Journal of Environmental Chemical Engineering 3 (2015) 662–669

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

Biosorption of fluoride on Neem (*Azadirachta indica*) leaf powder

Ranjan Kr. Bharali *, Krishna G. Bhattacharyya

Department of Chemistry, Gauhati University, Guwahati, Assam 781014, India

ARTICLE INFO

Article history:
Received 27 September 2014
Accepted 9 February 2015
Available online 17 February 2015

Keywords:
Azadirachta indica
Neem leaf powder
Fluoride biosorption

ABSTRACT

Neem leaf powder prepared from mature, dried Neem (*Azadirachta indica*) leaves was investigated to assess its ability to remove fluoride from aqueous solutions using batch adsorption process. Effects of solution pH, contact time, adsorbent amount and solution temperature on fluoride sorption had been investigated. The biosorbent was effective at the pH range of 5.0–7.0 and its fluoride removal capacity was found to be above 80%. The equilibrium time for fluoride sorption was found at 60 min and the process followed the second order kinetic mechanism. The adsorption process was exothermic in nature and obeyed Freundlich, Langmuir and Temkin isotherm models. SEM study of the biosorbent showed a morphological change of the surface after sorption and FTIR study indicated the involvement of some surface functional groups in fluoride sorption. These results indicated that Neem leaf powder might be an effective adsorbent for treatment of water contaminated with fluoride.

Introduction

Fluoride has been considered as an essential micro-nutrient in human body, because very trace amount of fluoride is beneficial for the production and maintenance of healthy bones and teeth in human body [1]. However, excessive presence of fluoride in drinking water influences the metabolism of elements such as Ca and P in human body and causes dental and skeletal fluorosis [2]. For optimal dental health, the World Health Organization recommended a level of fluoride from 0.5 to 1.5 mg/L as the permissible limit of fluoride concentration in drinking water [3]. A concentration higher than this limit can lead to fluorosis. Fluorosis due to excessive presence of fluoride in drinking water has been reported from different regions of the world, which has increased the importance of defluoridation studies throughout the world.

During the last few years, adsorption on suitable solid matrix has received much importance as a possible measure to bring down fluoride concentration within the permissible limit. Several adsorbent materials including activated alumina [4], zeolites [5], brick powder [6], $KMnO_4$-modified activated carbon [7], bauxite [8], Kanuma mud [9] and many more had been studied and reported for fluoride removal from aqueous medium. Besides, several plant-based biosorbents such as dried orange juice residue [10], tamarind (*Tamarindus indica*) fruit shell carbon [11], *Morringa indica*-based activated carbon [12], etc., have been studied very recently by various investigators and reported for fluoride removal from water with different degrees of success.

In the present work, Neem leaf powder (NLP), developed from the mature leaves of Neem (*Azadirachta indica*) trees has been shown to be an active biosorbent for removal of fluoride from water.

Materials and methods

Preparation of the biosorbent

The biosorbent was prepared from mature leaves of Neem tree. Clean and dust free leaves were first sun dried for 3–4 days and then allowed to dry in an air oven at 60–70 °C for a long time. The dry leaves was then crushed into fine powder, Neem leaf powder (NLP) using a mechanical grinder. The powder was then sieved and fractionated using a series of sieves and the 74–105 micron fractions were selected. NLP contains various water soluble amino acids, carbohydrates and pigments, which get dissolved during shaking in batch process and may hamper in spectrophotometric detection of fluoride ions. Therefore, NLP were washed with distilled water in a glass vessel at room temperature for several times to remove all the water soluble pigments and other materials. Initially the washings were turbid, but after several washings, the washings became clear and at this point washing was stopped. The washed powder was

* Corresponding author. Tel.: +91 9707385762.
E-mail address: rbharali84@gmail.com (R.K. Bharali).

http://dx.doi.org/10.1016/j.jece.2015.02.007
2213-3437/

dried for several hours at room temperature and was preserved as the biosorbent in plastic bottles.

Chemicals and reagents

All the chemicals used in the present work, including sodium fluoride, SPADNS [sodium 2-(parasulfo-phenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate], zirconyl oxychloride, copper chloride, ethylene diamine, sodium hydroxide, hydrochloric acid were of pure analytical grade. A stock solution of adsorbate (NaF) was prepared by dissolving 0.221 g of NaF in 1.0 L of distilled water (concentration of fluoride, 100 mg/L), which was further diluted to required concentration during the experiments. The mixed SPADNS reagent used in the experiments was prepared by mixing equal volume of SPADNS reagent and Zirconyl-oxychloride reagent.

