Design and Development of $NiFe_2O_4$ based Nanomaterials for Removal of Organic Pollutants from their Aqueous Solutions

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By

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Chapter – 8

Concluding remarks

8.1 Summary

This final chapter gives an overview of the thesis work. It is based on the crucial results found from the different investigations. There is a growing possibility of detecting phenolic compounds, antibiotics and dyes such as phenol, BPA, CIP and MG pollutants in our nearby water sources due to improper disposal of hospital waste, routine antibiotic use in humans and livestock, domestic washing of synthetic fabrics, and discharge from printing/textile workshops. These pollutants often enter drains that lead directly to rivers or lakes without adequate treatment, resulting in severe hazardous consequences. This thesis conducts a combined experimental and computational approach to the simultaneous adsorption of these organic pollutants by superparamagnetic $NiFe_2O_4$-based nano-adsorbents. The thesis also explores the Fenton and photo-Fenton catalytic properties of $NiFe_2O_4$-based nanomaterials through a combination of experimental and computational analyses.

In chapter 3, molecular dynamics simulations were conducted to investigate the adsorption mechanisms of phenol and BPA from aqueous solutions onto the (311) surface of $NiFe_2O_4$. This study described the different atom-type interactions (during adsorbent-adsorbate) dominating the investigated adsorption phenomena. Overall, the combined results from RDF and isotherm analyses suggest that the $NiFe_2O_4$ (311) surface exhibits a heterogeneous nature, as both phenol and BPA interact with specific active sites on the surface.

The next chapter investigates competitive adsorption CIP and MG from their aqueous solutions using magnetically recyclable $NiFe_2O_4$/GO composite. Composite formation was used to improve the adsorption performance of $NiFe_2O_4$ by loading them on GO sheets. Experimental results were combined with classical molecular dynamics simulations to understand the predominant molecular-level adsorbate-adsorbent interactions. The latter revealed the two adsorbates adsorb to distinctly different adsorption sites on the $NiFe_2O_4$/GO composite. Therefore, the simultaneous removal of two or more pollutants from an aqueous medium requires a composite adsorbent that can provide sites specific to different adsorbates.

Appropriate doping of such materials can alter their adsorption properties drastically.

Chapter 5 investigates the co-adsorption properties of $NiFe_2O_4$ nanoparticles doped with the higher valent Mo dopant. Molybdenum has higher electronegativity than Ni or Fe, which affects electron distribution in the doped material and results in different adsorption sites. DFT calculations also show that the Mo-dopant substitutes the Fe in the octahedral position of the $NiFe_2O_4$ lattice. NBO calculations indicates that substituting the octahedral Fe with the more electronegative Mo results in three adsorbent sites; one is Mo site, the tetrahedral Fe site and the oxygens coordinated to the Mo atom. Table 8.1 shows that the adsorption capacity of Mo doped $NiFe_2O_4$ was comparatively higher than $NiFe_2O_4$/GO composite for simultaneous adsorption of CIP and MG from their aqueous solution. No published reports that investigate the co-adsorption of CIP and MG from an aqueous medium solution could be found in the literature.

Table 8.1 Comparison of adsorption capacity (q_m, mg g^{-1}) of synthesized adsorbent for the simultaneous removal of CIP and MG from their aqueous solution.

Adsorbent	**q_m (CIP) (mg g^{-1})**	**q_m (MG) (mg g^{-1})**
$NiFe_2O_4$/GO	8.61	2.783
Mo doped $NiFe_2O_4$	22.70	18.95

The poor photo-Fenton properties of $NiFe_2O_4$, a magnetic material, can also be altered by appropriate metal ion doping. In this chapter, the same Mo - doped $NiFe_2O_4$ sample was used as photo-Fenton catalyst, which was used as adsorbent in previous investigation. Prior to that, it was necessary to investigate the photo-Fenton activities of bare $NiFe_2O_4$ itself. $NiFe_2O_4$ has negligible photo-Fenton TC degradation activity. Mo-doped $NiFe_2O_4$ has a reduced band gap (and the shifting of its band edges) show that the dopant Mo acts both as an electron trap and supplier, improving charge separation and carrier lifetimes during the photo-Fenton process. The photo-Fenton activities of these photocatalysts were evaluated for tetracycline (TC) degradation under cool white LED visible light irradiation. It is appropriate to highlight the use of low energy consuming 14W cool LED light source in all photocatalytic investigations of this thesis. Table 8.2 compares the TOF and HTOF values of Mo doped $NiFe_2O_4$ photo-Fenton catalyst with earlier reports on other doped photocatalysts. Moreover, DFT and TDDFT studies reveal that in the Mo-doped $NiFe_2O_4$ system, the HOMO shifts from Fe(Oct) in the ground state to Fe(Td) in the excited state. Additionally, Fe(Td) of Mo doped $NiFe_2O_4$ activates the O–O bond of H_2O_2 more effectively in the excited state, producing hydroxyl radicals. Therefore, the primary design criterion of an efficient photo-Fenton photocatalyst is that its nucleophilic center in the photo-excited state should effectively reduce H_2O_2 for hydroxyl radical generation.

