Preface

In recent years, the contamination of water sources with various organic pollutants such as antibiotics and dyes has become an increasingly pressing environmental concern. most research has focused on removing single organic pollutants, leaving the study of simultaneous adsorption/co-adsorption or competitive adsorption of multiple organic compounds relatively unexplored. Simultaneously removing more than one pollutant poses additional challenges due to potential interactions between the organic compounds.

Photo-Fenton catalysis also plays a significant role in resolving issues related to pollutant removal from water because of the lower costs and environment-friendly protocols. A photo-Fenton reaction is one in which light of a suitable wavelength can generate hydroxyl radicals from H_2O_2. Nonmagnetic adsorbents and photocatalysts pose challenges in wastewater treatment due to their separation and recovery difficulties after use. Superparamagnetic nanoparticles offer a promising solution, as they can be easily separated using a magnetic field and re-dispersed through sonication, enabling efficient reuse.

In this context, the present thesis uses $NiFe_2O_4$ to design various adsorbent and photo-Fenton catalysts. Thus, the thesis deals with the synthesis $NiFe_2O_4$/GO, Mo- doped $NiFe_2O_4$, and AgI/ $NiFe_2O_4$ samples. Among these, $NiFe_2O_4$/GO and Mo-doped $NiFe_2O_4$ were utilized as adsorbent, while Mo-doped $NiFe_2O_4$ and AgI/ $NiFe_2O_4$ used as photo-Fenton catalyst. These samples were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), Vibrating sample magnetometer (VSM), Brunauer-Emmett-Teller (BET) analysis and X-ray photoelectron spectroscopy (XPS). Bandgaps were determined using solid-state UV-visible diffuse reflectance spectroscopy (UV-DRS). Mott-Schottky (MS) and Nyquist plots were generated through electrochemical studies on an electrochemical workstation.

The thesis then evaluates the adsorption and photo-Fenton activities of the prepared samples. The absorbents were used for simulation removal of organic pollutants. Adsorption kinetics and isotherms were analysed to understand the adsorption phenomenon. The photocatalysts were used to degrade TC through photo-Fenton reaction. For a better comparison of photo-Fenton activities obtained in the present thesis with studies in literature, turnover frequencies (TOF) and H_2O_2 normalized TOF (HTOF) are reported in this thesis. Simultaneously, MD simulation and DFT calculations have been made to investigate the mechanisms involved in adsorption and photo-Fenton degradation of organic pollutants. The specific objectives of this thesis are outlined below.

Chapter 1 gives a brief introduction to adsorption and photo-Fenton catalysis. Special attention has been given to explain the adsorption and photo- Fenton activity of $NiFe_2O_4$ based materials. This chapter also contains a detailed literature survey on $NiFe_2O_4$-based adsorbents and photocatalysts. The in-depth knowledge gained from this literature survey enables the framing of the scope and the objectives of the present investigation. These have been highlighted at the end of this chapter.

Chapter 2 describes the experimental specifications, including materials used, photocatalytic methodologies, and instrumentation used to characterize the photo-Fenton catalysts prepared. It also includes the basics of MD simulation and DFT study.

Chapter 3 deals with the adsorption of phenolic pollutants on the $NiFe_2O_4$ (311) surface in the presence of many water molecules by large-scale classical MD simulations. This study does not have any experimental parts. It is entirely an MD study. The results of these investigations were qualitatively compared with the experimental results available in the literature.

Chapter 4 deals with the synthesis of $NiFe_2O_4$/GO nanocomposites for the simultaneous removal of CIP and MG pollutants. XRD, TEM, VSM, BET, and XPS techniques were used to investigate different aspects of adsorbent. The point of zero charge of adsorbent was calculated by salt titration method. Extended adsorption isotherm models have been utilized to depict the nature of adsorption process. Moreover, the superparamagnetic properties of the adsorbent facilitate easy recyclability. MD simulations were performed to investigate the adsorption of CIP and MG on the surface of $NiFe_2O_4$/GO. RDF analysis depicts the interaction of different atom types of adsorbent and adsorbate molecules.

Chapter 5 investigates the hydrothermal synthesis of Mo- doped $NiFe_2O_4$ nano-adsorbent. XRD, TEM, SEM, XPS, VSM, and BET were used to characterize these nano-adsorbent. Mo doping resulted in octahedron shaped particles with the same phase composition but increased surface area. These samples were used to simultaneous remove CIP and MG from their aqueous solution. An increase in adsorption activity of Mo- doped $NiFe_2O_4$ nano-adsorbent suggested that doping alters the electronic configuration and creates new active sites on the adsorbent surface. The location of Mo dopant in $NiFe_2O_4$ lattice was investigated by DFT calculations in conjunction with XRD and XPS analysis. NBO analysis depicts the electronic change in $NiFe_2O_4$ after Mo doping. Thereafter, interaction of CIP and MG with bare $NiFe_2O_4$ and doped $NiFe_2O_4$ cluster was investigated by DFT calculations.

Chapter 6 utilizes the synthesized Mo- doped $NiFe_2O_4$ samples as photocatalyst. The nanocomposites were characterized by UV-DRS, and Nyquist plots. MS plot quantifies the charge transfer resistance and band edges of photocatalyst. The Fenton and visible light photo-Fenton activities of this doped photocatalysts were evaluated for the degradation of TC. The nanocomposite shows enhanced activity towards photo-Fenton degradation of TC. The formation of defect level below conduction band enhances the charge separation, thus results in increased photocatalytic activity. The magnetic nanocomposites show excellent recyclability. DFT and TD-DFT calculations investigate the interaction of H_2O_2 with Mo-doped $NiFe_2O_4$ in ground state and excited state.

Chapter 7 includes the precipitation protocol to synthesize AgI/$NiFe_2O_4$ heterostructure. The nanocomposites were characterized by XRD, TEM, SEM, UV-DRS, VSM, and XPS. Nyquist and MS plot confirms the formation of heterojunction. The visible light photo-Fenton activities of this unique AgI/$NiFe_2O_4$ nanocomposite were evaluated for the degradation of TC. The nanocomposite shows enhanced activity towards photo-Fenton degradation of TC. The formation of z-scheme heterojunction enhances the charge separation, thus results in increased photocatalytic activity. Moreover, the nanocomposites show excellent recyclability. Additionally, DFT and TD-DFT calculations were also performed to understand the underlying photo-Fenton mechanism.

Chapter 8 summarizes the adsorption and photo-Fenton activities of $NiFe_2O_4$ based nano- adsorbent and photocatalyst prepared as a part of this thesis. The thesis ends with a short discussion on the future scope of this work.