

Remediation of different species of arsenic by adsorption process is becoming a growing exercise in present time. Nanomaterials are excellent choice for this purpose due to their high surface area, reactivity and selectivity. But tailoring of these materials over some supporting materials is an important concern for making them useful. Different functional polymers and biomass of some aquatic plants can act as an efficient scavenger of arsenic and other heavy metal ions from water. These materials have another advantage of immobilizing nanomaterials and thus, preventing them from agglomeration. This, further enhances sorption ability of the later as their surface integrity is maintained under different experimental conditions and they are transformed to efficient reclyable materials. Furthermore, those stabilizing materials also contribute to the sorption process and sometimes synergistically improve the sorption abilities compared to the component members.

This thesis is focused on the development of different composite/nanocomposite systems based on starch, chitosan biopolymer and water hyacinth root powder, for removal of arsenic contamination from water. Different nanomaterials chosen for the study were magnetite, iron oxyhydroxide, titanium dioxide and clay minerals. Properties of the materials under interest were tried to further upgrade by adopting different techniques such as surface functionalization of nanomaterials, modification of the polymeric systems, use of crosslinking agents, etc. To evaluate efficiency of the materials, influence of change in experimental conditions on removal of arsenic were determined and nature of sorption were predicted by employing numbers of sorption and kinetic models to the sorption data.

Contents of the thesis entitled “Study on Removal of Arsenic Contamination from Water by polymer nanocomposites” have been organized in four chapters dealing with different aspects of study. Brief overviews of those are given below-

1. Introduction: It deals with the background, motivation, scope, objective and plan of the investigation.
2. Experimental methods: It describes the starting materials used in the study and different methods adopted.
3. Results and discussion: It is related to the characterization of the prepared materials and efficiency evaluation of those in arsenic sorption.

4. Conclusion and future scopes: It summarizes the major findings obtained from the study and some of salient points on which further study can be done to make them more fruitful.

*Chapter 1* gives the general introduction and literature search pertaining to the study. A detailed analysis of cause for the dependence of people on ground water, its consequence in the form of hazardous arsenic intake, sources and distribution of arsenic contamination and health impacts are presented here. Merits and demerits of different conventional techniques used for arsenic treatment and advantages of adsorption technique over those are also discussed. Despite the excellent sorption ability of nanomaterials like  $\text{Fe}_3\text{O}_4$ , iron oxyhydroxide,  $\text{TiO}_2$ , clay, etc., they have some disadvantages in their normal form. Surface modification, stabilization over polymeric materials such as chitosan, starch, aquatic plant biomass, etc., and use of crosslinker are illustrated as a good alternative to overcome those difficulties. Role of polymer in their pristine as well as modified forms in arsenic sorption and in stabilization of nanomaterials in the form of composite/nanocomposite is also included. The aims and objectives along with the strategy of present work have been narrated in the last part of this chapter.

*Chapter 2* gives a brief introduction about starting materials used during the study and methods, techniques and instruments adopted to characterize the prepared materials and evaluate their efficiency during end use application. All the experimental methods applied to prepare different composite/nanocomposite systems are included. Procedure of batch experiments for removal of arsenic has been described. Application of numerous isotherm and kinetic models, thermodynamic parameters and computational calculations are also described.

*Chapter 3* is based on the characterization of prepared materials, their efficiency evaluation and interpretation in arsenic remediation. For systematic study the chapter is subdivided into three major sections-

*Section A* deals with two types of composites of chitosan biopolymer with MMT clay and magnetic  $\text{Fe}_3\text{O}_4$  nanomaterials. MMT based nanocomposite (*Section 3.1*) was prepared by well dispersing a clay suspension within chitosan solution followed by precipitation of the later by NaOH solution. Glutaraldehyde solution was used to crosslink the final product. A crosslinked chitosan material without clay was

also prepared by same way for comparison purpose. Incorporation of clay into the system enhanced sorption capacity as compared to chitosan alone. The delaminated structure of the clay mineral within the polymer matrix was explained by XRD and TEM micrographs. Also, during the processing, loss in crystallinity of the polymer was noticed as shown by XRD spectra. Successful adsorption of arsenic over the material was confirmed by FT-IR analysis and EDX spectra. A mechanism was also proposed to describe the formation of composite system and structural changes during arsenic sorption. The removal efficiency was studied as a function of contact time, material dose, initial As(V) concentration, etc. The sorption followed monolayer type of chemisorption pattern as described by Langmuir isotherm and was governed by a pseudo second order kinetics.

On the other hand, chitosan-  $\text{Fe}_3\text{O}_4$  composite (*Section 3.2*) was prepared by an ex-situ method.  $\text{Fe}_3\text{O}_4$  was prepared ex-situ by co-precipitation of ferrous and ferric salts which was then stabilized within chitosan matrix with the help of glutaraldehyde crosslinker. The material could efficiently perform several cyclic runs with high As(V) removal efficiency and its advantages over many established method is mentioned. Different characterization techniques were performed to investigate the binding, structural and other properties of prepared materials. The study also focused on the effect of competing ions, viz. phosphate and chloride on removal efficiency. The initial As(V) concentration (0.6 mg/L) was found to decrease to less than 0.01 mg/L at a contact time of 120 min with an adsorbent dose of 1g/L. Influence of different experimental conditions similar to previous discussion were also studied. The sorption followed a Langmuir monolayer sorption at low concentrations and then heterogeneity appeared at higher arsenate concentrations. The maximum adsorption capacity calculated from Langmuir isotherm was found to be 10.81 mg As(V)/g at room temperature and neutral pH. The sorption process was found to be governed by pseudo second order kinetics.

