

### Overall Conclusion of the Present Work

In spite of the demerits such as agglomeration, low stability and high risk of leaching of nanomaterials during arsenic treatment, due to their excellent sorption ability, special emphasis has been given to design nanocomposites. In present study, iron, titanium and clay based nanomaterials were added with starch, chitosan, etc. (during the formation of nanocomposites). Biomass based materials were also stabilized for successful utilization in arsenic mitigation. These may open up a new area in terms of long term recyclability as well as high arsenic sorption ability.

The significant out comings of this thesis and scopes for further improvement of those works can be summarized as follows-

Incorporation of clay into chitosan followed by crosslinking with glutaraldehyde showed significant improvement in As(V) removal as compared to clay free crosslinked chitosan as described in *Section 3.1 in Results and discussion*. The delamination of the clay layers within the polymer matrix was clearly observed as explained by XRD and TEM study. FT-IR spectrum described the probable binding of As(V) with the sorbent. The agglomerated structure of MMT/Ct/Glu as shown by SEM pictures became little bit smoother after treatment with As(V). The sorption of As(V) was affected by material dose, contact time and initial arsenic concentration. pH was another deciding factor and in present case acidic pH was found to be favourable. But stability of the nanoparticles at acidic pH was a problem. For an initial As(V) concentration of 0.4 mg/L, at neutral pH, a dose of 2.0 g/L of MMT/Ct/Glu was sufficient to bring down the As(V) concentration below 0.01 mg/L in 90 min. The arsenic binding process was found to be mainly due to amine functionality of chitosan, Lewis acid sites ( $Al^{3+}$ ) and Bronsted acid sites ( $AlOH_2^+$  and  $H^+$ ) on clay mineral. Hydrogen bonding, exchangeable cations and iron may also contribute in arsenate binding. The equilibrium data were fitted to both Langmuir and Freundlich adsorption isotherm. Langmuir isotherm model showed better fitting compared to the Freundlich model as judged by their equilibrium data. The pseudo second order kinetic model showed better correlation than pseudo first order model for sorption of As(V) on MMT/Ct/Glu. This chitosan based composite material could be considered as a biocompatible and bio degradable material for arsenic treatment.

In *Section 3.2* another chitosan based nanocomposite with magnetite particles (FeN) was characterized and successfully employed for arsenic remediation. The material being magnetic in nature, could be separated by using a bar magnet. Coating of FeN particles with chitosan was quite good as reflected in the TGA analysis and that also reduced the agglomeration of FeN nanoparticles which was confirmed from the SEM micrographs. The sorption of arsenic on the surface of CTN was explained by FT-IR and EDX data. The sorption of As(V) was observed to be dependent on material dose, contact time and initial arsenic concentration. For an initial As(V) concentration of 0.6 mg/L and at neutral pH, a dose of 1.0 g/L of CTN was sufficient to bring down the level of As(V) concentration to below 0.01mg/L in 120 min. Maximum removal efficiency of arsenate ions from solution was observed at a pH range of 3 to 4. Coating resulted in a long term usability of the material. From the equilibrium sorption studies, monolayer chemisorption pattern was observed at low ion concentrations but at higher concentration heterogeneity of binding surface was appeared. The pseudo second order kinetic model showed better correlation than pseudo first order model for sorption of As(V) on CTN. This type of materials can be employed as an efficient recyclable tool and are associated with least cost of energy and other materials and minimum time is required for separation of material from the treated water.

A dramatic improvement in dispersibility of TiO<sub>2</sub> particles in water was obtained on modification of TiO<sub>2</sub> particles with CTAB which was also accompanied by significant improvement in rate of arsenic removal (*Section 3.3*). Those modified particles were stabilized within starch matrix to gain an efficient recyclable material for arsenic remediation. The phase of TiO<sub>2</sub> remained unaltered during the modification or coating process. Both CTAB modified TiO<sub>2</sub> (CMT) and starch coated CMT were capable of bringing down the As(V) concentration from 400 µg/L to less than 10 µg/L. But the amount of material taken in present experiment is not sufficient in the case of Starch coated CMT nanocomposite. The successful adsorption of arsenic over the material was explained by FT-IR and EDX data. Langmuir isotherm model was found to be more fitted to the equilibrium data than the other two models which predicted a monolayer chemisorption pattern. The pseudo second order kinetic model showed better correlation than pseudo first order model for sorption of As(V) on CTN. Competition ions like phosphate and sulphate reduced the arsenate removal rate by CMT. Sorption of As(V) was found to be significant for all the materials viz.

unmodified titanium dioxide, CMT and SPC. But SPC showed the best result when efficiency, reusability and integrity all are taken under consideration. Thus, coating with starch biopolymer could convert TiO<sub>2</sub> nanoparticles into an efficient and long term usable material for arsenic treatment.

