CHAPTER 2

Materials and Methods

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The materials and techniques used for the synthesis, applications and characterisation of iron-based nanoparticles are discussed in this chapter. Along with this, the methods used for the removal studies of Cr(VI) and dyes are also discussed.

2.1. Materials used

Chemicals	Manufacturer
• Acetone	Merck, India
• Copper sulphate pentahydrate	Sigma Aldrich
• Chitosan	Sigma Aldrich
• Demineralised water	Nice, India
• Diphenylcarbazide	Sigma Aldrich
• Hydrochloric acid	Merck, India
• Hydrogen peroxide (30% W/V)	Merck, India
• Iron(III) chloride hexahydrate	Sigma Aldrich
• Malachite green	Merck, India
• Methyl blue	Merck, India
• Methyl orange	Merck, India
• Methylene blue	Merck, India
• Nickel(II) sulphate hexahydrate	Merck, India
• Nitric acid	Merck, India
• Potassium dichromate	Merck, India
• Sodium borohydride	Sigma Aldrich
• Sodium hydroxide	Sigma Aldrich
• Sulphuric acid	Merck, India
• Titanium dioxide (nanopowder)	Sigma Aldrich
• Natural zeolite	Sigma Aldrich
• Zinc nitrate hexahydrate	Sigma Aldrich

All the experiments were conducted using pure and analytical grade chemicals that were used directly without further purification. In order to remove the water content in ethanol, the rectified ethanol was refluxed in the presence of CaO and followed by a reaction with magnesium ribbon and iodine solution. Demineralised water was used in all the experiments.

Plant materials used in this study such as *Abrus precatorius* (AP), *Strychnos nux vomica* (SN), *Terminalia chebula* (TC), *Terminalia belerica* (TB) and *Phyllanthus emblica* (PE) were collected from the local market.

2.2. Application of iron-based nanoparticles

2.2.1 Cr(VI) removal studies

The dissolved Cr(VI) ion concentration in the aqueous solution was determined spectroscopically using diphenylcarbazide as the complexing agent in acidic medium. Cr(VI) stock solution was prepared by dissolving 141.4 mg of dried $K_2Cr_2O_7$ in 1000 mL deionised water (1 mL = 50 µg Cr). The complexing agent, diphenylcarbazide, was prepared by dissolving 250 mg of 1,5-diphenylcarbazide in 50 mL acetone. After reacting with Cr(VI), the diphenylcarbazide formed a red-violet complex which was measured at an absorbance of 540 nm. 5 mg/L of Cr(VI) solution was used for the batch experiments prepared by diluting 10 mL of Cr(VI) stock solution to 100 mL. To determine the unknown concentration of the Cr(VI), a standard calibration graph was constructed using a known Cr(VI) concentration. For this, 9.5 mL of different concentrations (0 to 7 mg/L) of known Cr(VI) solution were prepared by dilution and transferred to a 50 mL beaker. To this, 0.2 mL of diphenylcarbazide was added and mixed gently. Then, 10 % H_2SO_4 was added to adjust the pH of the solution to 2 and the solution was diluted to 10 mL using demineralised water. A red-violet complex was formed within a few minutes and its absorbance was measured using a UV-visible spectrophotometer at a wavelength of 540 nm. A reference solution was prepared by the same procedure, where demineralised water was used instead of Cr(VI) solution. A calibration curve was made by plotting the absorbance against the Cr(VI) concentration.

For the Cr(VI) removal study, a specific amount of iron-based nanoparticles was added into 10 mL of Cr(VI) solution of the desired concentration. After sonication for a previously determined time, the solution was centrifuged and 9.5 mL of the Cr(VI) solution was transferred into a 10 mL vial. 0.2 mL of diphenylcarbazide was added to this

and mixed it gently. 10 % H_2SO_4 was added to get the solution with pH 2 and diluted to 10 mL using demineralised water. The solution was kept for 5 to 10 minutes for complete colour development. After measuring the absorbance, the mg/L of chromium present in the solution was determined using the calibration curve.

The effect of various parameters such as nanoparticle dosage, initial concentration of Cr(VI), initial pH of the solution and contact time were also studied for the removal of Cr(VI). The Cr(VI) removal efficiency was estimated using the formula,

$$Percentage\ of\ removal\ efficiency(\%) = \frac{C_0 - C_t}{C_0} * 100 \qquad (2.1)$$

C_0 and C_t were the initial and final Cr(VI) concentrations in the aqueous solution.

2.2.2   Dye removal studies

The dye removal efficiency of iron-based nanoparticles was evaluated using malachite green (MG) as a model dye. MG stock solution of 500 mg/L was prepared in demineralised water. The UV-visible spectrophotometer was used to determine the concentration of MG dye at a wavelength of 617 nm. The working solutions for batch experiments were prepared by diluting the stock solution. To determine the unknown concentration of the MG dye, a standard calibration graph was constructed using a known MG concentration. For this, different concentrations of MG solution were prepared by dilution and its absorbance was measured. A calibration curve was made by plotting the absorbance against the MG concentration.

In dye removal experiments, a specific amount of iron-based nanoparticles was added to a definite concentration of MG dye. After sonication for a previously determined time, the solution was centrifuged and absorbance was determined using a UV-visible spectrophotometer. The remaining MG concentration present in the solution was determined from the calibration graph. The influence of various parameters such as initial dye concentration, nanoparticle dosage, initial pH of the dye solution and contact time were also studied regarding MG dye removal. The removal efficiency of iron-based nanoparticles for MG dye removal was calculated by the formula,

$$Percentage\ of\ removal\ efficiency(\%) = \frac{C_0 - C_t}{C_0} * 100 \qquad (2.2)$$

C_0 and C_t were the initial and final concentrations of dyes in the aqueous solution.

In some chapters, the removal study of dyes methyl blue (MB), methylene blue (MLB) and methyl orange (MO) are also reported in addition to MG dye. The characteristic absorbance of MB, MLB and MO was measured at 595 nm, 668 nm and 464 nm. The procedure used for MG dye removal was followed for the other dye removal too.

2.3.   Characterisation and analytical techniques used

The prepared nanoparticles were lyophilised using Operon FDU 7003 lyophiliser for the characterisation purpose. Particle size and morphology of the prepared compounds were analysed using Jeol/JEM 2100 High-resolution transmission electron microscopy (HRTEM) and FEI Inspect S50-SEM scanning electron microscopy (SEM). Binding energies of the nanoparticles were investigated via X-ray photoelectron spectroscopy (XPS, Kratos Analytical, Ultra axis). Fourier transform infrared spectra of the compounds were investigated through Spectrum Two Fourier transform infrared spectrometer (ATR-FTIR, Perkin Elmer, USA) and SHIMADZU IR Affinity-1 in the frequency range 4000 – 600 cm^{-1}. XRD data were collected using PANalytical Aeris X-ray diffractometer using Cu Kα radiation of wavelength $\lambda = 0.15406$ nm in the scan range $2\theta = 5$ - 90º. The absorbance of the solution was measured using a UV-visible spectrophotometer (SHIMADZU UV 1800) and the UV absorbance of solid samples was done by UV-visible spectrometer UV-2600, Shimadzu, Japan. Elemental analysis and mapping of the compounds were done using energy dispersive X-ray analysis (EDAX) by Jeol 6390LA/OXFORD XMX N and Bruker Nano GmbH, XFlash detector 6/100.