

Various Options for Removal of Fluoride from Drinking Water

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ABSTRACT

Excessive fluoride concentrations have been reported in groundwaters of more than 20 developed and developing countries including India where 19 states are facing acute fluorosis problems. Various technologies are being used to remove fluoride from water but still the problem has not been rooted out. In this paper, a broad overview of the available technologies for fluoride removal and advantages and limitations of each one have been presented based on literature survey and the experiments conducted in the laboratory with several processes. It has been concluded that the selection of treatment process should be site specific as per local needs and prevailing conditions as each technology has some limitations and no one process can serve the purpose in diverse conditions.

Keywords: Fluoride; Fluorosis; Ground water; Soil water; Drinking water; Treatment

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I. INTRODUCTION

The rapid increases in the human population and the rapid pace of Industrialization in India have created problems of waste disposal with the recent past. In general the domestic wastes and the industrial effluents are being by and large, indiscriminately discharged in the nearby fresh water resources without any treatment. Therefore, a rapid Degradation of water quality has been envisaged in the past years and Concrete steps are required to be taken immediately to abate water Pollution. Keeping the above aspect in view to cope with the problems the Present investigation has been undertaken. In the present study our Effort is to evaluate the feasibility of generating the condition suitable for bioremediation of induction wastewater in industrial areas of Kanpur district. **Mercury, arsenic, fluoride, nitrate, nickel and organic waste phenol** are a significant environmental toxin that can be deadly to humans.

1.1. Fresh Water Crisis

Water is, literally, the source of life on earth. About 70 percent of the earth is water, but only one Percent is accessible surface freshwater. The one percent surface fresh water is regularly renewed by rainfall and other means and thus available on a sustainable basis and easily considered accessible for human use. Water is the biggest crisis facing the world today. In India the crisis in terms spread and severity affects one in three people. As per an estimate in 2000, there were 7,800 cubic meters of fresh water available per person annually. It will be 5,100 cubic meters (51, 00,000 liters) by 2025. Even

this amount is sufficient for human needs, if it were properly distributed. But, equitable distribution is not possible India, which has 16 percent of world's population, 2.45 percent of world's land area and 4 percent of the world's water resources, has already faced with grave drinking water crisis. Water is the single largest problem facing India today. Years of rapid population growth and increasing water consumption for agriculture, industry and municipalities and other areas have strained Indian fresh water resources. In many parts of our country chronic water shortages, loss of arable land, destruction of natural habitats, degradation of environment, and widespread pollution undermine public health and threaten economic and social progress. By 2050 more than 50 percent of population is expected to shift to the cities and the drinking water scarcity will be acute. In the developed world, for example, the United Kingdom must spend close to \$60 billion building wastewater treatment plants over the next decade to meet the new European water quality standards. The World Bank has estimated that over the next decade between US \$ 600 to 800 billion will be required to meet the total demand for fresh water, including that for sanitation, irrigation and power generation. A water short world is inherently unstable world. Now the world needs another revolution, i.e., a Blue Revolution for conservation and proper maintenance of freshwater.

One in eight people in the world today lack access to clean drinking water. A child dies every 15 seconds from a lack of clean water. One in four children who die before age five worldwide, die of a water related disease. Most people without access to

clean water live right above it. In many cases the only thing preventing access to clean water is money¹. Access to clean water is the foundation of development. Food, health, hygiene, habitat, education, employability, productivity are all dependent upon access to water. Without clean water, none of these is possible and poverty is inevitable. Majority of these people are in the developing world.

Over the years, India has made improvements to both the availability and quality of municipal drinking water systems. However the exponentially growing population has stressed existing water systems and resources. The pressures of urbanization have stretched government solutions. Rural areas are still left out. Many water sources are contaminated with both bio and chemical pollutants, and over 21% of the country's diseases are water-related.

The Department for International Development (DFID) leads the UK Government's fight against global poverty. To take this agenda forward DFID is establishing a research programme to help engage with those new and emerging technologies with the potential to impact on poverty in a way that enables developing countries to take advantage of what they have to offer. Through this research, Technology and Action for Rural Advancement (TARA) seeks to identify key challenges and barriers that may reduce the impact of technologies such as Nanotechnologies for providing clean drinking water reaching the underprivileged in developing countries, it's possible environmental implications and remedial measures.

