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DEFLUORIDATION OF WATER BY METAL OXIDE AND HYDROXIDE ADSORBENTS: A REVIEW

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ABSTRACT

Fluoride pollution in drinking water is a widespread issue, particularly in regions like Rajasthan, India. Fluoride, a negatively charged contaminant, seeps into water sources through natural geological processes or human activities. Human activities, such as the disposal of industrial wastewater into water bodies, contribute to this problem. To address this issue, a variety of traditional and innovative methods are being employed to remove fluoride from water sources.

The review analyzed different adsorbents and their modifications as reported in reputable research publications to evaluate their adsorption capabilities under varying conditions. The impact of additional impurities on the removal of fluoride was also examined. The findings of this comprehensive study indicate that certain adsorbents, particularly binary and trimetal oxides and hydroxides such as alumina, magnesia, and zirconia, show promising potential for effectively removing fluoride from water sources.

Keywords: Adsorption, Fluoride, Adsorbents, Defluoridation, Water

INTRODUCTION

Fluoride is a powerful ligand, creating a wide range of organic and inorganic compounds present in different natural settings like soil, rocks, air, plants, and animals. Several of these compounds are easily dissolved in water, resulting in the occurrence of fluoride ions in both surface and groundwater sources **[1, 2]**.

BIS has set Fluoride limit as1 mg/L **[3]** while WHO has set its limit to 1.5 mg/L **[4, 5]**.

Drinking water is the main source of fluoride entry to human body. It causes many diseases and disorders like immunological defects **[6, 7]**, dental and skeletal fluorosis **[8]**. Fluoride sources are food, industrial exposure, drugs, cosmetics, *etc*.

The level of fluoride in water is influenced by various factors such as pH, total dissolved solids (TDS), water hardness, and alkalinity. Superphosphate fertilizer industry **[9, 10]**, glass and ceramic industry **[11]**, aluminum and zinc smelters **[12-14]**, and in municipal waste incineration plants, fluorinated textiles or CaF2 decomposition in waste sludge **[15]** etc. are also the significant cause of fluoride contamination.

Numerous effective defluoridation adsorbents have been documented in various reputable publications. The following are a few examples of such materials: Activated alumina **[16]**, activated carbons **[17-19]**, hematite **[20, 21]**, bauxite **[22, 23]**, resins **[24-26]**, pumice stone **[27, 28]**, rice husk **[29-31]**, red soil, charcoal, fly ash, modified ferric oxide &hydroxide **[32-34]**, titanium-derived adsorbent **[35-37]** and zeolites **[38, 39]**.

OXIDE AND HYDROXIDE ADSORBENTS

It is evident from reports thatmetal oxides and hydroxides are being widely used for fluoride removal. Iron oxide a good adsorbent is widely used to eliminate heavy metals, anions, and hazardous elements from wastewater **[40]**.

Binary oxide of Iron and aluminum $FeAlO_xH_y$, aluminum oxy hydroxide AlO_xH_y and iron oxyhydroxide FeO_xH_y were tested to evaluate their removal efficiency for arsenic and fluoride. As compared to FeO_xH_y and AlO_xH_y, $FeAlO_xH_y$ exhibits better results for simultaneous removal of arsenic and fluoride and may be used to treat water containing both As and F.

Poursaberi *et al.* **[41]** synthesize and characterize a new adsorbent having 3-aminopropyl triethoxysilane (APTES) coated magnetic nanoparticles which were functionalized with a zirconium (IV) porphyrin complex Zr (TCPP)Cl_2 [TCPP: tetrakis(4-carboxyphenyl) porphyrin]. Synthesis of Fe_3O_4 nanoparticles was done by co-precipitation of Fe^{2+} and Fe^{3+} in an ammonia solution and surface modification was done with APTES and Zr(TCPP). This nanoadsorbant was tested for a set of optimal conditions (fluoride concentration of 10 ppm, contact time: 20 min, pH: 5.5, and nanosorbents dosage: 100 mg) the percentage of the extracted fluoride ions was 92.0 ± 1.7%.

This developed adsorbent has proven to be efficient in treating wastewater samples obtained from the glass industry.

Dou *et al.* **[42]** used the extrusion method to prepare granular zirconium-iron oxide which are amorphous and nano-scale oxide particles and studied and evaluated its adsorption characteristic for fluoride removal. Ground water sample with initial fluoride concentration 10–150 ppm and pH 3–11, was tested by batch and column tests. Adsorption of Fluoride on granular zirconium-iron oxide follows pseudo-second-order kinetics and can be described by the Freundlich equilibrium model.