In the successive chapter, DFT and TD-DFT calculations were performed and it was found that the nucleophilic center in the photo-excited state of the $AgI/NiFe_2O_4$ composite interacts effectively with H_2O_2 for hydroxyl radical generation. DFT and TD-DFT calculations showed that the HO-OH bond (in H_2O_2) showed maximum activation when H_2O_2 interacted with the $NiFe_2O_4$ part of the model of the composite in excited state. The optimum TC degradation photo-Fenton activity was observed on the 30AgINIF composite, and its TOF value is significantly higher than earlier reports on other photocatalysts. Table 8.3 shows the comparison of TOF and HTOF of $AgI/NiFe_2O_4$ photo-Fenton catalyst with earlier reports on other photocatalysts. Overall, the TC degradation TOF and HTOF of $AgI/NiFe_2O_4$ photo-Fenton catalyst is found to be the best among the two studies in this thesis. Moreover, TOF and HTOF of $AgI/NiFe_2O_4$ also appears to be the best among the TC degradation photo-Fenton studies reported in the literature.

Table 8.2 Comparison of TOF and HTOF of differently heterogeneous photocatalysts (reported) with our synthesized Mo doped $NiFe_2O_4$ photocatalysts.

Catalyst	Working Conditions	TOF (μmol g^{-1} h^{-1})	H_2O_2 normalized TOF (10^{-6} mg^{-1} h^{-1} L)	References
Surface oxygen vacancy and carbon dopant co-decorated $ZnFe_2O_4$	TCH* - 100ml of 20mg/L, Catalyst- 0.5g/L, Time- 50 min, Light Source- Xenon lamp (300W), H_2O_2-10 mM	90.63 μmol g^{-1} h^{-1}	9.06	[260]
Hollow Fe doped In_2O_3	TC- 50ml of 20mg/L, Catalyst- 0.4g/L, Time- 60 min, Light source- Xenon lamp (300W), H_2O_2-10mM	112.50 μmol g^{-1} h^{-1}	11.25	[261]
3D hierarchical Fe doped $Bi_4O_5I_2$	TC- 40ml of 20mg/L, Catalyst- 0.75g/L, Time- 80 min, light source- Xenon lamp (500W), H_2O_2-17.4 mM	42.30 μmol g^{-1} h^{-1}	2.43	[262]
Ni doped $BiFeO_3$	TC- 50ml of 10mg/L, Catalyst - 0.7g/L, Time- 120 min, Light source- 500W xenon lamp, H_2O_2- 4 mM	15.43 μmol g^{-1} h^{-1}	3.86	[264]

1MNIF	TC- 10mg/L, Catalyst- 0.1mg in 3ml of TC solution, Time- 130 min, Light source- Cool white LED, H_2O_2-16.13 mM	309.991 µmol g^{-1} h^{-1}	19.22	**Our work (Chapter 6)**

Table 8.3 Comparison of TOF and HTOF of differently heterogeneous photocatalysts (reported) with our synthesized $AgI/NiFe_2O_4$ photocatalysts.

Catalyst	**Working Conditions**	**TOF (µmol g^{-1} h^{-1})**	**H_2O_2 normalized TOF (10^{-6} mg^{-1} h^{-1} L)**	**References**
Fe-g-C_3N_4/Bi_2WO_6	TC- 10mg/L, Catalyst- 0.4g/L, Time- 120 min, Light Source- Xenon lamp, H_2O_2-1mM	10.57 µmol g^{-1} h^{-1}	10.57	[296]
$MnFe_2O_4$/bio-char	TC-40mg/L, Catalyst- 0.5g/L, Time- 90 min, light source- Xenon lamp (300W), H_2O_2-100mM	111.603 µmol g^{-1} h^{-1}	1.12	[298]
Ce_4O_7 modified Bi_4MoO_9	TC-10mg/L, Catalyst- 0.4g/L, Time- 300min, Light source-5W white LED, H_2O_2-3mM	28.07 µmol g^{-1} h^{-1}	9.36	[299]
(FeNi-LDH)/Ti_3C_2	TC- 20mg/L, Catalyst - 0.2g/L, Time- 90 min, Light	142.055 µmol g^{-1} h^{-1}	7.11	[300]

	source- 300W xenon lamp, H_2O_2- 20mM			
30AgINIF	TC- 10mg/L, Catalyst- 0.1mg in 3ml of TC solution, Time- 100 min, Light source- Cool white LED, H_2O_2-16.13 mM	401.9 μmol g^{-1} h^{-1}	24.92	**Our work (Chapter 7)**

8.2 Future scope of this work

The future scope of this work points out the following aspects.

- The scale-up experiments will be conducted involving more than two organic pollutants to further evaluate the practical applicability of the $NiFe_2O_4$/GO composite and Mo doped $NiFe_2O_4$ adsorbents for their potential implementation in industrial-scale wastewater treatment.
- The simultaneous removal of metals and anions from aqueous medium should also be investigated using these adsorbents.
- The comparative adsorption and Fenton/ photo-Fenton activity of $NiFe_2O_4$ stabilized by other macromolecules (such as metal / covalent organic framework, biomaterials, 2D materials having high surface area etc.) should also be investigated.
- Reactive MD studies can further be carried out on $NiFe_2O_4$ based catalyst surface to uncover all potential reaction pathways and intermediates, providing valuable insights into the underlying mechanisms of photocatalysis.
- Electrochemical studies of previously prepared adsorbents and catalysts can be investigated.