Only 2.53 % of earth's water is fresh, and some two-thirds of that is locked up in glaciers and permanent snow cover. Nearly one billion people - one in eight persons in the world - lack access to safe water supply. Over 3.5 million people die each year from water-related disease; 84 % are children. 98 % occur in the developing world. Sixty five million people are at risk of arsenic poisoning in the Bangladesh, India and Nepal area. The water and sanitation crisis claims more lives through disease than any war claims through guns [2].

Indian government surveys reveal that only 30 % of the rural population had access to safe drinking (tap) water in the country. 55 % depend on tube well or hand pumps to meet their drinking water requirement. 15 % of rural populations were still looking for a dependable source of water. In urban areas, 74 % depend on tap water and 18 % on tube well/hand pump [2].

Altogether the cost of environmental damage is estimated to be \$9.7 billion per year, of the most vital is the health impacts of water pollution accounting for 59% of the total value of degradation. Waterborne diseases (the consequence of a combination of lack of clean water supply and inadequate sanitation) cost the Indian economy 73

million working days a year. Water quality is a major problem in both ground and surface water. Although in their upper reaches most rivers are of good quality, the middle and lower reaches of almost all rivers face major degradation. Some of the key pollutants and their sources are summarized below.

Microbial contamination (faecal) mainly arises from inadequately treated or untreated sewage. Lack of sanitation and sewage treatment facilities is the main cause for this.

· **Heavy metal** contaminated waste water from industrial activities such as electroplating, textile dyeing; tanneries etc reach the surface or ground water sources if it's inadequately treated. In addition leaching from solid waste dumps (e.g. fly ash ponds, sludge from above industries) also contributes towards heavy metal accumulation.

· **High salinity** arises from decreasing groundwater levels and seawater intrusion. This is also aggravated by agricultural run offs, which are rich in salts.

· **Arsenic, fluoride, nitrate, nickel and organic waste phenol** contaminants enter groundwater aquifers from their presence in the sediments of the region. This has been further aggravated by excessive groundwater withdrawals.

· **Micropollutants** include **pesticides, endocrine disrupting substances, and surfactants**. These arise from agricultural run offs and from sewage.

Water that does not meet drinking water standards should be treated to ensure that the health of the consumer or community is not compromised through exposure to toxic pollutants. Water supply systems in urban India are mainly centralized and managed by municipal bodies. Certain levels of treatment and purification occur at source before distribution via a piped network. Chlorination is the most common measure. Rural India depends on varied localized sources to meet its water needs. Traditionally households boil water before consumption. Urban markets today are flooded with household water purifiers catering to the middle and upper classes. The technologies used vary from reverse osmosis to UV purification to ionization, iodine filters, etc.

Polluted water is often treated by conventional or pressure-driven membrane processes to make it comply with drinking water standards. Conventional water treatment process consists of several stages. These include pre-treatment, coagulation, flocculation, sedimentation, disinfection, aeration, and filtration. The pre-treatment stage removes suspended solids. Coagulation and flocculation are carried out to precipitate dissolved impurities through sedimentation. The water is then filtered to remove any suspended particles. One of the disadvantages of the conventional water treatment method is that it cannot remove dissolved salts and some soluble inorganic and organic substances.

The DFID Research Strategy 2008 – 2013 recognizes a key role for research to help anticipate and respond to future trends with respect to new and emerging cutting edge technologies that could have a real relevance to the needs of poor people. The Research Strategy also recognizes that the challenge for DFID lies not in the development or commercial application of these technologies, but in translational research to support the longer term development agenda. Research is needed into the most effective, safe and affordable approaches to applying these new technologies in developing country situations and to ensuring the benefits are derived by the poorest. Purifying drinking water is one of the strategic areas for the research with a special focus on nanotechnology. TARA has undertaken this research to identify the key challenges and barriers that may be reducing the impact of these technologies on the lives of poor people and help to identify some of the key technologies that could form the basis of further work.

