Journal of Energy Research and Environmental Technology (JERET)
p-ISSN: 2394-1561; e-ISSN: 2394-157X; Volume 3, Issue 1; January-March, 2016; pp. 34-37

http://www.krishisanskriti.org/Publication.html

Comparative Studies between Conventional and Polymer based Adsorption for Defluoridization for Drinking Water

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Abstract—*This study was carried out to evaluate the effectiveness of rural based defluoridation technique - Nalgonda and other technique and amine based polymer adsorbent. The most widely used technique - Nalgonda technique held above other techniques due to its easy construction of the reactor, operation & maintenance and its effectivity when the fluoride concentration is above 20 mg/L. The generation of acid or alkali water however restricts its practical applications along with residual aluminum, soluble aluminum fluoride complexes and fluoride contaminated sludge. The leakage of sulphate as aluminium sulphate with concentration as high as 400 mg/L in treated water also makes it un-potable and caused pitting effect on RCC reservoir/reactor or container. On the other hand, Amine based adsorbent polyaniline was studied and observed fluoride binding due to electrostatic attraction between protonated amine and anionic fluoride. The complexity of co-precipitaion in Nalgonda technique for sludge removal is highly minimised in polyaniline adsorbent case which also further add advantage due to its reusability and thereby increasing the fluoride uptake value. However polyaniline binds fluoride at acidic pH thereby requiring the addition of base to increase the pH to convert into potable. Cement paste is also employed by several researchers for effective removal of F- due to high concentration of Ca^{2+} and additional adsorption of the remaining F- into amorphous calcium phosphate. But hardness due to lime makes it unfit for drinking. This paper deals with the comparison with emphasis to potable water.*

Keywords: *Defluoridation, Nalgonda technique, Polyaniline, Co-Precipitation*

1. INTRODUCTION

The emergence of fluoride ions (F^-) above the permissible/desirable limit (1.5 mg/L) in ground water during the last few decades have affected worldwide and at least 62 million people in India with dental and skeletal fluorosis and even tumors. Fluoride bearing mineral in the host rock, is the main source however, effluent from industries such as aluminum smelthers, steel, phosphate fertilizer, automobile and thermal power plants also generates of about 500–2000 mg/L of F^- and contributed to surface & ground water pollution. A recent assessment of surface water on periphery of industries from ten various location of Delhi reveals F^- contamination within the range of 2.4 - 22 mg/L against the desirable limit of 2 mg/L **[1]** causing ground water contamination as high as 3.1 mg/L and made unfit for consumption. Nalgonda techniques, activated carbon, bone char methods used for deflouridation of water are used basically in rural areas, which is community based. Nalgonda process did not achieve a great degree of success in field application as it removes only a smaller portion of fluoride (18–33%) in the form of precipitates and converts a greater portion of ionic fluoride (67–82%) into soluble aluminium fluoride complex ion, and therefore this technology is erroneous. Adoption of Nalgonda technique for defluoridation of water is not desirable due to use of aluminium sulfate as coagulant, the sulfate ion concentration increases tremendously and in few cases, it crosses the maximum permissible limit of 400 mg/L, which causes cathartic effect in human beings. The residual aluminium in excess of 0.2 mg/L in treated water causes dangerous dementia disease as well as pathophysiological, neurobehavioural, structural and biochemical changes. It also affects musculoskeletal, respiratory, cardiovascular, endocrine and reproductive systems. On household scale it is introduced in buckets or drums and at community. For larger communities a waterworks-like flow system is developed, where the various processes of mixing, flocculation and sedimentation are separated indifferent compartments.

