

Review on adverse effects of water contaminants like arsenic, fluoride and phosphate and their remediation

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This review presents removal of three major anionic contaminants (arsenic, phosphate and fluoride) in water by adsorption/precipitation method using both synthetic and natural materials. A discussion is also made on interfering co-radicals (silicate, sulphate, nitrate, bicarbonate, chloride, etc.).

Keywords: Arsenic, Co-ion effect, Contaminants, Fluoride, Phosphate

Introduction

Usually drinking water collected from wells, rivers, ponds, lakes, etc. is bio-contaminated. Although, tube well water is free from bacterial contamination, but usually present are some toxic anions (fluoride, arsenate, arsenite, phosphate, chromate and selenate), which also cause various diseases. Since most of the rural people use water without any pretreatment, development of cost effective and simple technology is very much essential to purify water obtained from natural sources. This review presents removal of major anionic contaminants (arsenic, phosphate and fluoride) in water.

Sources of Contaminants

Arsenic, phosphate and fluoride are three major contaminants present in ground water. Arsenic is introduced into water through dissolution of minerals and ores. It is used in semiconductor manufacturing, petroleum refining, wood preservatives, animal feed additives and herbicides. So, industrial effluent also contribute arsenic to water in some areas^{1,2}. Phosphate that occurs naturally in rock formations in earth's crust leaches out of rocks by rainfall. Due to its high nutritive value, phosphates are used in fertilizers and animal feeds. It is also a major component in industrial chemicals, pharmaceuticals and detergents. This results in high phosphate concentration in industrial effluents. Fluoride enter into ground water by natural weathering and

leaching, besides anesthetics, antibiotics, automobile wheel cleaning products, contaminated beverages and food products, insecticides (containing NaF) and tooth paste factories are major source of fluoride pollution in water³. As specified by World Health Organization (WHO) and Environmental Protection Agency(EPA), permissible concentrations of contaminants in public drinking water system are as follows: arsenic , 0.01; fluoride , 1.5; and phosphate, 0.05 mg/ dm³.

Remediation Processes

Many methods (ion exchange, reverse osmosis, coagulation, cementation, precipitation, nano-filtration, distillation, etc.) are being used for removal of anionic contaminants from drinking water⁴⁻⁶. Cost effective chemical precipitation/adsorption technology are being given first priority for treatment of contaminated water using natural and synthetic materials.

Arsenic (As)

Co-precipitation of As (V) with ferric ion [Fe (III)] is very much effective⁷, when Fe(III)/As(V) molar ratio is at least 3 and preferably > 4. At low concentration of As (V) and a high concentration of Fe(III), co-precipitation of As occurs with ferrihydrite (FH), (FeOOH, 5H₂O). It is probably most effective method for removal of As from aqueous solution and it forms a solid phase, which can be stable for at least a year. At higher As concentration, As (III) reacts faster than As(V) with ferrihydrites, whereas a reverse trend is observed at low As concentration. Whole range of iron minerals starting

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from amorphous ferrihydrite to hematite are capable of adsorbing As(III) and As(V) as arsenite and arsenate, respectively^{8,9}. Pierce *et al*^{10,11} studied As adsorption on amorphous iron hydroxide at low concentrations over a wide pH range. Naturally occurring oxides/hydroxides of other metals are also used as low cost material for As mitigation. Oxides/hydroxides surfaces that are positively charged in natural system due to protonation of surface sites¹² play an important role in adsorption of anions. A low cost ferruginous manganese ore (FMO, containing mainly pyrolusite and goethite) can adsorb both As (III) and As(V) without any pretreatment. Presence of bivalent cations enhances adsorption capability of FMO¹³. Traces of As can be selectively removed from drinking water by adsorption processes using natural manganese dioxides in column experiments^{14,15}. Some biomaterials or their derivatives also can remove As from their aqueous solution¹⁶. Some other natural solids (zeolites, volcanic stones and the cactaceous powder) can also be used for As removal¹⁷.

Activated alumina, a granular form of aluminium oxide (Al_2O_3), can remove As from solution. Activated alumina is very efficient in removing As(V), whereas As(III) is poorly removed¹⁸. So, As (III) is pre-oxidised before reacting with activated column. As (III) sorption by activated alumina has been studied for various adsorption parameters¹⁹. Sand/polymeric materials coated with natural minerals can also be used for removal of As from ground water^{20,21}. Manganese dioxide coated sand (MDCS) prepared by reacting KMnO_4 with manganese chloride in presence of sand in an alkaline condition can be used for As(III) and As (V) removal for home treatment units. Modification of polymeric materials (polystyrene and poly high internal phase emulsions) by coating their surface with appropriate adsorbing agents (iron hydroxide) improves its As uptake capacity leading to its residual concentration below $10 \mu\text{g}/\text{dm}^3$.

