CHAPTER 8

Summary and Conclusion

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The effective handling of water pollutants is a thrust area of research since only one percent of the water on earth is fit for use. Conventional water treatment methods like filtration, coagulation, chemical methods, aerobic and anaerobic treatments require high operational cost, less efficient and reliable, pretreatment requirements and formation of potentially toxic by-products. The application of nanotechnology contributes significantly to environmental and climate protection by saving raw materials, energy and water and reducing greenhouse gases and hazardous wastes. The nanomaterials have high reactivity and strong sorption properties due to their unique size-dependent properties, such as incredibly large surface area and quantum confinement effect.

For the past few years, iron-based nanoparticles have been considered a cost-effective solution for environmental clean-up problems. Iron-based nanoparticles typically include zero valent iron, iron oxides and iron oxy-hydroxides. They are considered practicable and environmentally friendly materials, owing to their easy availability, relatively cheap, low toxicity and simple preparation methods. Zero valent iron (Fe^0) has a unique position among iron nanoparticles due to its high reactivity and large surface area. The successful field application of Fe^0 nanoparticles makes them an attractive area for researchers. However, the rapid oxidation and agglomeration of Fe^0 nanoparticles and toxic effects of chemicals used during the synthesis act as barriers in the development of Fe^0 based environmental remediation. Developing stable and efficient Fe^0 based nanoparticles with low secondary pollution is the key objective of all the lab-scale studies. To achieve these goals, this thesis emphasises different methods to enhance the reactivity, stability and dispersibility of the Fe^0 nanoparticles. The study also reports green synthesis methods for the preparation of Fe^0 nanoparticles.

A review of various types of nanomaterials used for the remediation of water pollutants and iron-based nanomaterials is discussed in chapter 1. The properties, synthesis and modification methods and application of Fe^0 nanoparticles are also discussed in this chapter. Chapter 2 discusses the materials used in this work and the methods followed for the batch experiments of hexavalent chromium and dye removal studies.

The enhancement of reactivity of Fe^0 nanoparticles by bimetallisation is examined in chapter 3. Fe^0 nanoparticles and catalytic metal (Cu, Ni and Zn) loaded Fe^0 nanoparticles were prepared using the liquid-phase reduction method and applied to remove toxic hexavalent chromium and organic dyes. XRD and HRTEM confirm the formation of Fe^0 and bimetallic Fe nanoparticles. Fe/Cu and Fe/Ni nanoparticles show high reactivity for the Cr(VI) and malachite green dye removal among the prepared nanoparticles. The better efficiency of Fe/Cu and Fe/Ni bimetallic nanoparticles was assumed due to the direct electron transfer, hydride formation and formation of reactive oxygen species. The reduction and precipitation of Cr(VI) were established through EDAX. The degradation mechanism for malachite green was confirmed through GC-MS/MS and LC-MS/MS analysis.

In chapter 4, Fe^0 and bimetallic Fe/Ni nanoparticles were prepared using a biopolymer, chitosan, as a stabilising agent. Chitosan reduces the particle size and agglomeration of the Fe^0 and Fe/Ni nanoparticles and provides more stability. The formation of chitosan stabilised iron-based nanoparticles were confirmed by HRTEM and XPS. The deposition of Ni on Fe^0 makes CS-Fe/Ni nanomaterials more efficient in Cr(VI) and triphenylmethane dye removal than CS-Fe nanoparticles.

Chapter 5 discussed the preparation of TiO_2-zeolite-Fe^0 composites with different percentages of TiO_2. The TiO_2-zeolite composite was prepared by sonication of ingredients followed by the hydrothermal method. The incorporation of Fe nanoparticles into TiO_2-zeolite composite was done using wet impregnation followed by the liquid-phase reduction method. The characterisation of prepared nanoparticles was done by XRD, HRTEM, FTIR, UV-visible spectroscopy and EDAX. The photocatalytic nature of TiO_2-zeolite composite reduced the oxidation tendency of Fe^0 nanoparticles and made Fe^0 active for more extended periods. Due to the synergetic effect of TiO_2, Fe^0 and zeolite, the TiO_2-zeolite-Fe composite exhibits high efficiency for Cr(VI) and malachite green removal.

