Abstract — Water is one of the most vital and indispensable commodities of our everyday life. Progression of this natural resource plays a crucial role in socio-economic scenario. With only 1% available potable component, it is by and large adequate to meet all the demands of mankind. However its quality and dissemination over different regions of the world is uneven and causes problems of scarcity and appropriateness. Thus it is overbearing that one develops requisite low cost remediation and management practices for the rational and efficient use of this scarce commodity as much as possible. In order to execute this task, accurate and adequate information must be available about the quality of this natural resource under constantly changing human pressures and natural forces.

Keyword — aqueous media, Biological adsorbent materials, inorganic contaminants, natural resources, remediation.

INTRODUCTION

Importance of water as a finite natural resource is never underrated but due to its depletion and pollution there is scarcity of potable water. According to available statistics nearly 1.1 billion people in the developing world do not have access to minimum quantity of safe drinking water. One of the major reasons for this is high cost of water supply and purification technologies. 70% of India’s surface water resources and groundwater reserves have been contaminated by biological, organic and inorganic pollutants. The diffuse and point pollution sources including agricultural runoffs due to inorganic fertilizers and pesticides and natural contamination of water by fluoride, arsenic and dissolved salts due to geo-chemical activities which contribute majorly to this disturbing picture. Fluoride and nitrate are amongst main water pollutants causing major health concerns. In Accordance with the World Health Organization norms, the maximum permissible concentration of fluoride ions in drinking water should be below 1.5 ppm. Below this limit fluoride is useful as it has favorable effect on teeth. However if taken in excess and for longer duration, it can cause fluorosis of the teeth and bones [1-3]There is an urgent need of remediation of water using low cost, biodegradable biopolymers like chitosan [4]. An attempt has been made to consolidate the studies done at international and national level in this field.

INTERNATIONAL SCENARIO

Studies have been conducted by several authors with synthetic polymer supported chitin and chitosan. This is due to the fact that chitosan can be molded in several shapes, membranes, microspheres, gel beads, films, nanoparticles and nanofibers and is able to provide a ratio: surface area/mass that maximizes the adsorption capacity and minimizes the hydrodynamic limitation effects, such as column clogging and friction loss [4-7]. Polymeric supports have benefits such as easy usage and adaptability. Also it is possible to obtain homogeneous, porous, malleable and mechanically–chemically resistant biocomposites. There are many options available to support these biopolymers which include mineral materials such as hydroxyapatite, binary metal oxides, magnesia, hydrotalcite, alumina, rare earth metals, etc with high F removal capacity [8–13]. Charcoals that contain calcium compounds were synthesized by impregnating wood with calcium chloride followed by carbonization at 500 °C, 650 °C or 900 °C. (Tchomgui-Kamga E. et al 2010) [14] The charcoals were characterized by SEM, EDAX, XRD and chemical titrations. Their performance for fluoride removal from aqueous solution was evaluated by batch experiments. A new medium, granular ceramic, was developed for fluoride removal from water by Chen et al 2010 [15]. Granular ceramic is a solid-phase medium that produces a stable Al–Fe surface complex for fluoride adsorption. BET, SEM, and EDS were used to characterize the physical attributes (particle size, pore size and distribution, surface roughness) of the granular ceramic. Fluoride adsorption characteristics were studied in a batch system with respect to changes in initial concentration of fluoride, pH of solution, and coexisting ions. Fluoride adsorption was found to be pH dependent and the maximum removal of fluoride was obtained at pH 5.0–8.0. Equilibrium adsorption data were obtained at 293, 303, and 323 K, and interpreted in terms of the Langmuir and Freundlich isotherm equations.
Electrocoagulation (EC) process using aluminum electrodes was used for removing fluoride from treated industrial wastewater originated from steel industry (Khatibikamal V. 2010) [16]. After treatment, the fluoride concentration was reduced from initial 4.0–6.0 mg/L to lower than 0.5 mg/L. The pH of the influent is found as a very important variable which affects fluoride removal significantly. The optimal range for the influent is 6.0–7.0 at which not only effective defluoridation can be achieved, but also no pH readjustment is needed after treatment.

