International Journal of Researches in Biosciences, Agriculture & Technology | January 2014 Issue-2, Volume-1 | ISSN No. (Online) 2347-517X

APPLICATION OF NEW EMERGING NANO DIMENSIONAL MATERIALS FOR DEFLUORIDATION OF WATER

D. Marghade[1] , S. U. Bhonsule[2]
[1] Priyadarshini Indira Gandhi College of Engineering
[2] Priyadarshini College of Engineering

ABSTRACT

Chronic fluoride intoxication (fluorosis) is a worldwide health problem and India is endemic to fluorosis in 17 states. Fluorosis is originated mainly due to the consumption of drinking water containing high fluoride concentration. Among the available different deflouridation technologies, adsorption is one of the best due to its easy handling, low cost and high efficiency. Nowadays Nanosorbents are widely used as separation media in water purification to remove inorganic and organic pollutants from contaminated water. Two vital properties make nanoparticles highly lucrative as sorbents. On a mass basis, they have much larger surface areas compared to macro particles and they can also be enhanced with various reactor groups to increase their chemical affinity towards target compounds. In this work, synthesis and applications of various nano Dimensional materials for defluoridation of water are reviewed.

INTRODUCTION

Water is a mythical substance whose material existence is secondary compared to the symbolic value as it is manifested in our mind as the symbol of life. Sustainable supplies of clean water are vital to the world's health, environment and economy. Currently the human society is facing a tremendous crunch in meeting rising demands of potable water as the available supplies of freshwater are decreasing due to extended droughts, population growth, decline in water quality particularly of groundwater due to increasing groundwater and surface water pollution, unabated flooding and increasing demands from a variety of competing users. Today availability of safe drinking water is a concern

India is a vast country having diversified geological, climatological and topographic set-up, giving rise to divergent groundwater situations in different parts of the country. Unsustainable uses of resources and indiscriminate applications of pesticides, fertilizers, industrial pollutants are continuously disturbing the status of purity of groundwater. Major water pollutants include microbes (like intestinal pathogens and viruses), nutrients (like phosphates and nitrates), heavy metals and metalloids (like arsenic, fluoride, lead, and mercury), organic chemicals (like DDT, lubricants, industrial solvents), oil, sediments and heat. Virtually all industrial and goods-producing activities generate pollutants as unwanted by-products. Heavy metals can contaminate the aquifer and subsequently can bioaccumulate in the tissues of humans and other organisms

In the present context the recent advancement of nanoscale science and engineering is opening up a hitherto unknown and novel gateway to the development and deployment of effective defluoridation process.

Indian Scenario of Fluoride Pollution:

Fluoride is one of the most abundant anions present in groundwater worldwide and is one of the most important toxicological and geo-environmental issues in India. India is one of the 23 nations, which is reported to be endemic to fluorosis in 17 states and about 60–65 million people drink fluoride contaminated groundwater (UNICEF 1999). It indicates that endemic fluorosis is one of the most alarming public health problems of the country, especially in Rajasthan, Madhya Pradesh, Andhra Pradesh, Tamil Nadu, Gujarat, and Uttar Pradesh. The WHO (1997) recommendation has placed a highest desirable limit at 0.5 mg/L and the permissible limit at 1.5 mg/L for fluoride in the potable water. Fluorine is the most electronegative and highly reactive. India has 14.1% of total fluoride deposits on the earth's crust. The weathering of rocks and leaching of fluoride bearing minerals are the major reasons for high concentrations of fluoride in ground water. Its concentration in groundwater depends upon reaction times of rock water interactions.

Fluoride and Health:

The presence of smaller quantities of fluoride in drinking water are usually considered good to have a beneficial effect on the rate of occurrence of dental carries, particularly among children (WHO 1997; Rao 2009). Due to its strong electronegativity, fluoride is attracted by positively charged calcium ions in teeth and bones. Excessive intake of fluoride results in pathological changes in teeth and bones, such as mottling of teeth or dental fluorosis followed by skeletal fluorosis (Shusheela 1993; WHO 1997) and also lead to muscle fiber degeneration, low hemoglobin level, excessive thirst, headache, skin rashes, nervousness and depression (Meenakshi 2006). It was reported that various types of cancer were actually associated with fluoride (Yang et al. 2000). The severity of fluorosis depends on the concentration of fluoride in the drinking water, daily intake, continuity and duration of exposure, and climatic conditions.