II. MATERIALS AND METHODS

2.1 Chemicals and reagents

All chemicals which were used in the experiment, including sodium fluoride, lanthanum nitrate, ALC, sodium chloride, sodium hydroxide, glacial acetic acid, hydrochloric acid, sodium acetate, sodium carbonate, sodium bicarbonate, sodium nitrate, sodium sulfate, acetone, were of analytical grade and obtained from Ranbaxy India.

It was studied the polyacrylic anion exchange resin Amberlite IRA458, which is a gel type acrylic resin, with 1.25 eq/L exchange capacity and 35°C maximum temperature operation. Prior to the experiments, the resin was kept under water so that swelling could be achieved.

Batch experiments.

These experiments aimed to define the optimum conditions for sulfate sorption and the effects of (i) sulfate concentration and (ii) pH on the resin loading were studied. The experiments were performed by mixing 1mL of the resin with 100 mL of a synthetic solution containing sodium sulfate (100 - 1200 mg/L), in an orbital shaker (New Brunswick) at 180 min⁻¹, during 5 hours. When the effect of pH on sulfate loading was assessed, the solution pH was controlled at pH 2, 4, 6, 8, or 10. For the kinetic experiments, 10 mL of the same resin was mixed with 1 liter of a solution containing 800 mg/L sulfate, at 200 min⁻¹, 26 °C and pH 2. Sampling was performed at different contact times and after chemical analysis the resin loading was determined by mass balance. Following, fitting to pseudo first order, pseudo second order and intraparticle diffusion model was tested. Sorption isotherms were also produced from equilibrium loading experiments. The

experimental data were fit to both the Langmuir and Freundlich models. In all batch runs, as the experiment was finished the solution resin pulp was filtered and the sulfate concentration in the aqueous phase was determined by ICP-OES (Varian, 725).

Elution from the loaded Amberlite IRA458 resin was also studied. To achieve that 1mL of the loaded resin (34.4 mg SO₄²⁻ /mL - resin) was eluted with 100 mL of either sodium chloride (500 mg/L or 1300 mg/L) or sodium hydroxide (pH 10 and 12). The flasks were kept under agitation at 180 min⁻¹, for 24 hours at 34°C. All experiments were done at least twice and the average values are reported.

Fixed-bed experiments. These experiments were carried out in a 13 mm diameter × 142 mm long column, loaded with 10 mL of the Amberlite IRA458 resin (Vres) previously conditioned at pH 2 with hydrochloric acid. A 1000 mg/L and pH 2 sulfate solution was fed upwards at 10 mL/min (Q) and 26 °C. Sampling was carried out at every 10 minutes and the sulfate concentration in the column effluent was determined by ICP-OES (Varian). Following, the breakthrough data were modeled. The height of the resin bed was 9 cm, and the upflow velocity (U) was 1.37 cm/min.

2.2 Method

Fluoride Removal Methods

Various treatment techniques for fluoride removal have been studied. There appear to be only two (2) methods: ion exchange with activated alumina; and reverse osmosis that can economically reduce fluoride levels to drinking water standards. Listed below, not necessarily in order of applicability, are the available unit operations for the removal or reduction of fluoride in water.

Activated alumina (BTGA*) • Reverse osmosis (BTGA*)

- Bone char • Electrodialysis
- Alum coagulation / flocculation • Ion exchange
- Lime softening

*BTGA = “Best Technologies Generally Available”, as defined by USEPA in the 1986 amendments to the Safe Drinking Water Act

Alumina

Since the 1930's, it has been known that contact of fluoride-containing water with activated alumina would remove fluoride. Continued research into this phenomenon has led to increased knowledge about the removal of fluoride by this means, and there are a number of full-scale activated alumina fluoride removal treatment plants in operation in the India.