Phosphate

Phosphate can be removed from drinking water by natural and synthetic adsorbents as well as waste materials. Glimsing *et al*²² studied phosphate and glyphosate removal by hematite and ferrihydrite through adsorption method. Phosphate removal efficiency of 13 natural pumice rock samples obtained from different regions of Turkey has been investigated²³. Samples with high CaO content had high phosphate uptake capacity. Natural ores like Calcite [CaCO_3 (99% Ca)] and

Dolomite [CaAlFeCO_3 (30% Ca)] have also phosphate removal capacity. Calcite samples have higher efficiency than that for Dolomite. So, it implies that higher Ca content acts as active sites for phosphate adsorption²⁴. Adsorption removal of phosphate onto various clays and clay minerals has also been extensively studied²⁵. Presence of iron oxides on clay surface plays a major role in phosphate adsorption.

Adsorption of phosphate from aqueous solution by active red mud has been studied²⁶. Red mud has high TiO_2 and Fe_2O_3 contents, which are active components for adsorption of anionic pollutant. Red mud activated by heat treatment/ acid heat treatment showed that treated red mud sample using acid heat method at 80°C with $0.25 \text{ mol}/\text{dm}^3$ HCl for 2 h achieved highest phosphate removal capacity. Gas concrete waste can be used to remove phosphate from aqueous solution. Huang *et al*²⁷ reported removal of phosphate from industrial wastewater by using metal loaded skin split waste. Column packed blast furnace slag can also be used for phosphate removal²⁸. Removal of phosphate by sea food (cuttle fish) processing waste sludge is also reported²⁹. Tamarind nut shell activated carbon^{30,31} can also be used for phosphate abatement.

Fluoride

Surface of oxide minerals, being positively charged, has capability of abating fluoride from water. Refractory grade bauxite showed best result towards fluoride adsorption among refractory grade bauxite, feed bauxite, manganese ore and hydrated oxides of manganese ores (WAD). Langmuir isotherm model and isosteric heat calculation showed that adsorption process followed a heterogeneous model³². Fluorides can also be adsorbed onto mixed rare earth oxides rapidly and effectively³³. Optimum (> 90%) adsorption occurred within first 5-10 min at pH 6.5. Adsorbed fluoride can also be desorbed by using an alkali solution of pH 12. Other natural materials that remove fluoride from water are kaolinite, natural phosphate rock and alumina³⁴⁻³⁶.

Fluoride removal from ground drinking water by adsorption onto bone char has been studied³⁷. Bone char was found to be a better fluoride adsorber in comparison to natural tourmalin and activated alumina. Bone char column adsorption experiments indicated that fluoride removal could be significantly affected by flow rate and bed height. Tang *et al*³⁸ studied fluoride adsorption onto active alumina using batch methods and at equilibrium contact time of 10 h. Ionic strength did not impact

fluoride adsorption in entire experimental pH range (5.0-10.5). Adsorption of fluoride on limestone (LS) and aluminium hydroxide impregnated limestone (AILS) was investigated using a batch adsorption technique³⁹. Activated carbon derived from Royal Gulmohor fruit shell can also be used for fluoride abatement⁴⁰. Physically and chemically activated carbon can be successfully used for removal of fluoride from water. Tripathy *et al.*⁴¹ reported fluoride removal from drinking water by adsorption onto alum impregnated activated alumina. Selective ion exchange resin for fluoride sorption has been identified⁴².

Fluoride and As can be removed simultaneously from drinking water by using cake alum, a polymeric anionic flocculent and activated alumina⁴³. Cosorption and desorption of fluoride and phosphate in an acidic red soil of China has been investigated⁴⁴. Aluminium loaded Shirasu-zeolite can also remove arsenate, phosphate and fluoride ions simultaneously⁴⁵.

Co-ion Effect

A particular adsorbent may be suitable for a particular anion. But, presence of co-ions in water may reduce efficiency of that particular adsorbent. So, knowledge of interfering radicals on a particular sorption process is very much essential.