Conventional Defluoridation methods:

The conventional approaches for fluoride removal include chemical precipitation, ion exchange, adsorption, electro-dialysis, Donnan dialysis and reverse osmosis (Sujana et al., 2009). Among all these methods, adsorption technique is economically favourable and technically feasible to separate fluoride from aqueous solutions as the requirement of operative controls are minimal (Raichur and Basu, 2001). Activated alumina is one of the most widely used adsorbents for fluoride removal in the drinking water treatment (Choi and Chen, 1979) due to its high affinity, resulting from the cause that the aluminum ion can form inner-sphere complexation. Tang et al. studied fluoride adsorption on to active alumina using batch methods and at equilibrium contact time of 10 hrs. Tripathy et al reported fluoride removal from drinking water by adsorption onto alum impregnated activated alumina. However, because of the high cost for the method of activation and low sorption capacity of activated alumina there is a necessity to develop adsorbent with enhanced adsorption capacity for application.

Nano materials used for defluoridation of water:

These days use of nanoparticles is becoming very attractive in the area of adsorption or recovery of metal ions from industrial wastes or natural water streams. The various nano dimensional material are synthesize and used for defluoridation of water.

Carbon Nano tubes: Aligned carbon nanotubes (ACNTs), a new kind of carbon material, were prepared by catalytic degradation of xylene via ferrocene as catalyst and used for the adsorption of fluoride from drinking water (Li et al. 2003). At pH 7, ACNT has an adsorption capacity of 4.5 mg/g fluoride at 15 mg/L of fluoride concentration. Li et al. (2003) also reported adsorption of fluoride on alumina supported on carbon nanotubes. The adsorption capacity of the Al_2O_3/carbon nanotubes was found to be 13.5 times higher than that of AIC-300 carbon and four times higher than that of γ-Al_2O_3 (Jagtab et al. 2011).

Nano dimensional MnO_2: Con et al. (2013) prepared nano dimensional MnO_2 by oxidation-reduction reaction of permanganate and manganese sulfate in water – ethanol solution and coated nano dimensional MnO_2 particles on natural pyrolusite grains to form a high performance sorption material. Figure 1 showed TEM image of MnO_2 nanoparticles have almost the same shape of spongy barbed spheres with dimension of 30 - 50 nm. Figure 2 showed surface of natural pyrolusite coating MnO_2 particles. At the SEM image, that is easy to recognize the nanoparticles of MnO_2 distributed all over pyrolusite grain surface

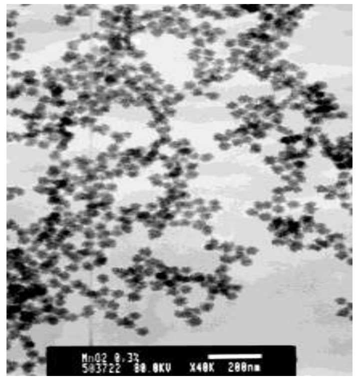

Figure 1. *TEM image of nano MnO_2 particles in the solution*

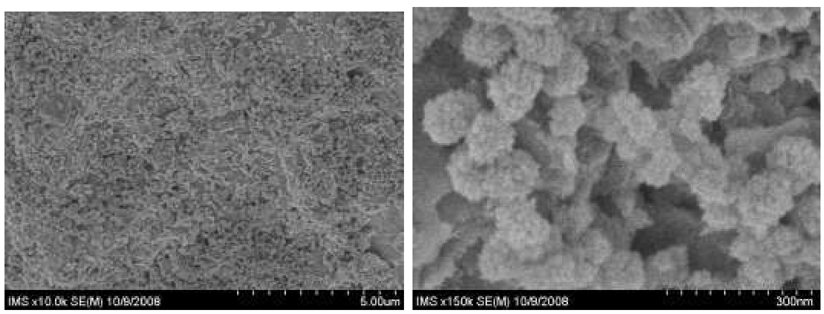

Figure 2. *SEM image of nanodimensional MnO_2 particles coated on calcinated clay surface*

Investigation of fluoride adsorption on nano MnO_2 coated on pyrolusite showed that, fluoride anions adsorbed on the material more complied with Freundlich isotherm and adsorption equilibrium time was only about 60 min. this is due dimerizeation, result in formation of multilayer adsorption of fluoride in the material.

Iron Nano materials*:* During the past few years , iron based novel sorbent with strong affinity towards fluoride have been developed for fluoride removal (Lin Chen *et al.*, 2009). Numerous techniques have been proposed to synthesize nano-sized Fe_2O_3 particles such as wet chemical method (Jiye fang *et al.,* 2003), hydrothermal (Song *et al.,* 2009), pyrolysis (Dghoughi *et al.,* 2006), sol gel (Markus Niederberger, 2007).