Activated alumina is used much the same way as are ion exchange resins. It is thought that

activated alumina removes certain species from water due to hydrolytic adsorption. Activated alumina is an amphoteric substance, with an isoelectric point of, approximately, pH 9.5. Below this pH it will remove anions, and above pH 9.5, cations. The affinity of alumina for anions seems to be inversely related to the solubility of its aluminum salt. Therefore, when treated with an acid solution, alumina behaves like an anion exchanger and fluoride is very high on the selectivity list. Activated alumina (and reverse osmosis, see below) remove arsenic and fluoride, among other impurities. Using activated alumina treatment, optimum removals for both contaminants may occur in a similar range of pH 5.5 to 6.0 (USEPA, 1985, USEPA, 2000). However, since arsenic V and silica are preferentially adsorbed by activated alumina media, the Effectiveness of activated alumina, where arsenic and fluoride co-occur, may require some investigation.

Activated alumina is a physically and chemically stable form of highly porous aluminum oxide, (Al₂O₃). Activated alumina is produced by exposure of hydrated alumina to caustic soda and heat treatment at about 750oF. The high porosities and large surface areas make alumina an excellent adsorbent. Activated alumina is chemically inert to all but the most corrosive gases and liquids, is non-toxic, and is quite abrasion and disintegration-resistant. The capacity of a continuous-flow activated alumina column for fluoride removal

1. **Initial Fluoride Concentration.** Studies (Choi, 1979) show that the capacity of activated alumina for fluoride removal *increases* with increased fluoride concentration.

2. **pH.** The pH of the influent water will influence the volume of water that can be treated until breakthrough occurs. An influent pH of 5.5 appears to be optimum, though the process is readily operable through a pH range of 5.0 to 8.0. At the optimum pH for fluoride removal, the alumina will also adsorb some organic molecules, as well as some metal ions, include.

III. RESULTS AND DISCUSSION

3.1 Batch experiments

Effect of pH on sulfate uptake. Fig. 1 depicts sulfate loading by Amberlite IRA458, at different pH and initial sulfate concentrations. Resin loadings increase with initial sulfate concentration in solution up to saturation, which is reached at ≈ 43.6 mg

SO₄²⁻ /mL - resin and pH 2. In this pH, HSO₄⁻ concentration is relevant (≈ 30%, taking pK_{a2} = 1.54, at 25°C and I = 0.1 mol/L (Martel and Smith 2003)) and contributed for increased sorption.

Resin loading is sensibly reduced as pH increases and the maximum loading at pH 10 is only 6 mgSO₄²⁻ /mL - resin. This behavior is typical of weak base resins in which the exchange capacity is function of pH. Nevertheless, as it is aimed to remove sulfate from acid drainage, the resin seems suitable.

Sulfate uptake kinetics was determined at Ph 2.0 for a solution containing 800 mg SO₄²⁻ /L and the results are shown in fig. 2. It can be noticed that sulfate loading is fast and levels out within 60 minutes, whereby a loading of 55 mg SO₄²⁻ /L - resin was achieved. The loading kinetics was modeled and from the three equations tested (pseudo first order, pseudo second order and intra particle diffusion) only the pseudo first order model showed good fit (R² = 0.97) with a rate constant (k) value of 0.072 min⁻¹. This suggests that, in the experimental conditions of the present work, film diffusion is likely the controlling step during sulfate uptake by Amberlite IRA458 resin, while poor diffusion is fast.

Following, sulfate elution was studied batch wise applying two different solutions at two different concentrations. As it can be seen in tab. 1, sodium hydroxide showed much better results as compared to sodium chloride solutions. This is because pH has an important effect on sulfate loading on this polyacrylic resin as can be seen in fig. 1. Furthermore, anionic resins have higher affinity for sulfate as compared to chloride because the electrostatic interaction is stronger (Inglezakis and Pouloupoulos 2006). Regardless, elution of sulfate loaded Amberlite IRA458 requires further research

Knowing the time required for equilibrium, sorption experiments were performed at different initial sulfate concentrations followed by data fitting to the Freundlich and Langmuir equations. The loading isotherm is presented in fig. 3 where Q_{eq} represents the equilibrium sulfate loading. It can be observed that both models can represent sulfate uptake by Amberlite IRA458. The Langmuir model showed a somewhat worst fit (R² = 0.95) with 41.3 mg SO₄²⁻ /mL - resin maximum loading as compared to that achieved with the Freundlich model (K_f = 12.64 L/mL - resin, n = 6.09, R² = 0.98).