Nitrate, due to its high water solubility, is possibly the most widespread groundwater contaminant in the world, imposing a serious threat to human health and contributing to eutrophication (Bhatnagar A 2011, 2010, 2009 Öztürk N., et al 2004) [17-20]. Among several treatment technologies applied for nitrate removal, adsorption has been explored widely and offers satisfactory results especially with mineral-based and/or surface modified adsorbents. In this review, an extensive list of various sorbents from the literature has been compiled and their adsorption capacities for nitrate removal as available in the literature are presented along with highlighting and discussing the key advancement on the preparation of novel adsorbents tested for nitrate removal. A physico-chemical investigation of the adsorption of nitrate by chitosan hydrobeads and beads conditioned with sodium bisulfate were conducted by Chatterjee et al 2010, 2009a, 2009b [21-23]. The adsorption of nitrate by chitoan hydrobeads was increased with a decrease in the pH of the solution. The adsorption process was found to be temperature dependant with an optimum activity at 30 °C. Adsorption capacity was found to decrease with increases in temperature after 30 °C, indicating the exothermic nature of this process. Surface modifications of natural zeolite were performed by coating it with a chitosan layer (Arora M et al 2010) [24]. The chitosan coated zeolite (Ch-Z) was protonated with either sulfuric or hydrochloric acid and tested for its suitability to capture nitrate from water at 20 and 4 °C. The surface characterization of the Ch-Z was done by SEM, FTIR, TGA and nitrogen adsorption tests. The results of these tests showed evidence of chitosan coating onto zeolite particles. Ch-Z has comparable capacity to other weak anion exchangers with a nitrate ion exchange capacity 0.74 mmol NO₃⁻ g⁻¹ (protonated with HCl). Nitrate, contained in surface or groundwater, can be removed by sorption on protonated cross-linked chitosan gel beads (Jaafar K et al 2004) [25]. The sorption capacity is large enough to meet the standard of drinkable water. The isothermal equilibrium curves are straight lines which were established for a contaminated groundwater. The sorption kinetics is not limited by pore diffusion and is well modelled by a phenomenological equation. The experimental partition coefficient and overall mass transfer coefficient were used for simulating a plug flow fixed bed adsorber. Selectivity coefficients for binding of negative and positive ions to chitosans of different chemical composition were determined by equilibrium dialysis (Vold IMN et al 2003) [26]. Chitosan with different fraction of acetylated units (Fₐ of 0.01 and 0.49) generally behaved similarly in their selectivity towards both negative and positive ions. No selectivity was found in the binding of chloride and nitrate ions, while chitosan showed a strong selectivity towards molybdate polyoxyanions, with selectivity coefficients around 100. Apart from chitosan the adsorption isotherms of nitrate on resin Amberlite IRA 400 at various pH, in the range 2–12, were experimentally determined by batch tests (Chabani M et al 2009) [27]. The experimental data have been analysed using the Langmuir, Freundlich, Redlich–Peterson and Sips isotherms models. In order to determine the best fit isotherm, two error analysis methods were used to evaluate the data: the regression correlation coefficient, and the statistic Chi-square test. In the range of pH tested, the Sips model was found to give the best fit of the adsorption isotherm data. The maximum adsorption capacity can be deduced from the obtained correlation coefficients and was found to decrease for increasing pH. The removal of chloride, nitrate and sulfate ions from aqueous solutions by a macroporous resin is studied through the ion exchange systems OH⁻/Cl⁻, OH⁻/NO₃⁻, OH⁻/SO₄²⁻, and HCO₃⁻/Cl⁻, Cl⁻/NO₃⁻, Cl⁻/SO₄²⁻. (Dron J et al 2011) [28].

