Conclusions

The water pollution with toxic metal ions (Cr, Hg, Cd, Ni, As, Pb) and their removal especially in low concentrations from industrial effluents are of great concern in terms of the protection of public health and environment. The immune system is suppressed by heavy metals, leading to the increased susceptibility to disease in human as well as in animals.

To identify the problem extensive literature search was carried out and it was observed that though a lot of work has been done in the various areas of water purification, only few reported work is on removal of low concentration of heavy metal ions.

Out of the variety of materials applied for water purification, polymeric nanofibers were chosen as they have unique characteristics, such as a large surface area per unit mass, high porosity, high gas permeability, and small inter-fibrous pore size. The application of nanofibers in water purification is desirable because the high specific surface area leads to a high adsorption rate and a high adsorption capacity compared to other types of materials, such as resins, foams, and conventional fibers.

For this study two types of polymers like Chitosan and Poly-acrylonitrile were chosen to prepare electrospun composite nanofibers. Chitosan being non-toxic, biodegradable, biocompatible and natural polymeric material presents an affinity for the heavy metal ions because of its free reactive hydroxyl and amino groups. But there are some constraints because of its inefficiency, poor stability, poor mechanical properties. In case of PAN the nitrile groups with a large dipole provide high cohesive energy density and chain stiffness, which result in excellent tensile strength.
Hence chosen polymeric nanofibers were modified to improve the efficiency and stability for the removal of heavy metal ions. For removal of heavy metal ions surface effectiveness can be increased by using high surface area adsorbent due to the formation of internal pores and by modification of adsorbent’s surface by inorganic materials. Rare-earth metals like cerium, zirconium and yttrium are reported to have a high adsorption capacity. They have been successfully used in the present work to purify contaminated water and display superior performance for removing heavy metal ions.

Electrospun PVA/CHT composite nanofibers were modified by Ce (III) nitrate hexahydrate and used for removal of As (III) and Hg (II). PAN nanofibers were modified by Zirconia and used for the removal of Hg (II). PAN/Zr composite nanofibers were further modified by orthophosphoric acid and applied for the removal of lead.

Heavy metal ions such as Arsenic, Mercury and Lead have been considered as priority pollutants by the U.S Environmental Protection Agency due to their toxicity, bio-accumulating tendency. Arsenic exists in two oxidation states; As (III) and As (V) but As (III) species is more difficult to remove from aqueous solution than As (V). Mercury possesses high level of toxicity even at low dosages and even difficult to remove by conventional adsorbents reported in literature. Therefore present investigation was focused on removing these ions from aqueous solution.
PVA/CHT/Ce Composite Nanofibers

Ce loaded PVA/CHT composite nanofibers were successfully prepared by electrospinning technique. The composite nanofibers possess high surface area while they are non toxic and biodegradable. The optimized ratio of PVA and CHT to obtain uniform and bead free composite nanofibers was 7:3. The optimized Ce content in PVA/CHT blend was 3.5% (w/w) to produce uniform, continuous and beads free composite nanofibers. The kinetic study of adsorption process reveals fast and efficient removal of As (III) and Hg (II). It was observed that more than 80% removal is achieved in first 10 minutes and maximum adsorption of As (III) and Hg (II) occurs within 60 and 75 minutes respectively. The experimental data were found to follow Langmuir isotherm and adsorption capacity of composite nanofibers for As (III) and Hg (II) were calculated to be 18.0 mg/g and 31.0 mg/g respectively. The pH is observed to play an important role in adsorption process and the adsorbent works in nearly neutral pH range of 6-7. The prepared composite nanofibers (CHT/PVA/Ce) purify water within the permissible limits prescribed by WHO/EPA from initial concentration (1500 µg/L) of As (III) and Hg (II). Besides this, CHT/PVA composite nanofibers are capable of removing the ultra low concentration of both the metal ions (<100 ppb) under study. As per Langmuir isotherm maximum adsorption capacity for As (III) and Hg (II) by PVA/CHT/Ce is 18.0 mg/g and 31.0 mg/g respectively. One of the important benefits of the developed material is that it does not require any oxidizing agent unlike the conventional materials which require an oxidizing or an adsorbing agent for removal of ionic species from water. Interference study for As (III) indicates that Pb²⁺, NO₃⁻ and SO₄²⁻ ions interfere with As (III) adsorption, whereas Ca²⁺, Zn²⁺, Mg²⁺, Cu²⁺ and Cl⁻ have very low interference on adsorption of As (III) by PVA/CHT/Ce composite nanofibers. In case of multi ions solution containing the adsorption of As (III) decreases by 25–35%. The presence of Na⁺, Ca²⁺, K⁺ and Mg²⁺ water do not affect much the Hg (II) adsorption, but adsorption of Hg (II) is affected up to
10% due presence of Fe$^{2+}$ and Cl$^-$ ions present in water. Other metal ions like (Zn$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Cd$^{2+}$ and Mn$^{2+}$)spiked in water also interferes in Hg (II) adsorption. It was also observed that the developed material is regenerable and can be effectively used for three consecutive cycles. The material can also be used in remote areas where there is a shortage of electricity as the process is non-energy intensive. A mechanism has been proposed to understand the adsorption of As (III) and Hg (II) over the surface of PVA/CHT/Ce composite nanofibers which is supported by the SEM & EDAX, FTIR, XRD and XPS. In addition, this material shows good antimicrobial activity against gram positive and gram negative bacteria, S. aureus and E-coli respectively.