Table 1 Effect of eluent type and concentration on sulfate elution from Amberlite IRA458 resin. Experimental conditions: 34° C, 180 min⁻¹, sulfate loading: 34.4 mg/mL -

Eluent solution	Elution efficiency (%)	Eluent solution	Elution efficiency (%)
NaCl (0.5 g Cl-/L)	3.6	NaOH (pH=10)	41.4
NaCl (1.3 g Cl-/L)	3.7	NaOH (pH=12)	44.8

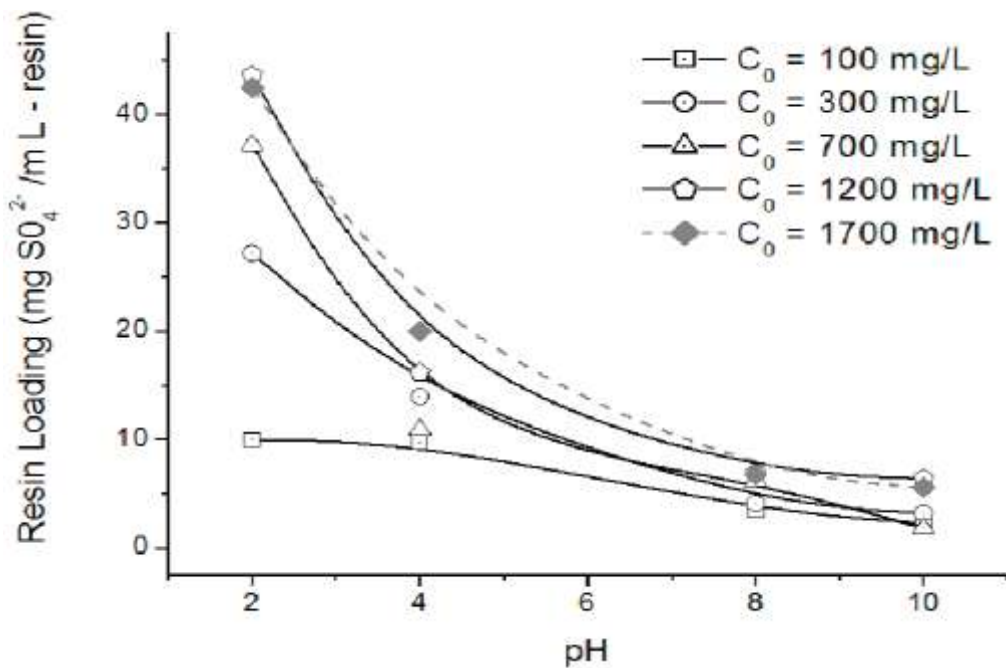


Figure 1 Sulfate loading in Amberlite IRA458, at different pH values. Experimental conditions: 34 • } 1° C, stirring speed 180 min⁻¹.