The present study was conducted to evaluate the feasibility of nano-alumina (Al₂O₃) for fluoride adsorption from aqueous solutions (Kumar E et al 2011) [29]. The nature and morphology of pure and fluoride-sorbed nano-alumina were characterized by SEM with EDX, XRD, and FTIR analysis. Batch adsorption studies were performed as a function of contact time, initial fluoride concentration, temperature, pH and influence of competing anions. Fluoride sorption kinetics was well fitted by pseudo-second-order model. The maximum sorption capacity of nano-alumina for fluoride removal was found to be 14.0 mg g⁻¹ at 25 °C. Maximum fluoride removal occurred at pH 6.15. The fluoride sorption has been well explained using Langmuir isotherm model. Fluoride sorption was mainly influenced by the presence of PO₄³⁻, SO₄²⁻ and CO₃²⁻ ions. Miretzyk P et al 2011 reviewed the recent developments in the F⁻ removal in water treatment, using chitosan derivatives and composites in order to provide useful information about the different technologies [30]. When possibly the adsorption capacity of chitosan derivatives and composites under different experimental conditions is reported to help to compare the efficacy of the fluoride removal process.

The application of neodymium-modified chitosan as adsorbents was investigated for the removal of excess fluoride from water [31]. The modified chitosan showed defluoridation capacity at neutral pH 7. The defluoridation capacity further increased with increasing
Studies were conducted to investigate the fluoride adsorption capacity of natural (raw) bauxite and clay which are the locally available, cost-effective, simple and abundant adsorbents on the region (Atasoy D. et al. 2013) [34]. Adsorption tests were carried out by Batch method for the adsorbents. Fluoride reached adsorption equilbrium within 3 h in bauxite and 5 h in clay. It was observed that the amount of fluoride adsorbed is decreased with the increase in dose. The maximum adsorption capacity was found to be 0.25 mg g⁻¹ and 0.30 mg g⁻¹ for clay and bauxite, respectively at a dose of 0.2 g/40 mL (2.5 g L⁻¹). Experimental data for fluoride adsorption in raw clay and bauxite agreed with both Langmuir and Freundlich equations.

Zhang Yi et al (2013) studied the effect of temperature, contact time and initial fluoride concentration [35]. Scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and Fourier-transform infrared spectrometry (FTIR) were used to characterize the adsorbent. The SEM analysis graph showed that the sizes of bentonite/chitosan beads were between 50 um and 150 um. The holes on the surface of beads could increase the adsorption sites. The EDAX spectra of the adsorbent showed the presence of elements in bentonite/chitosan beads. The emergence of fluoride peak in fluoride treated beads demonstrated the adsorption of fluoride onto adsorbent. The adsorption of fluoride onto the adsorbent followed Freundlich isotherm model and pseudo-second order kinetic model. The fluoride loaded adsorbent could be regenerated using sodium hydroxide.

The effect of chitosan immobilization of Scenedesmus spp. cells on its viability, growth and nitrate and phosphate uptake was investigated by Sashenka F et al 2008 [36]. Scenedesmus sp. (strains 1 and 2) and Scenedesmus obliquus immobilized in chitosan beads showed high viability after the immobilization process. Immobilized Scenedesmus sp. strain 1 had a higher growth rate than its free living counterpart.

