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Copper oxide incorporated mesoporous alumina for defluoridation of drinking water

Amit Bansiwal, Pradnya Pillewan, Rajesh B. Biniwale, Sadhana S. Rayalu *

Environmental Materials Unit, National Environmental Engineering Research Institute (Council of Scientific and Industrial Research), Nehru Marg, Nagpur 440020, India

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ABSTRACT

In the present study mesoporous alumina was modified by coating copper oxide to enhance the defluoridation of water. The copper oxide coated alumina (COCA) was synthesised by impregnating alumina with copper sulphate solution followed by calcination at 450 °C in presence of air. The COCA was thoroughly characterised using powder XRD, SEM and BET surface area analysis. It was observed that coating of copper oxide improves the adsorption capacity of unmodified alumina from 2.232 to 7.770 mg g^{-1}. Various adsorption isotherm and kinetic parameters were computed using batch adsorption studies to determine the adsorption capacity and to understand the mechanism of adsorption. The results revealed that the adsorption follows Langmuir isotherm and pseudo-second-order kinetic models. The adsorption capacity obtained from Langmuir isotherm plots were 3.155 mg g^{-1}. Assessment of the water quality before and after treatment with COCA also confirmed that the there is no leaching of copper and other parameters were also within permissible limits of Indian drinking water standard indicating that the COCA can be used for treatment of fluoride contaminated drinking water.

1. Introduction

Fluoride is an essential element for normal mineralisation of bone and dental caries, however excess intake of fluoride through contaminated drinking water lead to fluorosis, which is perhaps the most common drinking water related problem. Besides affecting the dental and skeletal system, various other adverse health effects namely muscle fibre degeneration, low haemoglobin level, deformities in RBCs, excessive thirst, gastrointestinal discomfort, etc., are also observed due to excess fluoride intake [1]. The problem of excess fluoride in drinking water is prevailing in 25 nations across the world and it is estimated that more than 200 million people are bound to consume fluoride contaminated water. In India 20 of 35 states and Union Territories are affected due to excess fluoride in groundwater covering more than 150 districts and 36,988 habitations [2]. Considering the severity of health problems due to excess fluoride in groundwater, the World Health Organisation (WHO) permissible limit of fluoride has been reduced from 1.5 to 1.0 mg l^{-1} in 1998.

Removal of fluoride from groundwater is the only remedy since source substitution is not possible due to non-availability of alternate sources. Various defluoridation techniques have been used to reduce the excess fluoride below the safe limits. These include coagulation and precipitation, membrane processes, electrolytic, ion-exchange and adsorption onto various adsorbents. The Nalgonda technique based on chemical precipitation using alum and lime is most comely used technique for defluoridation [3,4]. However, generation of aluminium and fluoride rich sludge and aluminium carryover in treated water are major disadvantages of precipitation-based techniques. To overcome the limitation of conventional techniques adsorption-based fluoride removal systems are emerging as the feasible option. Large numbers of adsorbents have been studied for removal of fluoride from water based on alumina [5], granular ferric hydroxide [6], geomaterials [7], chitin and chitosan [8–12] mixed metal oxides [13–15], clays [16], minerals [17] industrial wastes [18] cement [19,20], etc.

Activated alumina (AA) is the most extensively studied adsorbent for removal of fluoride from drinking water. Due to high affinity and selectivity of AA for fluoride, defluoridation processes based on AA have been used both at community and domestic level. AA is the granular form of aluminium oxide (Al_2O_3) with high internal surface area, typically in the range of 200–300 m^2/g. This high surface area allows the material a very large number of sites where adsorption can occur. The earliest study conducted by Savinelli and Black [21] has demonstrated the high potential of activated alumina for fluoride uptake [21]. Some researchers have concluded that removal was the result of ion-exchange as well as adsorption process, which follows both Freundlich and Langmuir isotherms [5]. AA has a great capacity for fluoride adsorption, which is dependent upon the crystalline form, activation process solution pH and alkalinity. Interference due to presence of other anions/cations also affects the fluoride removal capacities of AA. The use of activated alumina in a continuous flow fluidised system is an economical

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* Corresponding author. Tel./fax: +91 71272247828.
E-mail addresses: ak_bansiwal@neeri.res.in (A. Bansiwal), pradnya_pillewan@rediffmail.com (P. Pillewan), rb_biniwale@neeri.res.in (R.B. Biniwale), s_rayalu@neeri.res.in (S.S. Rayalu).

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and efficient method for defluoridating water supplies [5] and adsorption capacity of 1450 mg kg^{-1} at pH 7 can be achieved. However, the greatest disadvantage of fluoride removal by activated alumina is that the optimum fluoride removal capacity occurs only at a pH value of the solution below 6.0, which limits the practical applications of the AA heavily. Moreover, it has been reported that alumina begins to leach below pH 6 and poses severe threats to human health since the aluminium and its fluoride complexes are known to cause Alzheimer's disease and the other health effects are also well documented [22].

To overcome above limitations, various chemical modifications of AA have been suggested. One such attempt is reported by Maliyekkal et al. [23] wherein AA coated with manganese oxide was evaluated for removal of fluoride [23]. A significant increase in adsorption capacity and adsorption rate was observed as compared to unmodified AA. Tripathy et al. have also reported fluoride removal using alum impregnated AA [24]. Improvement in adsorption capacity was reported after impregnation of AA with alum as compared to unmodified AA. Recently Maliyekkal et al. [25] also reported modification of AA using magnesia which lead to improvement in the fluoride uptake capacity [25].