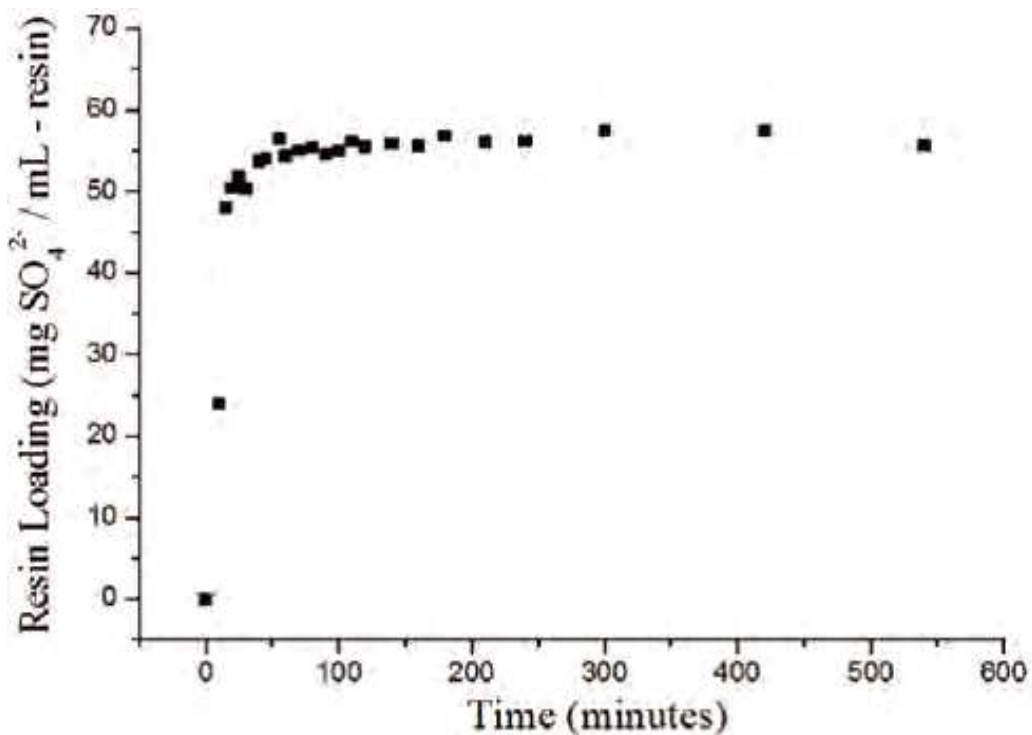


Figure 2 Resin loading kinetics bat pH 2 from 800mg/L sulfate concentration. Experimental conditions: 26 • } 1° C, stirring speed 200 min.

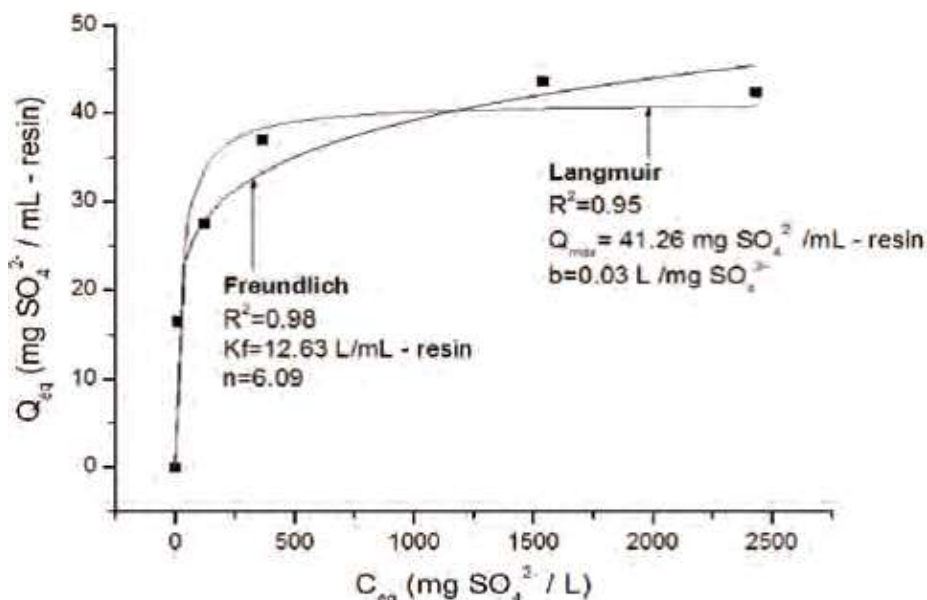


Figure 3 Loading isotherm for sulfate sorption on Amberlite IRA458. Experimental Conditions: pH 2.0, 34°C, stirring speed 200 min⁻¹.

3.2 Fixed-bed sorption

Fig. 4 depicts the breakthrough curve during sulfate loading on Amberlite IRA458. It can be observed that breakthrough is achieved after 40min where as saturation is observed after 90 min. In this condition, resin loading was 70 mg SO₄²⁻ /mL - resin. This value is slightly higher than the maximum exchange capacity (1.25 meq/mL - resin) if sulfate is the adsorbing species. As already stated, however, bisulfate concentration is relevant at pH 2.0 and indeed contributed for the high resin loading.