The promising applications of nanotechnology in contributing new or improved solutions to meet human development needs have been repeatedly stressed by researchers and scientists. Application of nanotechnology for water purification has been identified as a high priority area. Nano-AI-OH possesses a maximum fluoride capacity of 3259 mg F⁻¹ kg⁻¹, which is comparable with that of activated alumina. Maximum adsorption occurred at around pH 7, which makes nano-AI-OH a potential adsorbent for drinking water treatment. (Wang SG et al 2009) [37]. Environmental-responsive nanoparticles of chitosan- graft-poly(N-isopropylacrylamide) copolymers (CS-g-PNIPAAm) were prepared by the self-assembly method (Chuang Chung-Yang et al 2011) [38] The copolymer was first synthesized through polymerization of NIPAAm monomer in the presence of CS in an aqueous solution using cerium ammonium nitrate as the initiator. Then, the CS-g-PNIPAAm solution was diluted by deionized water and heated to a proper temperature for CS-g-PNIPAAm to undergo self-assembly. Micelles of CS-g-PNIPAAm were formed, and glutaraldehyde was added to reinforce the micelle structure to form nanoparticles. TEM images showed that a porous or hollow structure of nanoparticles was developed. The synthesized nanoparticles carried positive charges on the surface and their mean diameter could be manipulated by changing the temperature of environment. These nanoparticles possess environmentally sensitive properties. Three types of matrix nano composites were presented underlining the need for these materials, their processing methods and some recent results on structure, properties and potential applications, perspectives including need for such materials in future space mission and other interesting applications together with market and safety aspects. (Camargo PHC et al 2009) [39]

INDIAN SCENARIO
Considerable work has been done by Meenakshi S et al 2009a, 2009b, 2009c, 2009d, 2009e 2009f [40-45]. Activated alumina has been used by many as a defluoridation adsorbent (Chauhan et. al., 2007) [46]. Hydroxyapatite in bone char matrix may be used for defluoridation in both POE and POU devices in a cost effective manner. Graphite is yet another adsorbent for fluoride with some potential (Karthikeyan and Elango.2008) [47]. Application of these technologies is, however, subject to full scale field trial. Studies on fluoride removal from aqueous solutions using various reversed zeolites, modified zeolites and ion exchange resins based on cross-linked polystyrene are reviewed (Mohapatra M 2009) [48]. During the last few years,
layered double oxides have been of interest as adsorbents for fluoride removal.

The metal-binding property of chitosan is used by Jagtap S et al 2009, to incorporate titanium metal and applied as an adsorbent for fluoride adsorption. Titanium macroospheres (TM) were synthesized by a precipitation method and characterized by FTIR, SEM, and XRD [49]. The Langmuir and Freundlich adsorption models were applied to describe the adsorption equilibrium and the adsorption capacities were calculated. Thermodynamic parameters of standard free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) were also calculated. The effects of various physico-chemical parameters such as pH, initial concentration, adsorbent dose, and the presence of coexisting anions were studied.

A novel combustion synthesis for the preparation of Nanomagnesia (NM) and its application in water purification was described by Maliyekkal S.M. et al 2010, 2008 [50, 51]. The synthesis was based on the self-propagated combustion of the magnesium nitrate trapped in cellulose fibers. The fluoride scavenging potential of this 44s material was tested as a function of pH, contact time and adsorbent dose. The result showed that fluoride adsorption by NM is highly favorable and the capacity does not vary in the pH range usually encountered in groundwater. The effects of various co-existing ions usually found in drinking water, on fluoride removal were also investigated. (Sharma et al 2009a, 2009b, 2009c, 2010) used green amendments e.g., Rock Phosphate (RP) and Coal Fly Ash (CFA) to remediate heavy metal contaminated soils of Delhi [52-55]. This research work focused on the batch, bench and column scale demonstration of metal immobilization in contaminated soils using green amendments like Rock Phosphate (RP) and Coal Fly Ash (CFA).

RECOMMENDATIONS FOR BRIDGING THE RESEARCH GAP
Fluoride contamination of aqueous media is a global phenomenon. Limitations of existing remediation processes for fluoride and nitrate in drinking water underscore the need for new generation materials for holistic and total water quality solution. Although ongoing research in the field of chitosan based adsorbents, is extremely effective in remediation efforts, there are significant gaps in these adsorbents. Ideally these materials should be low cost, multifunctional and ecofriendly. The sludge generated on using these materials should be easily disposable in a safe and environment friendly manner. I propose to address these gaps

CONCLUSION
Maintaining and re-improving the quality of water, air and soil, so that the Earth will be able to support human and other life sustainably, are one of the great challenges of our time. Further research can reduce the environmental footprints of industrial and other agrochemical activities, the designing of remediation technologies using nanocomposites as amendments are really significant. The kinetic and thermodynamic studies of these interactions throw light on the selection, effectiveness and longtime feasibility of these remediation technologies.