In *Section 3.4*, a combined system of aminated starch, organoclay and oxyhydroxide was utilized in trivalent arsenic remediation. Starch was aminated using ethylene diamine via grafting with GMA. Interaction among the various components and intermediates were confirmed by different characterization tools. The oxyhydroxide acted as a crosslinking agent and also took part in As(III) sorption. The different analytical tools confirmed the preparation of the material and successful sorption of As(III) over it. Amination of starch was confirmed by the appearance of new band in the FT-IR spectrum of AmS near 1565 cm<sup>-1</sup> for -NH bending vibration, and at 1169 cm<sup>-1</sup> for -CN stretching vibration. On addition of iron oxyhydroxide, a new band at 534 cm<sup>-1</sup> appeared which was due to stretching vibration of Fe-O. Incorporation of optimum amount of clay (10%) further contributed to the sorption process. Sorption of As(III) was found to be dependent on the dose of the material, contact time, initial ion concentration and greatly on temperature. The sorption process was spontaneous which was governed by a pseudo second order kinetic model. Isotherm study proved that the sorption predominantly occurred through chemical interactions and ion exchange also contributed to it as predicted by the entropy study. The sorption was an endothermic one. High negative value of  $\Delta G$  proved feasibility of the process. Further, heat of sorption i.e.  $\Delta H$  value and activation energy confirmed the chemical nature of the sorption.

In *Section 3.5*, dried biomass of Water hyacinth root powder stabilized with citric acid crosslinker was established as a novel and eco-friendly material for arsenic sorption from contaminated water. Presence of arsenic in the prepared material after treatment with arsenic water was confirmed by FT-IR study and EDX spectra. Citric acid enhanced the stability of root powder of water hyacinth while using for water treatment and thus, reduced the extra step needed to remove the unwanted turbidity. The new system was found to decrease turbidity of the treated water and improve reusability of the material in diverse experimental conditions without hampering the efficacy. The material could bring down the arsenic concentration below maximum permissible limit set by world health organization. Material dose, treatment

time, initial ion concentration and pH had immense influence on the sorption rate. The sorption followed a monolayer chemisorptions pattern as predicted by pseudo second order model. The equilibrium sorption study further supported the monolayer chemisorptions pattern of sorption. The intraparticle-diffusion model predicted that the transport of arsenic ions from solution to the surface of the adsorbent material followed a slow diffusion path to the interior of the material, which is the rate determining step. Thus, the sorption was a multistep process and diffusion was the rate determining step. Crosslinking improved the stability and decreased the turbidity of treated water. This was evidenced by reusability test.

In the last part (*Section 3.6*) another state of art material of water hyacinth root powder in combination with chitosan and stabilized with glutaraldehyde crosslinker was developed for arsenic mitigation. Preparation of the material was very simple and very good interactions occurred among the different components. The sorption of As(III) over those materials was explained by different spectroscopic tools. Moreover, those information were further supported by the theoretical study. Variation of composition of component materials significantly influenced the sorption process. Different parameters like material dose, treatment time, initial arsenic concentration, etc., also had remarkable influence on the efficacy of the prepared material on arsenic sorption. The sorption capacity of the material was found to be a function of initial arsenic concentration and increased with the increase in ion concentration. For an initial As(III) concentration of 0.4 mg/L, a material dose of 3 g/L was found to be sufficient to bring the concentration below acceptable limit. The sorption preferred a monolayer chemisorption pattern as described by Langmuir adsorption isotherm. The sorption of As(III) over the material was mainly via the different functional moiety. The findings were explained by pseudo second order kinetic model and confirmed by DFT study.

