Journal of Environmental Management 212 (2018) 424–432

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Fixed bed column study for water defluoridation using neem oil-phenolic resin treated plant bio-sorbent

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A R T I C L E I N F O

Article history:
Received 30 October 2017
Received in revised form
29 January 2018
Accepted 8 February 2018
Available online 22 February 2018

Keywords:
Defluoridation
Bio-sorbents
Fixed bed study
Cost analysis
Regeneration

A B S T R A C T

Fluoride has both detrimental and beneficial effects on living beings depending on the concentration and consumption periods. The study presented in this article investigated the feasibility of using neem oil phenolic resin treated lignocellulosic bio-sorbents for fluoride removal from water through fixed bed column study. Results indicated that treated bio-sorbents could remove fluoride both from synthetic and groundwater with variable bed depth, flow rate, fluoride concentration and column diameter. Data obtained from this study indicated that columns with the thickest bed, lowest flow rate, and fluoride concentration showed best column performance. Bio-sorbents used in this study are regenerable and reusable for more than five cycles. The initial materials cost needed to remove one gram of fluoride also found to be lower than the available alternatives. This makes the process more promising candidate to be used for fluoride removal. In addition, the process is also technically advantageous over the available alternatives.

1. Introduction

Fluoride is one of the commonly found elements in groundwater. Volcanic rocks, calcium poor ores, disposal of fluoride-rich liquid spent from alumina smelters, fly ash disposal release sufficient enough fluoride content in the water resources and pollute them. Consumption of drinking water with lesser than 1.5 mg/L of fluoride is beneficial for proper growth and strengthening of our teeth enamel and bone. However, consumption of higher level of fluoride (more than 1.5 mg/L) containing water could lead to severe health hazards. Fluoride transforms hydroxyapatite (one of the major components in teeth and bone) into stronger fluorapatite. Overconsumption of fluoride produced high amount of fluorapatite which makes the teeth enamel stronger and brittle. This results molting of teeth and in severe condition, it develops dental and skeletal fluorosis leading to permanent deformation of a skeleton. The effects of fluoride intoxication are severe in school going kids and old people (Wang and Reardon, 2001; Hichour et al., 2000).

Groundwater of most of the Asian countries, part of Africa and Australia contain fluoride than the WHO permissible limit. Till date, different types of techniques, e.g., coagulation and precipitation, electro-coagulation, ion exchange, membrane separation and adsorption, have applied for fluoride removal from water (Ayoob et al., 2008; Bhatnagar et al., 2002; Mohapatra et al., 2010; Gill et al., 2014, Waghmare and Afrin, 2015). Among all these processes adsorption-based processes used mostly as they are simple, easy to handle and inexpensive. Till date, different types of adsorbents have been tested and reported for their high fluoride removal efficacy. Recent reviews summarized adsorption based water defluoridation (Habuda—Stanić et al., 2014; Mondal and George, 2015; Wambu et al., 2016). These reviews indicated the major disadvantages of the adsorbents. The adsorbent based processes are suffering from either poor removal efficiency, or high processing cost, or availability of raw materials, poor regeneration or production of toxic sludge difficult to dispose of. To tackle these issues researcher used inexpensive biomasses (Ramanaiah et al., 2007; Sathish et al., 2007; Davila-Rodriguez et al., 2009; Thakre et al., 2010; Mondal et al., 2012; Paudyal et al., 2013; Manna et al., 2014, 2015; Amin et al., 2015; Kestkar et al., 2016; Mondal and Kundu, 2016; Hiremath and Theodore, 2017; Saikia et al., 2017;

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https://doi.org/10.1016/j.jenvman.2018.02.037
0301-4797/

Mondal, 2017). In addition to this, researchers had developed biomasses based advanced materials for fluoride removal (Roy et al., 2017a,b). Many of the bio-sorbents showed higher defluoridation capabilities; even in some cases, they are better than the available alternatives to parametric influences. However practical application of these adsorbents for industrial and household wastewater treatment in large-scale is yet to explore. Any materials having defluoridation capacity in different parametric influences is eligible for large-scale water treatment with data analysis by using appropriate mathematical models. In addition, applicability of the biomass should verify by a pilot scale study.

The study presented in this article described the column defluoridation study and mathematical modeling of neem oil—phenolic resin treated bio-sorbents. The defluoridation ability of neem oil—phenolic resin treated bio-sorbents in different parametric influences was established previously by our group (Manna et al., 2015). Current study presented the applicability of the neem oil—phenolic resin treated bio-sorbents in large-scale defluoridation. Defluoridation capabilities of neem oil—phenolic resin treated bio-sorbents in fixed bed column and data analysis with mathematical modeling have been presented in this paper. Also, adsorption-desorption mechanisms of the process have been discussed in details with proper characterization techniques.

The main aim of this study is to establish the feasibility of neem oil—phenolic resin treated bio-sorbents for fluoride removal from wastewater in large scale. In addition, this study also was undertaken to understand the desorption mechanism involved. For this, detailed column studies have been carried out with fluoride containing distilled water and groundwater. The exhausted bio-sorbents were regenerated by washing them with a mild acid solution. The liquid spent generated during the acid wash and the bio-sorbents (before and after acid wash) were analyzed with FTIR spectroscopic analysis for understanding the desorption mechanisms.

