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FLUORIDE REMOVAL FROM WATER ADSORPTION USING SOIL

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ABSTRACT

The fate of excessive fluoride in water is cause for serious public health concerns worldwide. Fluorine is the lightest member of the halogen group and is one of the most reactive of all chemical elements. It is not, therefore, found as fluorine in the environment. It is the most electronegative of all the elements. Which means that it has a strong tendency to acquire a negative charge, and in solution forms F^- ions. Other oxidation states are not found in natural systems, although uncharged complexes may be. Fluoride ions have the same charge and nearly the same radius as hydroxide ions and may replace each other in mineral structures. Fluoride thus forms mineral complexes with a number of cations and some fairly common mineral species of low solubility contain fluoride.

KEYWORDS- Water, Fluoride, Soil, Air.

INTRODUCTION

Water de-fluoridation using various technologies therefore continues to attract disproportionate research interest from around the world. De-fluoridation study using soil adsorbents, in particular, have remained the focus of intense our research. since the last few decades. So as to assess the research status in this area, soil adsorbents commonly reported for water de-fluoridation over the last few decades were reviewed. Fluoride has beneficial effects on teeth at low concentrations in drinking water, but excessive exposure to fluoride in drinking water, or in combination with exposure to fluoride from other sources, can give rise to a number of adverse effects. These range from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases. Crippling skeletal fluorosis is a significant cause of morbidity in a number of regions of the world.

Excessive water fluoride continues to pose serious public health concerns world over. Detrimental effects of long term exposure to excessive dietary fluoride range from mild colorization of teeth surfaces to staining, pitting and loss of the tooth enamel, and severe crippling skeletal deformations and death may result in chronic cases. The associated non-skeletal effects include neurological, kidney, endocrine, thyroid and liver disorders, and chronic disruption of metabolic processes occurs when the fluoride doses are very high. Nonetheless, fluorosis is still the most noxious effect of prolonged consumption of excessive dietary fluoride. Sustained consumption of high fluoride water when safer drinking water is not readily available remains the main pathway by which people get exposed to excessive fluoride. At the moment, technologies used in de-fluoridation of water include reverse osmosis and nano filtration, dialysis and electro-dialysis and adsorption. However, adsorption appears to be the most appropriate solution because it is cost-effective, simple to operate and it produces high-quality treated water. Currently, activated alumina, rare earth oxides and

activated carbon are the most plausible adsorbents for fluoride removal from water. They are, however, expensive, require a delicate balancing in adsorption parameters, and are strongly affected by the anions in water. The alternate adsorbents desired for safe and easy treatment of high-fluoride water must not only be affordable and efficient but also simple to use and robust enough to regenerate in several cycles of reuse without considerable loss of their de-fluoridation capacities (DCs). Unsurprisingly, soil adsorbents have continued to attract unequalled research attention in the area of water de-fluoridation, especially over the last few years. This is because soils, ordinarily, have good natural sorptive properties, and they are chemically stable, readily available in abundance, and usable in a wide range of water conditions. As a consequence, large volumes of research data continue to accrue in the field of water de-fluoridation based on sorbent soil media.

Water de-fluoridation has been the subject of intense literature reviews, especially in the most recent years. Several of these reviews have been devoted to the use of adsorption technology in water de-fluoridation with a significant proportion of them being dedicated to fluoride removal from water by adsorption based on specific types of adsorbents such as nano filters, chitosan derivatives and calcium containing materials. Despite the intense research interest being generated by soil adsorbents in water de-fluoridation, there has been no such review that has been devoted solely to providing deeper insight into the role of soil adsorbents in water de-fluoridation. Furthermore, previous reviews of water de-fluoridation and of water de-fluoridation by adsorption have given only a casual treatment to the role of soil adsorbents in water de-fluoridation. As a consequence the overall direction of science, insofar as the use of soil adsorbents in water de-fluoridation is concerned, remains unclear. An in depth review of fluoride soil adsorbents is therefore desirable for a deeper understanding of the role of soil adsorbents in the on-going search for robust adsorbents for easy and safe de-fluoridation of drinking water. This would in turn inform more focused studies towards innovative technological approaches to management of community exposure to excessive fluoride through drinking water.

