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Arsenic, Fluoride and Nitrate in Drinking Water: The Problem and its Possible Solution

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Abstract: This research has been designed to remove the toxins specifically Arsenic, Fluoride and Nitrate from drinking water. Integrated combined technique i.e., ion exchange resins and activated alumina were used to remove these toxins. Aqueous solution of arsenic was prepared and checked by atomic absorption spectrophotometry whereas aqueous solution of fluoride and nitrate prepared and checked by ion analyzer by using ion selective electrodes. Results showed that the integrated combined technique of ion exchange resins and activated alumina were found to be most feasible than other purifications technologies, based on engineering economics and regulatory criteria. This technique will be pilot tested and effective to remove arsenic, fluoride and nitrate from drinking water at large scale.

Key words: Drinking water, arsenic, fluoride and nitrate contents removal, ion exchange resins and activated alumina

INTRODUCTION

Arsenic is common, naturally occurring drinking water contaminant that originates from arsenic containing rocks and soil, transported to natural water via erosion, dissolution and air emission (Ahmed and Rehman, 2000; Bajpai and Chaudhari, 1999). In areas where drinking water supply contains unsafe level of arsenic, the immediate concern is finding a safe source of drinking water. There are two main options i.e., finding a new safe source and removing arsenic from contaminated source (Bellack, 1971). Arsenic occurs in both organic and inorganic forms, however the inorganic form is more prevalent in water and considered more toxic (Bonnin, 1997; Ahmed and Rehman, 2000). The Environmental Protection Agency (EPA) has established arsenic as a Class A human carcinogen with low arsenic exposure (less than 0.05 mg L⁻¹) linked to cancer of skin, liver, lungs and bladder (Clifford, 1986).

Nitrates and nitrites are nitrogen-oxygen chemicals unit, which combines with various inorganic compounds (Chen *et al.*, 1999; Driehaus *et al.*, 1998). An excessive level of nitrates in drinking water has caused serious illness, sometimes death (Bajpai and Chaudhari, 1999). The serious illness in infants is due to conversion of nitrate in the body, which can interfere with the oxygen carrying capacity of child blood, which is an acute condition in which health deteriorates rapidly over the period of days (Munter *et al.*, 1999; Pentchuk, 1986). Main causes of toxicity of nitrate in drinking water include shortness of breath and blueness of the skin. Above disease are short-term basis where in long term basis person suffers from diuresis, deposition of starchy compounds and hemorrhaging of spleen. On site ion exchange studies investigated the combined removal of As (V) and nitrate from drinking water (Bellack, 1971). Experimental results showed that conventional sulphate selective resins were better than special selective resins for removal of combined As (V) and nitrate from drinking water.

Fluoride in drinking water and toothpaste attracts public attention nowadays whereas fluoride as a strong oxidant is added to many drinking waters in small quantities to prevent dental caries (Bonnin, 1997). Generally, fluoride is carcinogen (Pentchuk *et al.*, 1986) a bone seeker and is linked to hip fractures and brittling of bones. All salts of fluorine are toxic but some of them more or some less. Research of several investigators during the last 5-6 years has proved life long impact and accumulation of fluorides causes not only human skeletal and teeth damage, but also changes in the DNA (Deoxy ribonucleic acid) structure, paralysis of volition, cancer etc. because of toxicity of fluoride and over dosing, fluoridation of drinking water has been stopped in many countries (Buswell, 1943). For fluoride consumption by humans 3 mg per day is a figure that should never be exceeded and of course sodium fluoride in toothpaste should be replaced with calcium fluoride, which are much less toxic (Chen *et al.*, 1999; Yang *et al.*, 1999).

Permissible limits of arsenic, nitrate and fluoride in drinking water recommended by Environmental Protection Agency (EPA) in 2001 as follows (Clifford, 1999) Arsenic 10 ppb (i.e., 10 $\mu\text{g L}^{-1}$) Fluoride 4 ppm (i.e., 4 mg L^{-1}) and Nitrate 10 ppm (i.e., 10 mg L^{-1}).

In present investigation, the study of removal of arsenic, nitrate and fluoride from drinking water by ion exchange technique and activated alumina has been undertaken with the view to the suitability and compatibility of ion exchange resins and activated alumina for the removal/ adsorption of arsenic, nitrate and fluoride from the drinking water.