Breakthrough modeling. Four different equations were applied to model the breakthrough curve produced during sulfate sorption on Amberlite IRA458, namely: (i) Bohart-Adams (1920), (ii) Thomas (1944), (iii) Yoon and Nelson (1984), (iv) Dose-response models (Yan et al. 2001). The latter is an empirical equation widely used in the pharmaceutical industry, which was also applied in biosorption studies (Calero et al. 2009; Senthilkumaret al. 2006).

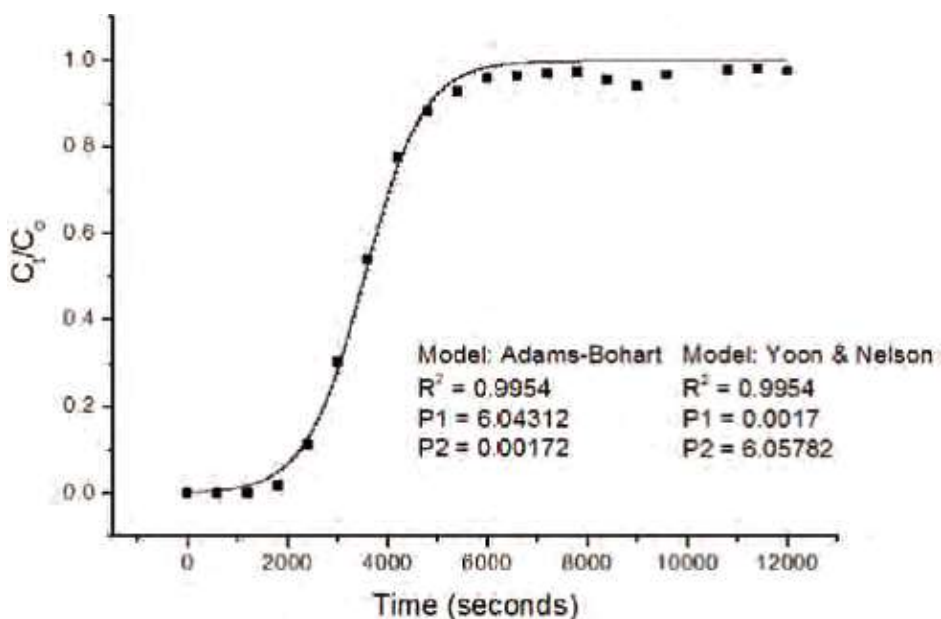


Figure 4 Breakthrough curve observed during fixed-bed sorption. Experimental Conditions: 26 °C, pH 2.0, upflow velocity 1.37 cm/min.

Summarizing, all model were found to be suitable for describing the dynamic behavior during sulfate sorption on the anionic polyacrylic ion exchange resin. Further studies are addressing sulfate sorption by other resin types as well as the application of cationic resins so that a process can be devised to treat mine affected waters. This resin shows high sorption capacities in acid solutions similar to that observed with resins containing polystyrene matrixes (Guimaraes 2010), but the latter seem more indicated for less acidic capacity.

IV. CONCLUSIONS

The literature survey and the laboratory experiments have 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. Therefore, any technology should be tested using the actual water to be treated before implementation in the field.

A large number of factors and geological conditions influence the correlations between different pairs of physico - chemical parameters of water samples directly or indirectly. All the physico-chemical parameters of Ganga river water at Kanpur for pre monsoon, monsoon and post monsoon for year 2012 are within the highest desirable limit or maximum permissible limit prescribed by WHO except turbidity, Fe contents and pH which recorded high values in all seasons, pre monsoon and monsoon season and pre monsoon season respectively . From the results of present study we conclude that Ganga water of Kanpur is though fit for drinking purposes yet it need treatment to minimize the contamination especially turbidity and Fe contents . To minimize the contaminations of Ganga River water at Kanpur the values of correlation coefficients and their significance level will help in selecting the proper experimental methods used for treatment of water. To create increasing awareness among the people to maintain the Ganga river water at its highest quality and purity levels, the present study may prove to be useful in achieving this goal.