FLUORIDE DISTRIBUTION IN WATER

Fluoride is found in all natural waters at some concentration. Seawater typically contains about 1 mg l⁻¹ while rivers and lakes generally exhibit concentrations of less than 0.5 mg l⁻¹. In ground water, however, low or high concentrations of fluoride can occur, depending on the nature of the rocks and the occurrence of fluoride-bearing minerals. Concentrations in water are limited by fluorite solubility, so that in the presence of 40 mg l⁻¹ calcium it should be limited to 3.1 mg l⁻¹. It is the absence of calcium in solution which allows higher concentrations to be stable. High fluoride concentrations may therefore be expected in ground water from calcium-poor aquifers and in areas where fluoride-bearing minerals are common. Fluoride concentrations may also increase in ground water in which cation exchange of sodium for calcium occurs.

Fluorosis has been described as an endemic disease of tropical climates, but this is not entirely the case. Waters with high fluoride concentrations occur in large and extensive geographical belts associated with

- a) Sediments of marine origin in mountainous areas,
- b) Volcanic rocks and
- c) Granitic and gneissic rocks.

A typical example of the first extends from Iraq and Iran through Syria and Turkey to the Mediterranean region, and hence from Algeria to Morocco. Other important examples come from the southern parts of the USA, southern Europe and the southern parts of the former USSR. High ground water fluoride concentrations associated with igneous and metamorphic rocks such as granites and gneisses have been reported from India, Pakistan, West Africa, Thailand, China, Sri Lanka, and Southern Africa.

Endemic fluorosis remains a challenging and extensively studied national health problem in India. In, 13 of India's 32 states and territories were reported to have naturally high concentrations of fluoride in water but this had risen to 17 by 1999. The most seriously affected areas are Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh. The highest concentration observed to date in India is 48 mg l⁻¹ in Rewari District of Haryana. The high concentrations in groundwater are a result of dissolution of fluorite, apatite and topaz from the local bedrock, and Handa noted the general negative correlation between fluoride and calcium concentrations in Indian ground water. Efforts to address the problem of fluoride in rural water supplies in India have been led by the Rajiv Ghandi National Drinking Water Mission, with considerable support from external agencies, particularly UNICEF. However, even with the great interest in fluoride in India, it is not easy to arrive at an accurate or reliable estimate of the number of people at risk. This is because of the difficulty of sampling groundwater from India's many millions of hand pump. Existing sampling has been selective but unstructured, taking some villages from districts and some of the many pumps in each village. Further, there have been no comprehensive health surveys for dental fluorosis from which the overall extent of the problem could be assessed. Nevertheless, in the most affected states listed above, half or more of the districts have some villages with groundwater supplies having high fluoride concentrations. In these states, 10% to 25% of the rural population has been estimated to be at risk, and perhaps a total of 60–70 million people in India as a whole may be considered to be so.

EXPOSURE

Air

Due to dust, industrial production of phosphate fertilizers, coal ash from the burning of coal and volcanic activity, fluorides are widely distributed in the atmosphere. However, air is typically responsible for only a small fraction of total fluoride exposure. In non-industrial areas, the fluoride concentration in air is typically quite low (0.05–1.90 µg m⁻³ fluoride). In areas where fluoride-containing coal is burned or phosphate fertilizers are produced and used, the fluoride concentration in air is elevated leading to increased exposure by the inhalation route. High levels of atmospheric fluoride occur in areas of Morocco and China. In some provinces of China, fluoride concentrations in indoor air ranged from 16 to 46 µg m⁻³ owing to the indoor combustion of high-fluoride coal for cooking and for drying and curing food. Indeed, more than 10 million people in China are reported to suffer from fluorosis, related in part to the burning of high fluoride coal.