Chapters 6 and 7 emphasise the reducing and stabilising property of plant extracts to prepare the Fe^0 nanoparticles. In chapter 6, two novel plant extracts from *Abrus precatorius (AP)* and *Strychnos nux-vomica (SN)* were used to prepare Fe^0 nanoparticles. Different plant components reduce the Fe^{3+} ions differently and produce Fe nanoparticles. GC-MS/MS analysis identified the volatile bioactive components present in the prepared plant extracts. The formation of iron nanoparticles was confirmed by UV-visible spectroscopy and HRTEM, and the presence of plant components in prepared nanoparticles were confirmed through FTIR. The results from the SAED pattern suggest that AP-Fe nanoparticles have a mixture of Fe^0 and Fe_2O_3 nanoparticles and the SN-Fe nanoparticles mainly have Fe_3O_4 nanoparticles. In the presence of H_2O_2, the Fe nanoparticles act as a Fenton-like catalyst to degrade malachite green dye molecules. The high efficiency of AP-Fe nanoparticles over SN-Fe nanoparticles in the removal of Cr(VI) and malachite green dye is attributed to the composition of AP-Fe.

In chapter 7, the preparation of extracts from an ayurvedic composition *Triphala* (TP) and its components such as *Terminalia chebula*, *Terminalia belerica* and *Phyllanthus emblica* was discussed. The Fe nanoparticles prepared by these plant extracts were mainly iron oxides. The SAED pattern shows that TP-Fe is mainly composed of Fe^0 and FeO and the iron nanoparticles prepared from *Triphala* components individually consist of Fe^0 and Fe_3O_4. The formation of FeO is due to the improved antioxidation property of *Triphala* composition. The prepared nanoparticles act as an excellent Fenton-like catalyst for malachite green dye removal and it also exhibits high efficiency for Cr(VI) removal.

8.1. The practical significance of our work

- We have synthesised bimetallic Fe nanoparticles to determine the most efficient bimetallic Fe composition for the Cr(VI) and dye removal. Observed that the characteristics of the incoporated second metal influence the removal efficiency of water pollutants. Fe/Ni and Fe/Cu are the most efficient bimetal combinations for Cr(VI) and dye removal. The optimum percentage of second metal loading was also verified through the batch experiment study.
- The malachite green degradation mechanism by Fe^0 nanoparticles is not studied in detail before. We have found that at the early stage, the dye degradation occurs through reduction and later the oxidative degradation mechanism has prevailed.
- The thesis also gives more information on the application of biopolymer chitosan for the stabilisation of bimetallic nanoparticles. Our synthesis method gives the smallest chitosan stabilised iron/bimetallic and iron nanoparticles compared to previous studies.
- The synthesis of different percentages of TiO_2 loaded zeolite stabilized iron nanoparticles provides a significantly efficient material for Cr(VI) removal and dye

degradation. The reason for the improved efficiency of TiO_2-zeolite-Fe composite was also discussed.

- The thesis also identified two novel plant extracts for the preparation of Fe nanoparticles and their properties were examined. The Fenton-like degradation of malachite green using phytogenic Fe nanoparticles was studied in detail.
- The preparation of novel iron nanoparticles using ayurvedic composition *Triphala* and the comparative study of iron nanoparticles prepared by *Triphala* constituents give light to the synergistic effect of plant extracts for the preparation of iron nanoparticles.

8.2. Future scope of our investigation

Different modifications have been done on the Fe nanoparticles to improve their properties. However, the selection of modified materials/methods to be carefully considered for the field application of the Fe nanoparticles. In the natural environment, different parameters such as humic acid and different inorganic solutes significantly influence the reactivity of nanoparticles. The storage stability, transportation and toxicity of the nanoparticles are also important parameters in the natural environment. Our plan is to discover the most appropriate, non-toxic, cost-effective material/method for natural environmental applications.