Adsorption experiments with NLP

The sorption behaviors of fluoride on NLP were examined under the batch mode of operation. The batch adsorption was carried out in 100 mL polypropylene conical flasks by mixing a pre-weighed amount of the NLP with 50 mL of the aqueous NaF solution of particular concentration at 303 K. The flasks were then agitated in a thermo-stated water bath shaker for a pre-determined time interval at a constant speed. After adsorption was over, the mixture was filtered off and the fluoride remaining unadsorbed was estimated spectrophotometrically by SPADNS method [13], using a spectrophotometer (Shimadzu Spectrophotometer, UV-1800) with SPADNS reagent at λ_{max} = 570 nm. Effects of contact time and sorption kinetics sorption were studied by analyzing uptake of the fluoride by constant amount of biosorbent (3.0 g/L) at 303 K from aqueous solution at different time intervals of 5, 10, 20, 30, 45, 60, 90, 120 and 180 min. Isotherm studies were carried out by mixing various doses of biosorbent (from 1.0 to 5.0 g/L) to a particular concentration of fluoride solution and agitating the reaction mixture for the equilibrium time (min). Effects of pH on fluoride adsorption was studied by adjusting the pH of the reaction mixture from 2.0 to 11.0 at 303 K (NLP 3 g/L, fluoride concentration 3.0 mg/L, agitation time 60 min). The pH of the fluoride solutions were adjusted by adding 0.1 M (M = mol/dm^3) HCl and 0.1 M NaOH solutions and was measured using a pH meter. Influence of temperature on adsorption was studied in the temperature range from 298 to 318 K, by keeping the other parameters like amount of NLP (3.0 g/L), fluoride concentrations (from 3.0 to 15.0 mg/L), agitation time (60 min) constant.

The amount adsorbed per unit mass of the adsorbent (q_t) at time *t* was calculated using the following mass–balance relations:

$$q_t(\mathrm{mg/g}) = (C_o - C_t) \times \frac{V}{m} \qquad (1)$$

$$\text{Extent of sorption}(\%) = \left[\frac{(C_o - C_t)}{C_o}\right] \times 100 \qquad (2)$$

where, C_o and C_t were initial ($t = 0$) and final ($t = t$) fluoride concentrations in mg/L when the adsorption was carried out for a time interval of *t* min with '*m*' amount of sorbent (g) and *V* volume (L) of fluoride solution.

Results and discussion

Characterization of NLP

The specific surface area of the NLP was determined by Methylene blue adsorption method [14,15] and was found to be 32.94 m^2/g, which was higher than that of a number of plant-based adsorbents such as cotton cellulose (1.081 m^2/g) [16], coffee residue (2.57 m^2/g) [17], teak tree bark (17.45 m^2/g) and coconut husk (20.31 m^2/g) [18], chitosan (2.76 m^2/g) [19], but much less than that of most commercial activated carbons (800–1500 m^2/g) [20]. This result indicated that NLP provide considerable surface area for sorption of pollutants.

The cation exchange capacity (CEC) of NLP was 0.859 meq/100 g, which was determined by Cu(II) bis-ethylenediamine complex method [21]. This value of CEC is much lower than that of some other adsorbents such as commercial activated carbon (68.7 meq/100 g), activated carbon supported on K-type zeolite (113.8 meq/100 g) [22] and the clay mineral bentonite (75.3 meq/100 g) [23]. This indicated that in case of NLP, the CEC values only result from the polar functional groups at the surface.

The anion exchange capacity (AEC) of NLP was determined by conductometric method [24] and the AEC value for NLP was 1.5 meq/g, which was comparable to the AEC of reagent grade cellulose powder (0.69 meq/g) and cellulose based anion exchanger (1.81 meq/g) [24]. This result indicated that NLP could provide considerable numbers of exchangeable anionic sites to adsorb anions like fluoride. To determine the acidity/basicity of the NLP, the pH of 5% slurry of the powder (5.0 g NLP in 100 mL distilled water) was recorded with a pH meter (Systronics, 335) and the value was found to be 6.5. This indicated that the NLP was slightly acidic in nature.

Effects of pH

The pH of the fluoride solution had some significant influence on sorption of fluoride by NLP, because it can affect the surface charge of the adsorbent. As shown in Fig. 1, the biosorbent was effective in the pH range of 5.0–7.0 with a maximum sorption of 82.3% at pH 6.8, and the extent of sorption of fluoride decreased considerably above pH 7 or below pH 4. Since sorption was >80% at the natural pH of aqueous NaF solution as prepared (pH 6.8), therefore, all the subsequent experiments were carried out without adjusting the pH of the fluoride solution. The effects of pH on fluoride adsorption by NLP is similar to what has been observed for fluoride adsorption onto various other adsorbents like lanthanum incorporated chitosan beads [19] and tamarind fruit cover [25].

Effects of contact time and sorption kinetics

The effect of contact time on fluoride sorption by NLP at 303 K is shown in Fig. 2. It was found that the extent of sorption increased with the increase in time (min) up to 60 min and after this time interval, the sorption was almost constant.

This indicated that the time necessary for NLP–fluoride interactions to reach equilibrium was just over 60 min, which was found to be independent of initial fluoride concentrations.

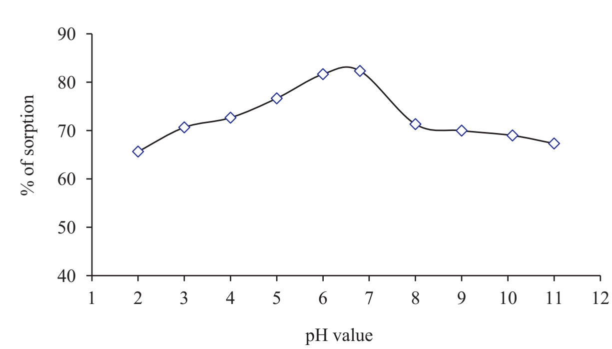

Fig. 1. Variation of the extent of sorption of fluoride with pH on NLP at 303 K.