Defluoridation using Activated Alumina (AA) has been one of the widely used adsorption/ ion exchange methods water and many reports are available on large-scale installations for townships, requiring supervision and skilled personnel. The quality of treated water from such facilities was assured. However, this approach was not immediately feasible because of increase hardness and surface loading (the ratio of total fluoride concentration to activated alumina dosage). The process is highly selective and is pH specific with low adsorption capacity, poor physical integrity, requires acidification and pretreatment and its effectiveness for fluoride removal reduces after each regeneration. Bone char, though cost effective with a defluoridation percentage of 62 to 66%, still posses limitations such as harbors of bacteria and hence unhygienic conditions. Without a regular fluoride analysis, nothing indicates when the material is exhausted and the fluoride uptake is ceased. Moreover, the use of bone-char will have psychological effects on consumers. In urban areas, peoples generally use R.O techniques to maintain the fluoride from groundwater source but it proves costly. Thus, these conventional techniques are not that much suitable for the urban areas, we need such a technique having economical cost and easily accessible.

One of the most technologically important conducting amine based commercially available polymer is polyaniline with good environmental stability, easy synthesis, and reversible acid/base doping/dedoping chemistry [2]. In the field of defluoridization, very few researchers had explored the potential of amine compounds. Recently, polyaniline was prepared with aniline in hydrochloric acid medium mixed with ammonium peroxydisulphate and employed through electro chemical process for F- removal obtaining uptake capacity of 20 mg/g [3]. However, the polyaniline when synthesized over the surface of alumina or chitosan, yields powdered adsorbents and showed lesser adsorption capacity value for F- adsorption with 6.6 mg/g and 5.9 mg/g respectively [4]. The mechanism of removal was identified as ion exchange of doped protonic hydrochloric acid chloride of polymer matrix and F-. Removal mechanism was also proposed as electrostatic attraction between protonated amines of both polyaniline and chitosans with anionic fluoride. However, during a parallel study on Cr(VI) removal, the same polyaniline was oxidized to pernigraline along with reduction of Cr(VI) to Cr(III) [5]. Such oxidation property (unstability) of polyaniline will hinder the long period storability and commercialization potential of polyaniline adsorbent. Besides, powder adsorbent has high hydrodynamic limitation effects such as column clogging along with restriction of flow of water to be treated. These finding raise the necessity to modify or develop a stable and inert amine based adsorbent with certain objectives that includes easy synthesis technique, rapid adsorption, desorbable, cost effective and easy separation after adsorption. Lately, another polyaniline polymer synthesized on surface of jute-fiber (PANI-jute) as support material with chain terminating agent para-phenylenediamine was employed for removal of hexavalent chromium effectively [6]. The presence of para-phenylenediamine was to increase the stability of the polymer and the study also confirms the non oxidation property of polyaniline in acidic solution or basic environment. Research & investigation on removal of F- by amine rich stable polyaniline synthesized with para-phenylenediamine are not yet reported and explored.

2. MATERIALS AND METHOD

In the process of Nalgonda Technique, alum (aluminium sulphate) and lime (calcium oxide) are added to and rapidly mixed with the fluoride contaminated water. Induced by a subsequent gentle stirring, “cotton wool”-like flocs develops (aluminium hydroxides) and is subject to removal by simple settling. The main contents of the fluoride are removed along with the flocs through combination of sorption and ion exchange with some of the produced hydroxide groups [7-9]. Activated alumina for defluoridization through adsorption involves preparation at low temperature dehydration. The fluoride uptake capacity of activated alumina depends on the specific grade of activated alumina, the particle size and the water chemistry (pH, alkalinity and fluoride concentrations) [8,9]. Bone char used for defluoridation involve sieving of bone char to the average particle diameters of 0.65, 0.79 and 1.29 mm, then washing it with deionized water, drying in a furnace at 100◦ C for 24 h and stored in plastic containers. The concentration of fluoride in an aqueous solution was determined by a potentiometric method. For polyaniline, adsorption was conducted in batch mode and estimation was done through ion meter.