**PAN/Zr Composite Nanofibers**

Zirconia loaded PAN composite nanofibers were successfully fabricated by electrospinning technique. PAN nanofibers were modified with Zr content (1-5%). Up to 5%, the composite fibers were found to possess smooth morphology. On increasing the concentration of Zr beyond 5%, beads and droplets were formed during production of the fibers. The pH$_{pzc}$ of composite nanofibers was found to be in the range of (6.25-6.36). The dispersion of Zirconia nanoparticles was found to have a positive effect on the stability of PAN nanofibers. SEM analysis confirmed that Zirconia nanoparticles were uniformly distributed on PAN nanofibers and their interaction was supported by FTIR analysis. The adsorption data of Hg (II) on PAN/Zr composite nanofibers is well fitted to Langmuir isotherm. As per Langmuir isotherm, this material is very effective in removing the very low (~50ppb) concentration of Hg (II) from water. This material efficiently purifies the water containing up to 1200μg/L to the permissible limits as prescribed by WHO/USEPA. The adsorption of Hg (II) occurs in the near neutral range. During interference study of PAN/Zr composite nanofibers easily removed Hg (II) (>95%) from municipal tap water which contain (Na$^+$ &Ca$^{2+}$ up to 1000ppm, K$^+$ & Mg$^{2+}$ up to 150ppm, Fe$^{2+}$ up to 2.5ppm and Cl$^-$ up to 30.5ppm etc.). While other metal
ions such as Pb$^{2+}$, Co$^{2+}$, Cr$^{3+}$ and Zn$^{2+}$ interfere during adsorption of Hg (II). Moreover, the PAN/Zr composite nanofibers can be easily regenerated and reused for repetitive Hg (II) adsorption. Fibrous structure of material is not affected by acid treatment during regeneration process and remains stable and do not degrade after repeated use. After the adsorption of Hg (II) on PAN/Zr composite nanofibers, surface of nanofibers became little rough without affecting the fibrous structure. The adsorption of Hg (II) was confirmed by EDAX, FTIR, XRD and XPS. The adsorption of Hg (II) takes place by forming the PAN/Zr- Hg (II) complex between Zr and Hg. Another part of study conducted on removal of As removal using PAN/Zr composite nanofibers suggest that these nanofibers are not effective in removal of As.

**PAN/ZrP Composite Nanofibers**

The PAN/Zr composite nanofibers were successfully modified introducing phosphate group to obtain PAN/ZrP composite nanofibers. Initially the Zr nanoparticles were treated with ortho-phosphoric acid by using different preparation routes and it was found that route c (hydrothermal treatment) was considered as best out of three used, showing the interaction of Zirconia and Phosphate group. After that hydrothermal treatment used for the modification of PAN/Zr composite nanofibers with ortho-phosphoric acid resulted in PAN/ZrP composite nanofibers. As per results obtained by the FTIR Analysis of ZrP and PAN/ZrP composite nanofibers revealed the introduction of Phosphate group. The clear adsorption band at 1052 cm$^{-1}$ confirmed the presence of P=O linkage in composite nanofibers. The modification of PAN/Zr composite nanofibers by phosphate group resulted in PAN/ZrP composite nanofibers with rough surface due to the distribution on ZrP particles on its surface. The elemental analysis also confirmed the presence of Phosphate in PAN/ZrP composite nanofibers. XRD studies suggest the amorphous nature of ZrP distributed in PAN Matrix. The adsorption study of PAN/ZrP composite nanofibers for lead removal followed the Langmuir isotherm well as
compared to Freundlich isotherm. The maximum adsorption capacity of lead was calculated as 17.0 mg/g. Lead adsorption onto PAN/ZrP was dependent on pH due to the ion-exchange mechanism, and adsorption kinetics of PAN/ZrP composite nanofibers followed the pseudo-second order model. Moreover, it can be easily regenerated by acid solution and can be successfully reused for six cycles with 70% removal of lead. The SEM analysis revealed that after adsorption of Lead on the surface of composite nanofibers becomes rough due to intake of lead in the pores of composite nanofibers. Additionally, EDAX confirms the adsorption of Lead on to the surface of PAN/ZrP composite nanofibers. FTIR, XRD and XPS further confirm the interaction of Lead with PAN/ZrP composite nanofibers.