The reverse micelle or water in oil (w/o) micro emulsions has received considerable attention for preparing nano- sized particles. By following this method, several studies have been carried out in recent years. Preparation of catalysts from micro emulsions and their applications in heterogeneous catalysts are well reviewed (Sara Eriksson et al., 2004). Sujana and Mohanty (2010) prepared microemulsion by taking water/n-hexanol/span 80 in the volumetric ratio of 5.5:90:4.5 and added 1M $FeCl_3$ solution in it. Then obtained microemulsion precipitated by aqueous ammonia solution. The precipitation continued till the pH of the solution reached 10 and then precipitate was cooled and separated by centrifuging at 5000 rpm. The synthesized powder was dried at 60^{o}C for 24 h and stored in an air tight container for further use. The transmission Electron Microscope images of the synthesized powder that the particle are very fine and were found to be < 10 nm (Fig.3).

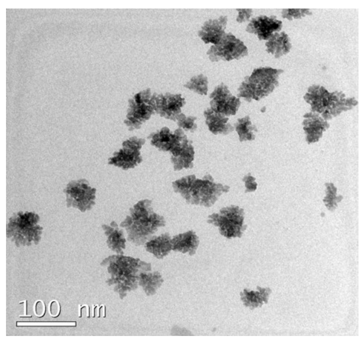

Figure. 3 *TEM image of iron oxide hydroxide nano particles*

Sujana and Mohanty (2010) studied the effect of pH on fluoride removal from aqueous solution by iron oxide hydroxide nano particles in the pH range of 2.5 to 9. They observed that the fluoride uptakecapacity of iron oxide hydroxide increased with pH up to 4, there after it showed decreasing trend with the increase of initial pH. The pHPZC of the prepared iron oxide hydroxide sample was found to be 5.3. This value is lower than the reported values for amorphous FeOOH (Balisterieri and Murray, 1981). Therefore, at pH lower than pHPZC iron oxide hydroxide becomes a strong anion exchanger. In the present study fluoride adsorption on the surface is coupled with a release of OH- ions, and favored at low pH values, decrease of adsorption with increase of pH (>4) may be because of stronger competition of hydroxide ions on adsorbent surface. It was observed that the pH of the equilibrated solution increased (1.0-1.8) in acidic pH range, while it decreased (1.0-3.0) when the initial solution was in alkaline range. The fluoride adsorption on iron oxide hydroxide surface is thought to be because of anion exchange at acidic pH and by Vander Waals forces at alkaline pH ranges. The fluoride adsorption on iron oxide hydroxide surface can be depicted as two step protonation/ligand exchange reaction mechanisms

$$\text{M-OH} + H^+ \leftrightarrow \text{MOH2}^+$$

$$\text{MOH2}^+ + F^- \leftrightarrow \text{MF} + \text{H2O}$$

This study confirms that the iron oxide hydroxide nano particles are suitable adsorbents for fluoride removal from aqueous solutions. Its adsorption kinetics is very fast and equilibrium was attained with in 1 hour. The results of kinetic modeling show that the pseudo second order kinetic model was better described the time effect on the fluoride adsorption when compared to the first order and intra particle diffusion models.

CONCLUSION

Research and development efforts made in the field defluoridation from drinking water have been shortly reviewed. Adsorption appears to be more conventional, low cost, easily applicable method for the removal of fluoride from water. Various nano dimensional materials were synthesized and their fluoride adsorption capacity was studied. The literature survey and the laboratory experiments have indicated that each of the discussed techniques can remove fluoride under specific conditions. But more development and deployment of effective defluoridation method is required to reduce extent of fluorosis problem in India.

REFRENCES

Choi W. W., and Chen K. K, 1979. The removal of fluoride from water by adsorption. Water Technology, Vol.10, pp. 562-570.

Con T.H., Thao P., Dai T.X. and Loan D.K. (2013), Application of Nano Dimensional MnO2 for High Effective Sorption of Arsenic and Fluoride in Drinking Water, Environmental Sciences, Vol. 1, no. 2, pp.69 – 77.

Dghoughi L., Elidrissi B., Bernede C., Addou M., Alaoui Lamrani M., Regragui M., and Erguig H., (2006). Physico-chemical, optical and electrochemical properties of iron oxide thin films prepared by spray pyrolysis. Applied Surface Science, Vol. 253, pp. 1823-1829.