3. RESULTS AND DISCUSSION

Conventionally, in India, F^- contaminated water has been treated generally by Nalgonda technique where alum [$Al_2(SO_4)_3$] and lime [$Ca(OH)_2$] are added to water followed by the coagulation/precipitation process and sedimentation of the $Al(OH)_3$ precipitate together with the adsorbed fluoride. Generation of acid/ alkali water, residual aluminum, soluble aluminum fluoride complexes and sludge with relatively higher fluoride concentration are however its main drawbacks [10,11]. High sulphate concentrations in treated water as high as 400 mg/L in this technique also cause the water un-potable and pitting effect on RCC. Cement paste is generally employed for effective removal of F^- due to highly elevated concentration of Ca^{2+} and additional adsorption of the remaining F^- into amorphous calcium phosphate [12]. However calcium (lime) creates the problem of hardness of effluent water and co-precipitation particle of CaF_2 are too fine to be sedimented without coagulation. Limitation of CaF_2 precipitation also includes it inability to reduce F^- concentration of less than 10- 20 mg/L against the theoretical solubility of 17 mg/L at 25^0C in water [13]. A study on electrocoagulation method by introducing bipolar aluminum electrodes showed effective removal of F^-. However, no $Al(OH_3)$ flocs was formed at acidic pH 2 due to amphoteric nature of aluminum hydroxide and no removal was observed unless the pH was increase to about 5- 7 [14]. Controlling pH at basic condition for F^- removal was very difficult during the process due to the defluordization reaction which changes the pH and also the applied current interfering with measurement of pH [15]. Electrocoagulation process also produces hydrogen gas at electrocoagulation cathodes resulting in problem of unsettling floc on leaving electrode. Another, recent studies on F^- removal by membrane technique such as reverse osmosis were reported with separation of F^- higher than 95% [16]. However, membrane based techniques such as ion exchanges required high installation and maintenance cost making them infeasible options. In the field of F^- adsorption, one of the most cost effective and widely used adsorbent is activated alumina. Slow rate of adsorption due to intra particular diffusion, accumulation of bacteria in the long run of commercially available activated alumina and production of fluoride contaminated alumina sludge however limits its use for treating large quantity of water. When activated alumina was coated with manganese oxide, the F^- uptake increased from 1.08 to 2.85 mg/g [17] due to formation of metal fluoride complex [18]. Nevertheless, the synthesis process was complex requiring heated at 150 ^{0}C for 5 hours and then 500 ^{0}C for 3 hours. One of the recently developed oxide based adsorbent also includes hydrous iron(III)-tin(IV) bimetal mixed oxide and achieved F^- uptake of 10.5 mg/g [19]. The oxides being in form of fine powder limits the practical application including difficulty in solid/ liquid separation after adsorption, low hydraulic conductivity and leaching of the metal/ metal oxides along with treated water. Presence of the H^+ during protonation on amines groups considers the amine base polymer as lewis acid and prefers to bind with F^- as it is the hardest Lewis base among all anions [20]. Therefore investigators explore the effectivity of F^- uptake by amine based chitosan derivatives & composites and that includes protonated cross-linked chitosan beads [21], magnesia-chitosan composite [22], alumina-chitosan beads [23], chitosan coated silica [24], Zr(IV) entrapped chitosan polymeric matrix [25] with maximum uptake of 7.32, 11.24, 10.41, 44.40 and 13.69 mg/g respectively. The adsorption mechanism suggested was H-bonding between protonated amine group (NH_3^+) and F^- ions. Regardless of its appreciable F^- uptake, the obtained flake and powder forms of chitosan are not suitable to be used as adsorbents due to their low surface area and no porosity[26].

The binding of fluoride by polyaniline is through electrostatic attraction of anionic fluoride and protonated amines of polyaniline at terminal end of the polymer. Due to chemical binding, kinetics is rapid and also desorption was possible. Through this, repeated adsorption was enhanced.

4. CONCLUSION

The literature survey has indicated that each of the discussed techniques can remove fluoride under specified conditions. The fluoride removal efficiency varies according to many site-specific chemical, geographical and economic conditions, so actual applications may vary from the generalizations made. Any particular process, which is suitable at a particular region, may not meet the requirements at some other place. Nalgonda technique, Activated Alumina, Bone Char is suitable technique for Indian rural communities. Thus we have to look for urban areas accessible methods for deflouridation which are economical and effective.

5. ACKNOWLEDGEMENT:

P. Albino Kumar would like to thank DST/WTI for the funding of the project DST/WTI/2K12/08.

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