MATERIALS AND METHODS

Study was carried out at Pakistan Council of Scientific and Industrial Research (PCSIR) Labs Complex Karachi, in May 2005 by preparing samples in laboratory. Sample solutions were prepared in deionized water, having conductivity below 1 $\mu\text{S cm}^{-1}$, sample solutions contain 50 ppb Arsenic, 10 ppm Fluoride and 50 ppm Nitrate. Two glass columns (having 1 inch internal diameter) join in series manner, one contain 100 mL mixed beds ion exchange resins (i.e., cation and anion exchange resins), at this stage resins were in form of sodium and chloride. Due to continuous adsorption of ions, resins become exhausted (i.e., loss the property of adsorption) then resins will be recharged or regenerated by specific regenerant (Faustand and Aly, 1983) i.e., sodium hydroxide and hydrochloric acid. Other column (have same internal diameter) contain 100 g of alumina (activated). Water sample passed first through column of resins and then activated alumina at 10 mL per min flow rate (Clifford, 1999). After exhaustion of resins, it would regenerated with 10% aqueous sodium chloride solution where activation of alumina was carried out with 0.1 N hydrochloric acid and regeneration with 0.1 N sodium hydroxide.

Operation conditions

Parameters	Ion exchange resins	Activated alumina
Effective size (mm)	0.4-0.6	2.0-2.5
Bed depth (m)	0.75	0.3
Bed mass (g)	100	100
Flow rate (mL min^{-1})	10	10
pH	6.8 \pm 0.17	7.5 \pm 0.2
Temperature ($^{\circ}\text{C}$)	19.5 \pm 2.0	20.7 \pm 1.1

The changes in water quality parameters during the experiments were followed. The concentration of arsenic, fluoride and nitrate in water was determined with atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Reverse Osmosis (RO) and Electro- Dialysis Reversal (EDR) efficiently removed the fluoride from drinking water upto 95%, where loss of water makes these technologies inefficient (Table 1). Ion

exchange technology had not ability to adsorb fluoride, as far as activated alumina media is concerned, this technique is efficiently adsorb the fluoride from drinking water up to optimum limit, without water loss. Therefore, activated alumina suitable for the removal of fluoride from drinking water.

Activated alumina (AA) is a porous, granular material that uses ion exchange properties to remove contaminants from a liquid stream (Driehaus *et al.*, 1998) Activated alumina preferentially removes ions, that is, the media will adsorb some contaminants before adsorbing some others. Activated alumina has following ion selectivity sequence.



Activated alumina removal efficiency is highly pH dependent, with optimal removal at pH 5.5-6.5, thus source water pretreatment with hydrochloric acid may be required (Kowalski, 1999). As the selectivity sequence shows, AA will adsorb arsenate As(V) more efficiently than arsenite As (III). AA is also a BAT (Best Available Technology) for fluoride removal (85-95% efficiency). The AA media can either be regenerated or disposed of and replaced with fresh media. Table 1-3

Table 1: Summary of technologies for fluoride removal

Technology	Removal efficiency	Water loss (%)	Optimal conditions	Operator skill
Activated alumina	85-95	1-2	pH 5.5- 8.3 (decreased efficiency at high pH);	Low
Reverse osmosis	85-95	40-60	<30 mg L ⁻¹ silica <15% water loss (per RO manufacturers.NO particulates)	Medium
Ion exchange	No	1-2	pH 6.5- 9.0 (decreased efficiency at high pH); <50 mg L ⁻¹ SO ₄ ²⁻ ; <500 mg L ⁻¹ TDS; <0.5 mg L ⁻¹ NO ₃ ⁻¹ ; <0.3 NTU turbidity	High
Electro-dialysis reversal	85-95	20-30	Treats most waters without preference; Process efficiency not affected by silica; Most economical for TDS of 3000-5000 mg L ⁻¹	Medium

Table 2: Summary for technologies for arsenic removal

Technology	Removal efficiency		Observations and Inference
	As (III)	As (V)	
Ion exchange resins	-	+++	Pilot scale in central and household systems, mostly in industrialized countries. Interference from sulphate and TDS. High adsorption capacity, but long perm performance of regenerated media needs documentations. Waters rich in iron and manganese may require pretreatment to prevent media clogging. Moderately expensive. Regeneration produces arsenic rich brine.
Activated alumina	+/	+++	Pilot scale in community and house hold system in industrialized and developing countries. Arsenite removal is poorly understood, but capacity is much less than for arsenate. Regeneration require strong acid and base and produces arsenic rich waste. Long term performance of regenerated media needs documentation. Waters rich in iron and manganese may require pretreatment to prevent media clogging Moderately expensive.
	++	+++	
Electro-dialysis reversal	-/	+++	Shown effective in laboratory studies in industrialized countries. Research needed on removal of arsenite and efficiency at high recovery rates, especially with low pressure membrane. Pretreatment usually required. Relatively expensive, especially if operated at high pressures.
Lime softening	+	+++	Proven effective in laboratories and at pilot scale. Efficiency of this chemical process should be largely independent of scale. Chiefly seen in central system in conjunction with water softening. Disadvantages include extreme pH and large volume of waste generated. Relatively inexpensive, but more expensive than coagulation with iron salts and alum because of larger doses required and waste handling.