Out of all these sorbents iron based materials i.e., chitosan-magnetic composite and starch-iron oxyhydroxide composite, were found to be very efficient on the basis of adsorption capacity. Iron oxyhydroxide also showed an early equilibrium stage (60 min) for As(III) as compared to others. But the preparation was a lengthy one. Again, if the sorption capacity is compromised, then water hyacinth root powder based materials were found to be very efficient on the basis of cost, processing and reusability. For Starch-TiO<sub>2</sub> composite remarkable arsenic sorption was obtained along with

recyclability. But relative to other sorbents except iron oxyhydroxide, processing of the material was quite lengthy. Chitosan-MMT composite showed high efficiency for As(V) removal which was also proved to be useful for regeneration. Moreover, material preparation was very simple and least chemical additives were used during preparation. The material also showed relatively faster equilibrium 60 min. Chitosan biopolymer as well as MMT clay have biodegradable properties and are proved to be antimicrobial. Most importantly, as both are biocompatible and very less amount of clay was taken, hence, even small amount of material leaching, rarely will cause any harm to our body. Thus, this system can be considered as the best one if all the criteria are considered together mentioned in the objectives of the thesis. Thus, Efficiencies of most of the materials were very good, but can be further improved and conditions are needed to be optimized for implicating in practical application.

### **Future Scopes**

With continuing advancement in the fields of material science and nanotechnology, there has been a growing interest in diverse applications of nanomaterials including water purification. The nanomaterials have gained interest because of their high efficiency, ease of processing and possibility of modifications as per requirements. Work presented in the thesis attempts to provide an insight into a number of systems based on polymeric and nanomaterials which can be successfully utilized as efficient recyclable tools for arsenic removal. Still several issues remain unexplored and this work can be further extended in various directions. Most of the materials presented, showed very good efficiency for removal of arsenic from water in the concentration range (low) of interest. But there are certain concerns which can be further upgraded. e. g.,  $Q_{\max}$  values are relatively low as compared to many literatures (high initial concentrations were taken in those cases) for water hyacinth root powder and its modified forms. To improve it, parameters like particle size, temperature conditions, amount of crosslinker etc. are needed to be further optimize. Again, in many cases, the equilibrium time was quite high and required to be minimized. Also, coating with polymeric materials, although enhance the possibility of recyclability of the material, sometimes it is required to compromise the removal efficiency, what actually happened in case of starch-CMT nanocomposite. Solubility of certain polymers (although have large number of sorption sites), is a big deal for processing them in composite preparation which may be associated additional steps and high cost. Another important concern is the reusability of the prepared materials. Although, most

of the materials were found to be efficient recyclable material, but for field applications, it is required to be further modify the prepared materials so that they could have maximum stability without affecting the sorption efficiency. As the thesis was mainly focused to establish some efficient adsorbing materials, hence some other important points regarding the secondary pollutants (turbidity, leaching etc.) which may be formed during treatment of water was considered only for few cases and needed to be critically studied along with other co ions those may be present in water. Also to apply in practical applications, it is necessary to reduce the equilibrium time, sorption capacity, reduce in material loss, etc. Some of the bright scopes those can be taken under considerations are as follows-

- The size of the nanomaterials can be controlled and effect of size on removal efficiency can be studied. Sorption being a surface phenomenon, size of the sorbent will greatly influences efficiency of the material. Size can be controlled by using surfactant, other chemicals, adjusting the agitation speed, etc. during the processing of the materials.
- Influence of amount of crosslinker on removal rate can be evaluated. Amount of crosslinker may affect the size of the nanomaterials which influence the removal efficiency. Moreover, the crosslinker binds through different functional groups may affect the sorption sites. Thus, optimization of crosslinking may be required.
- The study can be extended to generate a continuous flow system for arsenic treatment from contaminated water. For that, the materials are needed to be packed within the column with the help of some supporting materials like glass beads; glass wool etc., and different experimental conditions are required to be optimized with the help of batch experiments to experience the best results.
- The study can be extended for the removal of other water contaminants also, such as fluoride, microbial and other heavy metal ions.
- For appropriate and complete understanding of the usefulness of a system it is necessary to execute it in field trial. Systems which can give satisfactory result in column test can be evaluated with some field samples which may contain some other contaminants along with arsenic.

- Leachate produced during sorption-desorption experiment needed to handle carefully. Those leachates can be converted to some less toxic form by methylation or can be dumped into construction site from where it will rarely have the chance to mix with drinking water.