REFERENCES


32. Wang SG, Ma Y, Shi Y Jing, Gong Wen-Xin; “Defluoridation performance and mechanism of nano-scale aluminum oxide hydroxide in aqueous

Copyright © 2014 CTTS.IN, All right reserved 475
52. Sharma, Mamta Chhabra; Saxena, Reena; Sharma, Sandeep; Singh Suneeti “Modeling Of Heavy Metal Mobility In Delhi Soils Before And After Remediation With Rock Phosphate Using Sequential Extraction, TCLP and PBET” Asian Journal of Water, Environment and Pollution Accepted for publication, 2011
54. Sharma, Mamta Chhabra; Saxena, Reena; Sharma, Sandeep; Singh Suneeti “Green approach of chemical immobilization of lead in metal - contaminated soils of NCT of Delhi using rock phosphate” accepted for publication in Journal : Environmental Science : An Indian Journal, Volume 4(5) 2009
55. Sharma, Mamta Chhabra; Saxena, Reena; Sharma, Sandeep; Singh Suneeti “Green approach of Chemical Immobilization of Lead in metal - Contaminated Soils of NCT of Delhi Using Rock Phosphate and Coal Fly Ash” Journal : Environmental Science : An Indian Journal Volume 4(5) 2009

AUTHOR’S PROFILE

• Prof/Dr Sandeep K Sharma has received his PhD in Delhi University during the period of 1992. Currently, he is working as Associate Professor in Delhi University. He has successfully completed his Administrative responsibilities as Officer on Special Duty (ARSD College), Secretary – Staff Council, Chief Proctor, Teacher in Charge –Chemistry Department, Convenor – Admissions Committee, University Counsellor- SC/ST Cell, Member - Student Union Advisory Committee. His research has included Environment Chemistry and its socio-economic aspects, Green Chemistry, Analytical Chemistry. Recently he received a major research project from Ministry of Water Resources, Government of India. Based on this research and fellowship training he has received several awards and honors, such as: University Grant Commission Fellowship. He has authored over

Copyright © 2014 CTTS.IN, All right reserved

476
twenty research articles/books. He is a member of Green Chemistry Network. He has been honoured and is recipient of CSIR-UGC National Level Test For fellowship and Eligibility of Lecturership (NET), Junior Research Fellowship (JRF) and Senior Research Fellowship (SRF) Sponsored by UGC.

- Prof/Dr. Mamta Sharma has received her PhD in Delhi University during the period of 1994. Currently, she is working as Associate Professor in Delhi University. She has successfully completed her Administrative responsibilities as Convenor, Women Development Cell/Member, Governing Body. Her research has included Environment Chemistry and its socio-economic aspects, Polymer Chemistry. Based on this research and fellowship training he has received several awards and honors, such as: Innovation Projects from Delhi University, University Grant Commission Project, Department of Science and Technology (GoI) Project. She is serving as an expert Reviewers for journals like Journal of Polymer Science/Air, Soil and water research. She has authored over twenty five research articles/books. She is a member of Green Chemistry Network. She has honoured by All India Foundation for Peace and Disaster Management for Environmental Management Awareness, she is recipient of “Science Meritorious Award” third position in M.Sc. (University of Delhi), CSIR-UGC National Level Test For fellowship and Eligibility of Lecturership (NET), Junior Research Fellowship (JRF) and Senior Research Fellowship (SRF) Sponsored by UGC under CAS category, Silver Jubilee Scholarship” Miranda House, University of Delhi 1988.