+++; Greater than 90% removal; ++: 60-90 % removal; +: 30-60%; -: Less than 30%

Table 3: Summary of technologies for nitrate removal

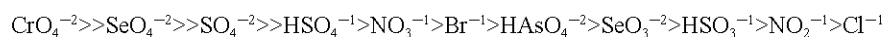
Technology	Removal efficiency	Water loss	Optimal conditions	Operator skill
Activated alumina	25-35	1-2	pH 5.5-8.3 (decreased efficiency at high pH);	Low
Reverse osmosis	85-95	40-60	<30 mg L ⁻¹ silica <15% water loss (per RO manufacturers. NO particulates)	Medium
Ion exchange	70-80	1-2	pH 6.5-9.0 (decreased efficiency at high pH); <50 mg L ⁻¹ SO ₄ ⁻² ; <500 mg L ⁻¹ TDS; <0.5 mg L ⁻¹ NO ₃ ⁻¹ ; <0.3 NTU turbidity	Low
Electro-dialysis reversal	65-70	20-30	Treats most waters without preference; Process efficiency not affected by silica; Most economical for TDS of 3000-5000 mg L ⁻¹	Medium

summarizes some of key technologies for fluoride, arsenic and nitrate removal with reference to optimal conditions and operator skill. Table 2 summarizes some of the key technologies for arsenic removal, with special reference to experience gained from field level application (Munter *et al.*, 1999). Research needs are also identified. Arsenic removal efficiency will vary according to many site specific chemical, geographic and economic conditions, so actual applications may vary from the generalization listed in Table 2. Because of many factors that can affect arsenic removal efficiency (including arsenic concentration, speciation, pH), any technology should be tested using the actual water to be tested, before the implementation of arsenic removal systems at the field scale (Inleva *et al.*, 2000; Huang and Liu, 1999; Faustand and Aly, 1983). Nitrates are considered to be toxic to human infants and ruminant animals such as cows. They occur naturally as a result of the decomposition of nitrogen containing waste matter, also as a result of farm run off from fertilizer. The maximum level of nitrates in potable water is usually limited to 10 ppm as a nitrogen. At level above 50 ppm nitrates as nitrogen can cause methemoglobinemia in infants, also known as blue baby syndrome. Technologies used for the removal of nitrates presented in Table 3 strong base anion exchange resins mostly used for the removal of nitrates from drinking water.

Synthetic ion exchange resins are widely used in water treatment to remove any undesirable dissolved solids, most commonly hardness, from water (Huang and Liu, 1999; Veressinina *et al.*, 2000). These resins are based on a cross-linked polymer skeleton called the matrix. The most commonly this matrix is composed of polystyrene cross linked with divinyl benzene. Charged functional groups are attached to the matrix through covalent bonding and fall into four groups:

- Strongly acidic
- Weakly acidic
- Strongly basic
- Weakly basic

The acidic resins are negatively charged and can be loaded with cations (e.g., Na⁺) that are easily displaced by other cations during water treatment. This type of cation exchange is most commonly applied to soften hard waters. Conversely strong basic resins can be pretreated with anions, such as Cl⁻ and used to remove a wide range of negatively charged species (Veressinina *et al.*, 2000). Following relative affinities of some common anions for strong base anion resins.



Different resins will have differing selectivity sequences and resins have been developed specifically to optimize removal of sulphate, nitrate and organic matter.

Filtration through ion exchange resins and activated alumina reduced the concentration of arsenic, fluoride and nitrate (Inleva *et al.*, 2000; Wu and Nitya, 1979). Filtration through these media did not influence other water parameters that indicate the selectivity of this medium towards arsenic, fluoride and nitrate ions (Wu and Nitya, 1979). When filter medium i.e., ion exchange resins and activated alumina was saturated with arsenic, fluoride (Singh *et al.*, 1999; Yang *et al.*, 1999; Thomas, 2001) and nitrate ions, the medium was regenerated with sodium hydroxide and hydrochloric acid and the filtration cycle was repeated. Unfortunately, after such regeneration the sorption capacity of alumina was not restored, due to formation of a ferric oxide film on the surface of alumina grains during the filtration of water containing definite concentration of iron. The film was not removed during the activating of alumina with hydrochloric acid (Jonston and Heijnen, 2002; Edward, 2005). In the next experimental series, in order to remove the ferric oxide from the surface of filtering media, then alumina was flushed with 5% hydrochloric acid until no brown precipitates of ferric oxide was visible (Jonston and Heijnen, 2002). Such an approach enabled restoration of the sorption capacity of alumina (Pentchuk *et al.*, 1986; Kowalski, 1999).

CONCLUSIONS

A feasibility study on the use of two filter media i.e., ion exchange resins and activated alumina, for the removal of arsenic, fluoride and nitrate from drinking water demonstrated that given technique suitable for removal of arsenic, fluoride and nitrate from drinking water. Uniqueness of this technique is that it is relatively cheaper than other technologies and very easy to handle.

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