Jagtap S., Yenkie M.K., Labhsetwar, N. and Rayalu S. (2010). Fluoride in Drinking Water and Defluoridation of Water, Chemical Reviews, dx.doi.org/10.1021/cr2002855.

Jiye fang, Amar Kumbhar, Weilie L. Zhou,and Kevin L. Stokes,(2003). Nano-needles of maghemite iron oxide prepared from a wet chemical route. Materials Research Bulletin. Vol. 38 pp. 461-467.

Li Y. H., Wang S. G., Zhang X. F., Wei J. Q., Xu C. L., Luan Z. K., and Wu D. H. (2003) Mater. Res. Bull., Vol. 38, pp. 469.

Li Y. H., Wang S., Cao A., Zhao D., Zhang X., Xu C., Luan Z., Ruan D., Liang J., Wu D., and Wei B. (2001) Chem. Phys. Lett., Vol. 350, pp. 412.

Lin Chen, Hai-Xia WuTing-Jie Wang, Yong Jin, Yu Zhang, and Xiao-Min Dou, (2009). Granulation of Fe-Al -Ce nano adsorbent for fluoride removal from drinking water by spray coating on sand in a fluidized bed. *Powder technology.* Vol. 193, pp. 59-64.

Markus Niederberger, (2007). Nonaqueous Sol–Gel routes to metal oxide nanoparticles. Account of Chemical Research. Vol. 40, No.9, pp 793–800.

Meenakshi, R.C. (2006). Fluoride in drinking water and its removal. Journal of Hazardous Materials, Vol. B137, pp. 456–463.

Raichur A.M. and Basu M.J., (2001). Adsorption of fluoride onto mixed rare earth oxides. Separation and Purification Technology. Vol. 24 pp. 121–127.

Rao, N.S. (2009) Fluoride in groundwater, Varaha River Basin, Visakhapatnam District, Andhra Pradesh, India. Environmental Monitoring and Assessment, Vol. 152, pp. 47–60.

Sara Eriksson, Ulf Nylen, Sergio Rojas, and Magali Boutonnet, (2004). Preparation of catalysts from microemulsions and their applications in heterogeneous catalysis. Applied Catalysis A: General. Vol. 265, pp. 207-219.

Shusheela, A.K. (1993). Prevention and control of fluorosis in India. Rajeev Gandhi National Drinking Water Mission. Ministry of Rural Development, New Delhi Health, Vol. 1, pp.20–22.

Song Ge, Xiangyang Shi Kai Sun, Changpeng Li Ctirad Uher James R. Baker, Jr., Mark M. Banaszak Holl and Bradford G. Orr, (2009) Facile hydrothermal synthesis of iron oxide nanoparticles with tunable magnetic properties. Journal of Physical Chemistry C. Vol.113, No.31, pp 13593–13599.

Sujana M. G. and Mohanty S. (2010) Characterization and fluoride uptake studies of nano-scale iron oxide-hydroxide synthesized by microemulsion method. International Journal of Engineering, Science and Technology, Vol. 2, No. 8, pp. 1-12.

Sujana M.G., Soma G., Vasumathi N., and Anand S., (2009). Studies on fluoride adsorption capacities of amorphous Fe/Al mixed hydroxides oxides from aqueous solutions. *Journal of Fluorine Chemistry*. Vol. 130, No.8, pp. 749–754.

Tang Y., Guan X., Su T., Gao N. and Wang J. (2009) fluoride adsorption onto activated alumina: Modelling the effects of pH ans some competing ions. Colloids & Surfaces, Vol. 337, pp. 33-38.

Tran Hong Con, Phuong Thao, Trinh Xuan Dai and Dong Kim Loan (2013) Application of Nano Dimensional MnO2 for High Effective Sorption of Arsenic and Fluoride in Drinking Water, Environmental Sciences, Vol. 1, no. 2, pp. 69 – 77.

Tripathy S.S., Bersillion J.L. and Gopal K. (2006) Removal of fluoride from drinking water by adsorption onto alum-impregnated activated alumina. Sepn. Purif. Technol., Vol. 50, pp. 310-317.

UNICEF (1999). State of the art report on the extent of fluoride in drinking water and the resulting endemicity in India. Report by fluorosis and Rural Development Foundation for UNICEF, New Delhi

WHO. (1997). Guideline for drinking water quality health criteria and other supporting information (2nd ed., Vol. 2). Geneva: World Health Organization.

Yang, C.Y., Cheng M.F., Tsai, S.S., and Hung, C.F. (2000). Fluoride in drinking water and cancer mortality in Taiwan. Environmental Research, Vol.82, pp.189–193.