ mg L}^{-1}$, $CO_2\text{--}0\text{--}1000\text{ mg L}^{-1}$, $\pm 2\%$ f.s.). Two sets of oxygen sensors using ZrO_2 solid electrolyte of limit current type (Fujikura Limited, FCX-MW, $0\text{--}95\%$ O_2 , $\pm 0.5\%$ f.s) and four mass flow controllers (MFC, HORIBA limited, Sections-E40, $\pm 1\%$ f.s) and also a 14 channels data logger taken at 1 s intervals. The obtained data were analyzed by the program created using IgorPro[®] and performed for the TG mass correction and synchronous processing along with fixed-quantity compensation processing of gas analysis (Sano, 2008). The specific surface of DDC500 was determined by nitrogen adsorption/

Download English Version:

<https://daneshyari.com/en/article/10144513>

Download Persian Version:

<https://daneshyari.com/article/10144513>

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