*Section B* reports two types of starch based nanocomposite systems using surface modified  $\text{TiO}_2$  nanoparticles (*Section 3.3*) and iron oxyhydroxide nanomaterials (*Section 3.4*).

In *Section 3.3* bare  $\text{TiO}_2$ , CTAB (N-cetyl-N,N,N – trimethyl ammonium bromide) modified  $\text{TiO}_2$  (CMT) and starch coated CMT were taken under consideration

for arsenic sorption. Modification with CTAB increased the dispersibility of TiO<sub>2</sub> particles in water and produced highest arsenic removal rate (~99% from 0.4 mg/L). But material loss was maximum in this case and hence, it was less efficient for regeneration. Bare TiO<sub>2</sub> also showed good removal efficiency, but coating with starch made the particle best for regeneration along with its high sorption ability. The materials were characterized with different analytical techniques and influence of experimental conditions on removal efficiency was evaluated. For a targeted solution of 0.4mg/L, a material dose of 2 g/L was found to be sufficient to bring down the As(V) concentration below 10 µg/L. Equilibrium was established within 90 minutes of treatment. The sorption pattern followed Langmuir monolayer pattern and the maximum sorption capacity was found to be 1.024 mg/g and 1.423 mg/g after starch coating and after CTAB modification, respectively. The sorption mechanisms were governed by a pseudo second order kinetics.

**Section 3.4** demonstrates the excellent arsenic adsorption property of a hybrid material of aminated starch, oxyhydroxide of iron and OMMT nanoclay. At first, starch was aminated with ethylene diamine via GMA (Glycidyl methacrylate) grafting. Thereafter, clay was incorporated in to it followed by the in-situ generation of iron oxyhydroxide from Fe(NO<sub>3</sub>)<sub>3</sub>. Most significant thing in the material was that besides sorption of arsenic, iron oxyhydroxide itself acted as crosslinker for the material. On the other hand, starch helped in the immobilization of clay as well as oxyhydroxide particles. Each step in preparation of the final material and sorption of arsenic over it were confirmed by different characterization techniques and further verified by molecular modeling on the basis of density functional theory. Clay was found to have definite contribution to arsenic removal. The material showed excellent sorption ability for As(III) from aqueous solution and could reduce its concentration below 10 µg/L. The thermodynamic parameters, viz. Gibbs free energy, enthalpy, entropy and activation energy determined feasibility of the process, its endothermic behavior and most importantly chemical nature of the sorption accompanied by ion-exchange to some extent. The sorption followed a monolayer chemisorption pattern as determined by Langmuir isotherm model with a  $q_{max}=2.04$  mg/g at 303 K. The binding of As(III) over the material was governed by a pseudo second order kinetic model and

dependence of rate constant values on temperature during the binding further supported the endothermic nature.

**Section C** describes the utility of dried biomass of water hyacinth root powder (WHRP) based materials in arsenic adsorption. Two types of materials, viz. citric acid (CA) crosslinked WHRP (**Section 3.5**) and Glutaraldehyde crosslinked WHRP/chitosan composite (**Section 3.6**) were evaluated for arsenic sorption.

In **Section 3.5** water hyacinth root powder was stabilized by crosslinking with citric acid. The process was carried out in water medium, where, minute amount of titanium dioxide played a significant catalytic role in crosslinking process. Incorporation of CA into WHRP enhanced its integrity and thus, removal efficiency remained unaffected after several cyclic runs. Also, turbidity which formed due to treatment with uncrosslinked WHRP was reduced to below the permissible limit. Change in experimental conditions, such as amount of CA, material dose, treatment time, initial ion concentration and pH were found to affect the sorption rate. An amount of 10% (w/w) CA was adequate to keep turbidity level below 2.5 nephelometric turbidity unit (NTU) without hampering the removal capacity/rate. A material dose of 5 g/L removed successfully total inorganic arsenic concentration to below 10 µg/L. The sorption process followed a monolayer chemisorption pattern and maximum adsorption capacity was found to be 28 µg of arsenic/g. The material was more efficient at acidic pH and it was governed by a pseudo second order kinetic model.

**Section 3.6** focused on a new composite system prepared by amalgamating dried *E. crassipes* root powder with chitosan biopolymer using glutaraldehyde as crosslinker. A comparative study between root powder and composite was also done. Different composite systems were prepared by varying the ratio of the components and their performance was evaluated. Composite with 1:2 wt ratio (Chitosan:WHRP) showed best results at least cost. Most significant part of this study was that the component materials synergistically enhanced sorption ability of the final composite. The composite could efficiently remove As(III) from water to below the permissible limit as prescribed by WHO. Different interactions arised during the composite formation and sorption of arsenic over it were analyzed and confirmed by different physico-chemical/ spectroscopic techniques and density functional theory (DFT) calculations. Maximum adsorption capacity for the material was found to be 7.11 mg of arsenic/g. The sorption

was chemical in nature and was governed by a pseudo second order kinetic model.

*Chapter IV* finally summarizes the salient observations of the entire work presented in this thesis and incorporates future prospects and outlook to improve and consolidate the research work.