REFERENCES

- [1] Haudrechy P et al. (1994) Nickel release from nickel-plated metals and stainless steels. Contact Dermatitis, 31:249-255
- [2] Morgan LG, Flint GN (1989) Nickel alloys and coatings: release of nickel. In: Maibach HI, Menné T, eds. Nickel and the skin: immunology and toxicology. Boca Raton, FL, CRC Press, pp. 45-54.
- [3] WHO-JMP-MDG Report; Meeting the MDG drinking-water and sanitation target: A mid-term assessment of progress 2004; http://www.who.int/water_sanitation_health/monitoring/jmp2004/en.
- [4] WHO Fact Sheet; Arsenic in drinking water; Fact sheet No.210; 1999; http://www.knowledgebank.irri.org/factsheets/PDFs/Health_and_Nutrition/who_FS_arsenic.pdf.
- [5] Dissanayake, C.B., 1991. The fluoride problem in the groundwater of Sri Lanka – environmental management and health. Int. J. Environ. Stud. 19, 195-203.
- [6] WHO, 1985. Guidelines for Drinking Water Quality, vol. 3. World Health Organization, Geneva, pp. 1-2.
- [7] Smet, J., 1990. Fluoride in drinking water. In: Frencken, LE (Ed.), Endemic Fluorosis in Developing Countries – Causes, Effects and Possible Solution: Report of a Symposium Held in Delft, The Netherlands. Netherlands Organisation for Applied Scientific Research.
- [8] NHMRC, 2004. Australian Drinking Water Guidelines. National Health and Medical Research Council. http://www.nhmrc.gov.au/publications/synopses/files/adwg_11_06_fact_sheets.pdf.
- [9] WHO, 1984. Guidelines for Drinking Water Quality. In: Health Criteria and Other Supporting Information, second ed., vol. 2. World Health Organization, Geneva
- [10] Czarnowski, W., Wrzesniowska, K., Krechniak, J., 1996. Fluoride in drinking water and human urine in Northern and Central Poland. Sci. of the Total Environ. 191, 177-184.
- [11] Agarwal, M., Rai, K., Shrivastav, R., Dass, S., 2003. Defluoridation of water using amended clay. J. Cleaner Produc. 11, 439-444.
- [12] Gaciri, S.J., Davies, T.C., 1992. The occurrence and geochemistry of fluoride in some natural waters of Kenya. J. Hydrol. 143, 395-412.
- [13] Chernet, T., Trafi, Y., Valles, V., 2002. Mechanism of degradation of the quality of natural water in the lakes region of the Ethiopian rift valley. Water Res. 35, 2819-2832.
- [14] Mjengera, H., Mkongo, G., 2002. Appropriate defluoridation technology for use in fluorotic areas in Tanzania. 3rd WaterNet

- Symposium Water Demand Management for Sustainable Development.
- [15] Moturi, W.K.N., Tole, M.P., Davies, T.C., 2002. The contribution of drinking water towards dental fluorosis: a case study of Njoro division, Nakuru district, Kenya. *Environ. Geochem. and Health* 24, 123–130.
- [16] Apambire, W.B., Boyle, D.R., Michel, F.A., 1997. Geochemistry, genesis and health implications of fluoriferous groundwaters in the upper regions of Ghana. *Environ. Geol.* 33, 13–24.
- [17] M.C. Bell, T.G. Ludwig, The supply of fluoride to man: ingestion from water, in: *Fluorides and Human Health*, WHOMonograph Series 59, World Health Organization, Geneva, 1970.
- [18] N. Mameri, A.R. Yeddou, H. Lounici, H. Grib, D. Belhocine, B. Bariou, Defluoridation of septentrional Sahara water of North Africa by electrocoagulation process using bipolar aluminium electrodes, *Water Res.* 32 (5) (1998) 1604–1610.
- [19] W.E. Shortt, Endemic fluorosis in Nellore District, South India, *Ind. Med. Gazette* (1937) 72–396.
- [20] Yadav, S., Khan, T.I., Gupta, S., Gupta, A.B. and Yadava, R.N. 1999 Fluorosis in India with special reference to Rajasthan. In: *Proceedings of the International Conference on Water, Environment, Ecology, Socioeconomics and Health Engineering (WEESHE)*, Seoul National University, 18–21st October, 3–10.

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