Arsenic

Silica at high levels ($\text{SiO}_2 > 20 \text{ mg/l}$) interferes adsorption at high pH. $\text{F}^- (> 5 \text{ mg/dm}^3)$, $\text{SO}_4^{2-} (> 100 \text{ mg/dm}^3)$ and $\text{PO}_4^{3-} (> 1 \text{ mg/dm}^3)$ also interfere As and F removal adsorptive process. When As is removed from water by iron chips, removal efficiency of arsenite [As (III)] in presence of other anions was in the order⁴⁶: $\text{SO}_4^{2-} > \text{NO}_3^- > \text{PO}_4^{3-}$. Similarly, order of anion suppression on arsenate removal on a molar basis⁴⁷ was found to be: $\text{PO}_4^{3-} > \text{SiO}_2 > \text{SO}_4^{2-} > \text{HCO}_3^-$. Although As can be removed from ground water using naturally occurring iron, presence of phosphate and silicate decreases removal efficiency. Removal mechanism indicates that phosphate is removed first by precipitating $\text{Fe}(\text{OH})_3$ and there is a competition for remaining adsorption sites between As and silicates⁴⁸. For As removal, generally silica is the most common and problematic interferant. Sulphate can interfere with very non specific adsorbents (anion exchange resins and activated alumina). Phosphate causes significant problems with adsorption using iron-oxide based media and moderate problem with titanium oxide (TiO_2) media. Vanadium and selenium also can act as

interfering radicals as they are adsorbed via a similar mechanism to that of As⁴⁹. Removal efficiency of As generally decreases, when there is an increasing concentration of phosphate and nitrate in aqueous solution⁵⁰.

Phosphate

Competitive adsorption of phosphate on goethite in marine electrolytes indicated⁵¹ that Mg^{2+} , SO_4^{2-} and F^- decreased phosphate adsorption at low pH, while Ca^{2+} increased adsorption at high pH. However, fluoride sorption can be improved in presence of phosphorous due to surface precipitation of (Al, Fe)-F-P⁴⁴.

Fluoride

Bicarbonate acts as a strongest interfering agent for As and fluoride removal adsorptive process. During adsorption of fluoride on activated alumina, co-anions reduced fluoride adsorption in the order of: $\text{HPO}_4^{2-} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$. Other toxic elements that might co-exist with fluoride in ground water (As and selenium) also reduced fluoride adsorption through competitions for same surface sites³⁸.

Field Study

New types of treatment technologies involving co-precipitation, ion-exchange and activated alumina filtration seem to be field tested.

Arsenic

KanchanTM Arsenic Filter (KAF), developed by Massachusetts Institute of Technology and Nepali NGO, Environment and Public Health Organisation, has been extensively tested in high As areas of Terai area in Nepal. Its foundation is a bio-sand filter (using either plastic/concrete base) that has been modified to include a diffuser basin on the top with iron nails. Rust from nails chemically interact with As and precipitate is filtered out in fine sand portion of the filter, which is easy to use and maintain⁵². Another plant, developed by Deptt of Public Health Engineering, Bangladesh, was based on oxidation of all aqueous As to arsenate [As (V)] and subsequent co-precipitation with alum. As removal plants have also been developed by All India Institute of Hygiene and Public Health, Kolkata, M/s Pal Trockner Pvt Ltd, PHED, Govt of West Bengal, M/s Adhlacon Pvt Ltd, Kolkata, School of Environmental Studies (SOES), Jadavpur University, Kolkata and CSIR, New Delhi, M/s RPM Marketing Pvt Ltd, and M/s Anir Engineers Inc.⁵³.

Phosphate

Permeable reactive barriers (PRB) can be used for phosphate removal. In this method, some selected mixtures are packed in a column. Generally, favourable mixtures contain silica sand, limestone and metal oxide⁵⁴. Volcanic ash soil mixed with Fe(II) sulphate at 500°C (Baked volcanic ash soil) has been used as an effective phosphate remover from secondary effluent in municipal wastewater treatment plant.

Fluoride

Nalgonda technique, used for defluoridation, involves addition of two simple readily available chemicals (lime and alum) followed by flocculation, sedimentation and filtration. Treated wastewater is passed through a micro-filtration membrane, which physically separates metal contaminant particles from wastewater. Solids are removed from membrane surface by periodically back flushing micro filtration membrane. Solid material within filtration vessel is also flushed into a holding tank for further processing of solids⁵⁵.

Conclusions

Presence of anionic contaminants (arsenic, fluoride, phosphate, etc.) in water is of serious concern to public health. It is highly desirable to form a research group to identify source and cause of anionic contaminants in water.

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