2. Materials and methods

2.1. Preparation of bio-adsorbent

Detail adsorbent preparation processes described in our article published elsewhere (Manna et al., 2015). The process is briefly described below. First, the plant matters were collected from local jute mill and washed with distilled water, followed by chopping into pieces (1–5 mm) and drying in an oven at 70 °C for 12 h (Saha et al., 2012). The dried plant matters were subsequently ground with a mixer grinder for 20 min and this is termed as UPB hereafter.

Ground UPB was then treated with 0.5% NaOH solution followed by steam treatment at 103 kPa for 30 min. The alkali steam treated plant matters were further treated with neem oil-phenolic resin. The resin was prepared as follows: first 23 mL of cashew nut shell liquid (CNSL), 15 mL of 37% formaldehyde and 10 mL of 0.5% NaOH aqueous solution was mixed by mechanical stirring over 15 min. Then 15 g of resorcinol and 175 mL of distilled water were added to the mixture and stirred again for 1 h maintaining the temperature between 28 °C and 30 °C. Thereafter, a required amount of distilled water was added to the solution for maintaining the solid content 2.0 g per 100 mL. The neem oil emulsion was prepared by mixing 10 mL of neem oil and 90 mL of alkaline water (containing 0.25 g of NaOH) with mechanical stirring for 30 min. Equal volume of neem oil emulsion and phenolic resin were mixed with continuous stirring. This neem oil-phenolic resin mixture was then used to treat alkali-stem treated plant matters. For this, the plant matters were soaked within the emulsion mixture for 18 h at room temperature (25–35 °C) followed by squeezing and curing at 105 ± 5 °C for 1 h in a hot air oven and termed as NPB hereafter. The treated and untreated plant matters were washed with ethanol to remove the unreacted chemicals and dried in an oven at 70 °C before their use for adsorption studies. The proportion of chemical used in this study was optimized with respect to the removal efficiency. The data was not shown in this paper.

2.2. Water used for the study

For fluoride removal by column studies, a range of synthetic sodium fluoride (NaF) solutions were used. The NaF solutions in concentrations between 5 mg/L and 20 mg/L were prepared by mixing NaF in distilled water following the procedures described in the report of the United States Environmental Protection Agency (USEPA, 1971).

Also along with synthetic water fluoride contaminated groundwater was also used during this study. The fluoride contaminated groundwater was collected from a well at Nashipur, West Bengal, India (Fig. 1). Nashipur area is underlain by old alluvial (red hardpan) with pH between 5.0 and 6.5, and average annual rainfall of about 1400 mm. The groundwater of this area is known to contain CO_3^{2-} (10–400 mg/L), HCO_3^- (10–600 mg/L), SO_4^{2-} (4–200 mg/L), NO_3^{2-} (3–200 mg/L), Cl^- (30–900 mg/L), F^- (0.18–6.88 mg/L), Ca^{2+} (4–600 mg/L), Mg^{2+} (3–400 mg/L), Na^+ (4–900 mg/L) and K^+ (2–300 mg/L) (Gupta et al., 2006). High bicarbonate and alkaline pH known to leach fluoride-containing minerals occasionally found in the rock formations of Chotanagpur plateau that reaches the western vicinity of Nashipur enhancing the fluoride concentration in groundwater. Many local residents continue to consume fluoridated groundwater despite the closure of many groundwater wells of the area by the government in an attempt to address public health issues related to high fluoride concentrations. Adverse effects of fluoride in drinking water were noticed amongst local residents during the collection of water. The physicochemical properties of the water were measured on spot using portable Eutech Multiparameter Tester 35.

2.3. Estimation of fluoride

Fluoride content of an aqueous medium was estimated as per USEPA (1971) using fluoride ion selective electrode supplied by Cole-Parmer, USA.

2.4. Preparation of fixed bed column and column study

All the column studies were done using polypropylene columns supplied by Tarson. The fixed bed columns were prepared using acid washed silica sand (with the specific gravity of solid grains of 2.65) and untreated (UPB) and treated plant bio-matters (NPB). First, the acid washed sand were loosely (at 14 kN/m^3 dry unit weight) packed within the column to a thickness of 50 mm. Then over the sand bed, 30 mm–70 mm thick plant matter layers were prepared by loosely packing the plant matters.

Fluoride-containing synthetic and groundwater were then percolated through the columns maintaining a constant flow rate. Synthetic aqueous solutions containing 5 mg/L to 20 mg/L of NaF and fluoride containing groundwater were passed through columns with a range of flow rate between 10 mL/min to 20 mL/min. The column diameter and column bed depth were also varied. Fluoride concentration in the effluent collected after every five minutes was estimated.

2.5. Regeneration and reuse

Fluoride saturated plant matters collected from column studies were regenerated to investigate its reuse potential. The