Dental products

A number of products administered to, or used by, children to reduce dental decay contain fluoride. This includes toothpaste (1.0–1.5 g kg⁻¹ fluoride), fluoride solutions and gels for topical treatment (0.25–24.0 g kg⁻¹ fluoride) and fluoride tablets (0.25, 0.50 or 1.00 mg fluoride/ tablet), among others. These products contribute to total fluoride exposure, albeit to different degrees. It is estimated that the swallowing of toothpaste by some children may contribute about 0.50 or 0.75 mg fluoride per child per day.

Food and beverages other than water

Vegetables & fruits normally have low levels of fluoride and thus typically contribute little to exposure. However, higher levels of fluoride have been found in barley, rice, taro, yams and cassava been found to contain relatively high fluoride levels. In general, the levels of fluoride in meat (0.2–1.0 mg kg⁻¹) & fish (2–5 mg kg⁻¹) are relatively low. However, fluoride accumulates in bone and the bones of canned fish, such as salmon and sardines, which are also eaten. Fish protein concentrates may contain up to 370 mg kg⁻¹ fluoride. However, even with a relatively high fish consumption in a mixed diet, the fluoride intake from fish alone would seldom exceed 0.2 mg F⁻ per day.

Milk typically contains low levels of fluoride, e.g. 0.02 mg l⁻¹ in human breast milk and 0.02–0.05 mg l⁻¹ in cow's milk. Thus milk is usually responsible for only a small fraction of total fluoride exposure. Tea leaves contain high levels of fluoride (up to 400 mg kg⁻¹ dry weight). Fluoride exposure due to the ingestion of tea has been reported to range from 0.04 mg to 2.7 mg per person per day (Murray, 1986). However, some

Tibetans have been observed to ingest large amounts of fluoride (e.g. 14 mg per day) due to the consumption of brick tea as a beverage. This type of tea is made from older leaves and contains much higher levels of fluoride than standard teas such as black or green tea.

It is also possible that other forms of tea will contribute to fluoride uptake, although data appear to be relatively limited. In one study 34% of the fluoride in black tea was shown to remain in the oral cavity but no data were presented on absorption from the gastrointestinal tract.

Water

Drinking-water is typically the largest single contributor to daily fluoride intake. Fluoride exposure (mg kg^{-1} of body weight per day) is determined by the fluoride level in the water and the daily water consumption (litres per day). Water consumption data are most readily available for countries such as Canada, the USA and the UK. More recently national figures can be obtained or computed from various compendia of environmental and water supply statistics such as World Bank. However, national consumption figures, especially for developing countries, may be of limited use for this purpose because there are likely to be major differences between urban communities with fully piped supplies and rural communities using wells and boreholes with hand pump. Consequently, data concerning exposure to fluoride are difficult to come by except for temperate regions. In the USA, young children who consume water containing 0.7–1.2 mg l⁻¹ fluoride are estimated to be exposed to approximately 0.5 mg fluoride per day; for those drinking 1 litre of water per day exposure may be up to 1.2 mg fluoride per day. Similar values would probably apply to other similar climatic regions.

For a given individual, water consumption increases with temperature, humidity, exercise and state of health, and is modified by other factors including diet. Roughly, the closer to the Equator, the higher the water consumption.

Total fluoride exposure

Based on the previous discussion, it follows that total daily fluoride exposure can vary markedly from one region to another. However, from several studies, a rough estimate of total daily fluoride exposure in a temperate climate would be approximately 0.6 mg per adult per day in an area in which no fluoride is added to the drinking water and 2 mg per adult per day in a fluoridated area. In many countries this can be potentially increased for children from the use of fluoridated dental products but there will be significant variation in individual exposure. In hot climates the much higher consumption of water will also increase the intake and this is frequently highly significant. In addition, fluoride exposure in many areas is considerably higher as a consequence of a range of practices, including the consumption of brick tea and the cooking and drying of food with high fluoride coal.

