Preface

Catalytic oxidation processes and adsorption on active surfaces are technically and economically feasible techniques of remedying water from organic pollutants. Furthermore, the nature of reactant adsorption on the catalyst surface plays an integral role in the mechanism of heterogeneous Fenton and photo-Fenton catalysis or adsorption techniques. In this context, any catalyst or adsorbent development depends on a thorough understanding of the interfacial reaction mechanism. The latter is essential for designing effective adsorbents, Fenton, and photo-Fenton catalysts for targeted environmental remediation applications. An appropriate combination of experimental and computational investigations can shed light on vital aspects of interfacial phenomena during adsorption, heterogeneous Fenton and photo-Fenton catalysis.

Superparamagnetic adsorbents, catalysts, or photocatalysts can ensure better recyclability. A series of experimental investigations have used magnetite and magnetite-based composite as adsorbent/catalysts targeting various organic pollutants. Carbon-based economical materials like graphene oxide (GO) have also been explored for these applications. GO has a tunable bandgap, excellent mechanical stability, elasticity, and very high specific surface area. But experimentalists have not addressed the molecular interaction feature during the adsorption process.

Furthermore, research on nanocatalysis from the perspective of interfacial reaction phenomena is scarce. Effective nanoparticle surface stabilization by organic moieties or loading them on supports can enhance selective reactant adsorption and Fenton activity towards a specific organic pollutant in different pH conditions. Fenton activity depends critically on the affinity of H_2O_2 towards the catalyst surface, and appropriate stabilization or composite formation can improve this aspect. Hence, this thesis attempts to elucidate these aspects through experimental and computational studies on magnetite, GO, and magnetite-GO-based nanocomposite.

Preface

Nanomaterials prepared in the thesis were characterized by XRD, FT-IR, SEM, TEM, UV-vis, solid-state UV-DRS. Gaussian calculations were investigated from the mechanistic point of view at the B3LYP level of calculation, with different basis sets using the Gaussian 16 program. Molecular dynamics simulations were carried out on LAMMPS software. A brief description of each chapter of this thesis follows.

Chapter 1 of the thesis introduces various methods for organic pollutants removal in the water remediation process. Strong emphasis has been given to understanding the nature of adsorbate-adsorbent interaction at the molecular level during the adsorption process. It also explains the Fenton and photo-Fenton mechanisms on magnetite nanoparticles and their composites towards organic pollutants. This chapter also includes a literature survey on the adsorption mechanism based DFT studies. However, fewer molecular dynamics studies were found to explain the molecular interaction between reactants in explicit solvents at the liquid-solid interface. The scope and objectives of the present thesis have been highlighted at the end of this chapter.

Chapter 2 presents the experimental and computational procedural particulars of the research carried out in this thesis. First, it illustrates the experimental details, including the instrumentation techniques used to characterize the prepared nanomaterials. It also gives the general photocatalytic protocols followed to study the degradation of various organic pollutants investigated in this thesis. Then the chapter explains the computational methods applied in the present work.

Chapter 3 investigates the adsorption mechanism of three organic pollutants (phenol, PCP, PNP) in the presence of many water molecules on magnetite (111) surface by large-scale classical

MD simulations. Various simulation systems were constructed with varying concentrations of pollutant molecules in water. Adsorption isotherms have also been generated using density profile data of the different systems. The MD investigations are qualitatively compared with the experimental results available in the literature. The adsorption mechanism of organic molecules onto iron and magnetic iron oxide surface is predicted through RDF's generated using long-time average MD simulation data. The results also predicted the adsorbent is more specific to the considered adsorbates.

Chapter 4 deals with the synthesis of magnetite and starch functionalized magnetite nanoparticles for the Fenton degradation of PNP. The prepared samples were characterized using different techniques. Parallelly, MD simulations under NPT conditions were performed to investigate the interfacial Fenton mechanism on magnetite and starch stabilized magnetite nanoparticles. Experimental results revealed that the functionalization of starch on magnetite nanoparticles increased the rate of Fenton degradation of PNP. Simulations explained the interactions between hydrogen peroxide and PNP molecules in aqueous surroundings over the nanocluster model through RDF analysis. MD results showed that starch stabilization facilitated increased proximity of H_2O_2 molecules to the magnetite surface. The simulation methodology gives a crucial stabilizer molecule selection criterion for designing an efficient Fenton nanocatalyst.

Chapter 5 investigates the photo-Fenton degradation of orange-G dye on GO. This study was a necessary prelude to the investigation of the Fenton and photo-Fenton activities of Fe_3O_4/GO nanocomposites. Two GO samples with different degrees of oxygen functional groups were prepared by varying the modified Hummer's method. SEM, XRD, and FT-IR were used to

characterize the GO nanomaterial. Both GO materials have bandgaps in the visible range. They demonstrate significantly better activity under visible light photo-Fenton conditions than the Fenton (in the dark) reaction condition. Simultaneously, GO models with different degrees of oxygen functionalities were also constructed for DFT calculation. The HOMO-LUMO gaps of the model structures led to the GO structure most susceptible to visible light activation. TD-DFT calculations were also carried out on this GO model. Frontier molecular orbital theory was used to locate the GO model's nucleophilic and electrophilic functionalities. Then large-scale classical MD simulations in an aqueous medium determined how different reactants interacted with particular oxygen functionalities on the GO structure. Finally, the experimental and computational results were combined to shed light on some critical aspects of heterogeneous Fenton and photo-Fenton mechanisms operating on a typical GO structure

Chapter 6 explores the Fenton and visible light photo-Fenton activities on magnetite-GO nanocomposite for PNP degradation. The stepwise synthesis protocol of the composite along with its use as a Fenton and photo-Fenton catalyst for PNP degradation has been discussed. Parallely, an appropriate GO-magnetite composite model was constructed and optimized by DFT calculation. Interaction energy calculation helped define the optimized model's stability, while NBO analysis elucidated the donor-acceptor interaction between GO and magnetite. MD calculations analysis explain the position of H_2O_2 and PNP from the magnetite-graphene oxide cluster. A combination of experimental, MD, DFT, and TD-DFT evidences helped understand the mechanism of Fenton and photo-Fenton degradation of PNP over magnetite-GO nanocomposite.

Chapter 7 summarizes the present study and ends the thesis with a short discussion on the future scope of this work.