In the present study, a new sorbent prepared by modifying activated alumina by copper oxide coating was evaluated for removal of fluoride from water. The newly synthesised copper oxide coated alumina (COCA) has been thoroughly characterised using XRD, SEM, FTIR and BET surface area analysis. Batch adsorption studies were conducted to determine various adsorption and kinetic parameters and to understand the mechanism of adsorption. Attempts were also made to study the effect of different anions commonly encountered in drinking water and to compare the fluoride removal efficiency with unmodified alumina, which was used as base material.

2. Materials and methods

2.1. Materials

Granular AA (PURALOX) used for preparing COCA was provided by SASOL, GmbH Germany. It was a high purity mesoporous alumina with pore size in the range of 50–200 Å. The alumina was in the form of spherical beads and was used as such after washing with deionised (DI) water (18 MΩ resistivity, obtained from MilliQ DI water system). Copper sulphate, sodium fluoride, sodium chloride, sodium nitrate, sodium sulphate, sodium carbonate, sodium bicarbonate were purchased from E. Merck India Ltd. A stock solution of 1000 mg l^{-1} fluoride was prepared by dissolving 2.2111 g of sodium fluoride in 1000 ml of DI water and working solutions of different fluoride concentrations were prepared freshly by appropriate dilution of stock solution by DI water. All chemicals used in this study were of analytical grade.

2.2. Synthesis and characterisation of adsorbent

Ten grams of AA was mixed with different concentrations of copper sulphate solution ranging from 0.001 to 0.05 M. The pH of solution was maintained at 4.5–5.0 by adding 0.1 N NaOH, and the solution was agitated for 16 h. After shaking, the material was filtered and the solid residue was washed thoroughly with DI water to remove excess copper sulphate. The washed material was air dried for 8–10 h. The dried material was calcined at 500 °C for 4 h in air atmosphere to convert the copper sulphate into copper oxide. The calcined material was again washed three times with DI water and air dried for 8–10 h. The final copper loading on the synthesised COCA was determined by digesting the COCA in aqua regia and analysis of copper by ICP-MS.COCA was synthesised using different concentration of copper sulphate to achieve copper loadings ranging from 1 to 20 mg/g (Fig. 1). It was found that the COCA with copper loading of 10 mg/g gave the best fluoride removal efficiency and hence was selected for further studies.

The synthesised COCA was thoroughly characterised using powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and BET surface area analysis. The powder XRD patterns were recorded using X-ray Diffractometer (Model Phillips: PW-1830). The operating target voltage was 35 kV and the current was 20 mA. The radiations of Cu Kα were generated using X-ray generator of model (PW 1729) of same make and the β radiation were filtered using monochromator. The sample was powdered and scanned for 2θ ranges from 10° to 110°. The SEM analysis was carried using Stereoscan S250 MK3 (Cambridge Instruments, UK) with different magnifications. The surface area determinations were carried out by N_2 adsorption isotherms using Micrometrics ASAP 2010 K surface area analyser.

2.3. Methods of analysis

Fluoride analysis was done by ion selective electrode method using ion meter (Thermoelectron, USA, Model 920A) coupled with fluoride ion selective electrode (Thermoelectron USA, Model 9609 BNWP). TISAB III was used as buffer for maintaining the pH and background ion concentrations during measurement. pH was measured using the same ion meter coupled with pH electrode. The concentrations of various co-ions and other physico-chemical parameters of treated and untreated water were determined using standard methods. Carbonate and bicarbonate alkalinity and total hardness were determined titrimetrically. The analysis of copper was done using ICP-OES (Perkin–Elmer, Model Optima 4100DV). Blank experiments were conducted throughout the studies and majority of the experiments were repeated twice and it was observed that the experimental error was within ±2%.

3. Results and discussion

3.1. Characterisation of adsorbent

The XRD patterns of unmodified AA and COCA presented in Fig. 2 shows few broad peaks characteristic of amorphous phases of alumina. Peaks at 2θ values of about 45°, 35° and 61° in both unmodified AA and COCA confirms presence of γ-alumina phases.

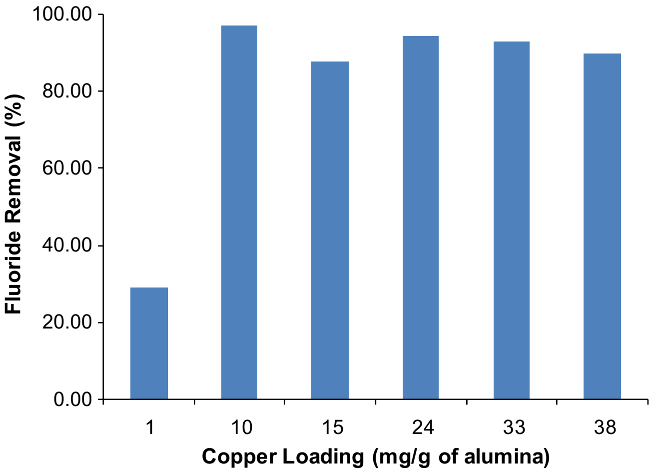

Fig. 1. Effect of copper loading on alumina for removal of fluoride (batch volume: 50 ml, temperature: 30 ± 1 °C, initial F concentration: 10.0 mg l^{-1}, contact time: 24 h, and adsorbent dose: 0.4 g/l).