FLUORIDE SOIL ADSORBENTS

The classes of soil minerals that have attracted the greatest research interest for de-fluoridation of water. Some of the minerals that have received the highest research attention in this area include the aluminosilicates, oxide minerals of Al and Fe, apatites, calcareous soil minerals, and carbonaceous geomaterials. Others are: sordic soils, red soil, serpentine mineral, fired clays soils.

SURFACE ACTIVATION OF SOIL ADSORBENTS

Natural soil systems ordinarily have low ion-exchange capacities because their surfaces are inherently saturated with replaceable groups which mask and neutralize the intrinsic surface charge to maintain the surface stability of the soil. The ion-exchange properties of the soil mineral can, however, be enhanced by pre-treatments that dislodge these masking ions from soil surface sites, and unblock the porous structure of the soil systems. This is important when the soil surfaces possess a net charge that would repel the adsorbate ions, which carry a similar charge to that of the soil surfaces. For anionic adsorption, surface charge reversal

for negatively charged soil adsorbents is achieved by impregnating the soil structure with multivalent cations or by hydrothermal activation in dilute acids among other physicochemical treatments. The latter approach is, however, the more popular because it is simpler and more cost-effective. Acid activation of soil adsorbents results in partial de-alumination of the clay structure. This increases the proportion of silica and the density of silanol (Si-OH) groups on the adsorbent surface, and increases the overall acidity and the net positive charge of the clay surface of the soil.

Owing to a high proportion of electronegative oxygen groups in the soil structure close to the adsorbent surfaces, many soil systems tend to carry a net negative charge, which is unfavourable to fluoride adsorption. In natural systems, this keeps fluoride in the soil solutions, from where it becomes easily available for easy uptake by plants. So as to enhance the potential of the soil adsorbents for fluoride adsorption, the adsorbent soil samples are pre-treated in dilute acid solutions to improve their surface positive charge. The surface charge reversal can then be confirmed by determination of the surface pH of the soil adsorbents by a variety of techniques, which include the alkali metric analysis.

CONCLUSIONS

In general the choice of a soil adsorbent for treatment of fluoride-contaminated water is controlled chiefly, among other factors, by the known adsorption capacities of the adsorbent for fluoride and the related adsorbates. The availability, cost, ease of preparation, simplicity of its application, and potential environmental and health hazards are the other factors that dictate suitability of an adsorbent for de-fluoridation of drinkable water. Certain potential adsorbents, which include palygorskite, pumice and montmorillonites, are not well distributed and could be difficult to procure for easy use in water de-fluoridation. Most distributed minerals in the humid tropical climates where high fluoride water is rampant include, laterites, hydroxyapatite, and silicate clays. The silicates and lateritic minerals are also the easiest to prepare and they are environmentally passive. This makes them first choice geo-materials for water de-fluoridation, especially among the developing countries within the tropics. On the other hand, despite its exceptional de-fluoridation capacity (DC) and large abundance in nature, natural apatite is among the hardest natural materials and is difficult to pulverize to usable forms for easy water de-fluoridation.

At the moment, the rare earth oxides and various nano sized adsorbents appear to have the highest water de-fluoridation capacity (DC). However, the current work reveals that the soil adsorbents could be the most promising media for isolation, processing and fabrication of robust adsorbents for the treatment of fluoride contaminated water. On the whole, the soil adsorbents have higher de-fluoridation capacity (DC) than most of the other categories of adsorbents including most alumina based adsorbents, activated carbons, bio-sorbents and biopolymers. They are stable, simple to prepare and use and they could be regenerated over several cycles of reuse not to mention that they are among, if not the cheapest materials to procure due to their ready availability in large quantities in nature.

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