Zhao *et al.* **[43]** also used extrusion method and prepared granulated Fe–Al–Ce hydroxide.Cross-linked poly vinyl alcohol was used as binder. This trimetal absorbent is tested for its efficiency of fluoride removal. Fluoride solutions with different initial concentrations 10–250 ppm and at pH = 7.0 were used. Column test with fluoridated tap water of average fluoride concentration 5.0 ppm, average pH = 7.8 and groundwater containing naturally elevated fluoride concentration an average fluoride concentration 3.7 ppm and average pH = 8.2 was also tested. Regeneration tests were also conducted using $NaAlO_2$ solution.

Chen *et al*. **[44]** synthesized a novel and costless bimetallic Fe—Ti oxide nano-adsorbent by co-precipitation of Fe (II) and Ti(IV) sulfate solution using ammonia titration at room temperature The optimized Fe—Ti adsorbent had a Langmuir adsorption capacity of 47.0 mg/g and showed a remarkable synergistic interaction. Formed Fe—O—Ti in Fe—Ti adsorbent provided active sites of Fe—O—Ti—OH.and Fe—O—Ti—F bonds were formed by adsorption of fluoride. The novel Fe—Ti oxide nano adsorbent is efficient and economical for fluoride removal from drinking water.

Titanium hydroxide gel derived from titanium hydroxide showed high adsorption abilities for fluoride ions even in the presence of coexisting chloride, nitrate and sulfate ions. The adsorbent successfully removed fluoride below 0.8 ppm from solution with an initial fluoride concentration of 50 ppm **[45]**.

Kang *et al*. **[46]** investigated the performance and mechanism of calcined Mg/Fe layered double hydroxides which were synthesized by co-precipitation method, for removal of fluoride and arsenate simultaneously from aqueous solution. Highest fluoride removal was observed when Mg/Fe layered double hydroxides were calcined at 400 °C. Langmuir isotherm model show maximum adsorption capacities of fluoride were 50.91 mg/g.

Wang *et al*. **[47]** prepared CeO2-ZrO2 nano cages by Kirkendall effect and tested it for fluoride adsorption using batch process. The porous CeO2-ZrO2 nano cages showed the maximum capacity of fluoride adsorption which was calculated to be 175 mg/g at pH = 4.0. Adsorptionisotherm is well described by Langmuir model. Co-existentof chloride and arsenate in high concentration has adverse effects on fluoride adsorption, while the presence of sulfate has no effect on the fluoride adsorption.

Activated alumina has remarkable adsorption properties for fluoride removal from natural water **[48]**. Activated alumina has been proved to be a very good adsorbent because of its high surface area, crystalline form, and activation process **[49]**, It is seen that it works effectively at pH < 6 **[50, 51]**. In a study, alum impregnated activated alumina was used for fluoride remediation of drinking water and showed remarkable removal efficiency of 99% at pH 6.5 **[52]**. Similar types of results are reported by another study for the adsorption equilibrium and kinetics of fluoride removal by using activated alumina adsorbent made by sol-gel method **[53]**.

In order to overcome the limitations of MgO for field applications Sairam Sundaram *et al* **[54]**. modified Magnesium oxide or magnesia (MgO) which is a well-known adsorbent and has extremely high defluoridation capacity, to MgO /chitosan composite. Chitosan is abundantly available biomaterial. MgO and MgO/ chitosan composite were studied for fluoride removal from aqueous solution with batch equilibrium experiments. MgO/Chitosan composite showed very good defluoridation capacity of 4440 mg/kg, as compared to MgO whics showed over two-times less capacity (2175 mg/kg) at equilibrium. The defluoridation capacity of tested adsorbents is not affected by pH and the presence of most of the co-anions except bicarbonate ion. The adsorption followed the Freundlich isotherm.

CONCLUSION

The concentration of fluoride in water can be influenced by various factors such as pH, temperature, TDS, alkalinity, and hardness. Currently, there are several methods used for removing fluoride from water, but adsorption processes have gained popularity due to their effectiveness, simplicity, and cost-efficiency.

The pH of water plays a crucial role in fluoride adsorption, with studies showing that adsorption increases from acidic to near neutral pH levels and then decreases as pH becomes more alkaline. The presence of other ions can also impact fluoride adsorption by occupying active sites on adsorbents, reducing both theoretical and practical adsorption capacities. Oxides and hydroxides, particularly those made of titanium, iron, and aluminum in binary or trimetal combinations, have demonstrated high fluoride removal capacities. Among these, activated alumina stands out as one of the most commonly used adsorbents due to its high adsorption capacity over a wide pH range.

While activated alumina is effective, it may not be easily accessible, especially in rural areas, and can be costly. There is a need for more affordable and readily available adsorbents with high adsorption capacities that can be easily handled and used in both household and industrial settings. Materials like alumina and magnesia show promise, but further research is needed to identify more suitable adsorbents that meet these criteria.

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