SYNTHESIS OF IRON(II) DOPED COPPER FERRITES AS NOVEL HETEROGENEOUS PHOTO-FENTON CATALYSTS

Theses of the doctoral (PhD) dissertation

By:

Engr. Asfandyar Khan

Supervisors:

Prof. Dr. Ottó Horváth, DSc

Dr. Zsolt Valicsek, PhD

Doctoral School of Chemical Engineering and Material Sciences

Research Group of Environmental and Inorganic Photochemistry

Center for Natural Sciences

University of Pannonia

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1. Introduction and aim of the research

Rapid growth in the global population leads to urbanization and industrialization, which has increased the demand for clean water, resulting in a water crisis. More water consumption leads to both a considerable increase in water pollution and a perceptible decrease in energy resources. Major water pollutants comprise certain organic and inorganic compounds, such as textile dyes and pigments, finishes, personal care products, pharmaceuticals, pesticides, herbicides, and some heavy metals (lead, nickel, mercury, silver, cadmium, etc.), which can be traced in the underground and surface water resources.

Various photocatalysts have been discovered and utilized in purification processes, and, among them, TiO_2 has been widely studied in eliminating some detrimental compounds from wastewater. The major limitation of TiO_2 in heterogeneous photocatalysis is its lower activity under visible-light irradiation due to its high band-gap energy. Hence, the researcher's attention has been diverted towards the synthesis of heterogeneous catalysts which can work under visible light, in a wider pH range, at low operating cost, with better performance, and are easy to separate after usage. Many metal oxides based on Cu, Fe, Zn, etc. were explored to overcome the limitations posed by TiO_2. Heterogeneous, ferrite-type catalysts can be applied in photo-Fenton, electro-Fenton, and photo-electro (PE) Fenton processes, and they can be reused many times under visible-light irradiation. For example, cobalt ferrites doped with nickel, zinc ferrites, aluminum doped zinc ferrites, and copper ferrites were successfully used for photocatalytic degradation of several dyes and other pollutants (e.g., nitroaromatic compounds). Few among them have antibacterial activity, too. According to these observations, doped, composite-type ferrites seem to exhibit better catalytic potentials than undoped ones.

Wastes from the textile, food, and leather industries contain extremely colored species which are toxic to humans and marine ecosystems. Methylene blue (methylthioninium chloride), a cationic dye in nature, exhibits numerous uses in the field of textile dyeing/printing, biology, and chemistry. There are hundreds of other hazardous organic compounds such as congo red, Rhodamine B, and several azo dyes, etc. are used in various textile industries. The removal of these compounds is crucial for the safety of living organisms.

According to a deep investigation of the published literate in the area of ferrites, no study has been reported about the synthesis of iron(II)-doped copper ferrites ($Cu^{II}_{(x)}Fe^{II}_{(1-x)}Fe^{III}_2O_4$) and their photocatalytic applications; therefore, the main aim of my research was the synthesis, characterization, and application of iron(II)-doped copper ferrites as novel catalysts for the degradation of Methylene blue (MB) and Rhodamine B (RhB) as model compounds. In addition, the simple oxides of the given metal ions, such as $Cu^{II}O$, $Fe^{II}O$, and $Fe^{III}_2O_3$, were also synthesized and investigated in heterogeneous photo-Fenton system individually as well as their simple composite ($Cu^{II}O/Fe^{II}O/Fe^{III}_2O_3$ without the common calcination to form ferrite).

2. Experimental methods

Iron(II)-doped copper ferrite nanoparticles (NPs) were synthesized with systematic alteration of the ratio of Cu^{2+} and Fe^{2+} in the composition given as $Cu^{II}_{(x)}Fe^{II}_{(1-x)}Fe^{III}_2O_4$ (where x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 for NP-1, NP-2, NP-3, NP-4, NP-5 and NP-6, respectively). NPs were synthesized by using a simple co-precipitation method. In this method, solution I was prepared by adding $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$, and $CuSO_4$ salts to 20 mL distilled water in stoichiometric amounts and sonicated for 30 min at room temperature, while solution II was 5 M NaOH (20 mL), which acted as precipitating agent. Solutions I and II were mixed together dropwise and were continuously homogenized by using a magnetic stirrer for 60 min. The dark precipitates obtained were filtered, dried, and calcined. In addition, simple metal oxides were prepared in a similar way for comparisons.

The final powdered catalysts were characterized by using Raman spectroscopy, X-ray diffractometry (XRD), scanning electron microscopy (SEM) combined with energy dispersive spectroscopy (EDS), inductively coupled plasma (ICP), Brunauer–Emmett–Teller (BET), and diffuse reflectance spectroscopy (DRS). Absorption spectroscopy was used for monitoring the photocatalytic degradation of MB and RhB under visible-light irradiation.

3. New scientific results

A) The synthesis of iron(II)-doped copper ferrites NPs with alteration of the ratio of Cu^{2+} and Fe^{2+} in the composition given as $Cu^{II}_{(x)}Fe^{II}_{(1-x)}Fe^{III}_2O_4$ (where x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 for NP-1, NP-2, NP-3, NP-4, NP-5 and NP-6, respectively) via simple co-precipitation technique as novel heterogeneous Fenton catalysts were characterized and their photocatalytic applications were investigated. Simple metal oxides ($Fe^{II}O$, $Cu^{II}O$, and

$Fe^{III}_2O_3$) were also prepared to compare their corresponding features to those of the doped ferrites.

I) The particle size investigation confirmed that NPs were of submicrometer size, predominantly in the 70–200 nm range, which was favorable for the preparation of homogeneous aqueous dispersions.

II) XRD confirmed that NPs exhibit inverse spinel structure: metal ions with +2 charge (Fe^{2+} or Cu^{2+}) are in octahedral position, while the half of the Fe^{3+} ions are in tetrahedral one. This structure does not change during the substitution of Cu(II) ions to Fe(II) in the iron(II)-doped copper ferrites. This is confirmed by the very slight change in the main peak at about 35 deg (2θ) in the XRD diffractograms. The Raman spectra of NPs also confirmed the inverse spinel structure. The vibrations under 600 cm^{-1} correspond to the M–O bonds at the octahedral sphere. Only one band belongs to the metal ions with tetrahedral coordination sphere—the symmetric stretching at 610 cm^{-1} (ν_s(M–O), E_g symmetry).

III) SEM confirmed the morphological changes occurred as a consequence of increasing Cu^{2+} ratio (x), the structure of NPs significantly changed from spherical (NP-1) to needle-like, embedded into clusters, in the case of NP-2 and NP-3. NP-4 formed larger needles on the surface, while NP-5 and NP-6 have some needle like crystals along with hexagonal crystals originating from a secondary nucleation. The EDS confirmed that major part of NPs were composed of Fe, Cu, and O, while some impurities in the form of Na and Cl were also present in some cases.

IV) An increase in the Cu^{2+}: Fe^{2+} ratio resulted in lower band-gap energies. NP-1 showed higher E_{bg} of 2.02 eV (613 nm), while NP-6 much lower E_{bg} of 1.25 eV (995 nm). It confirmed that copper ferrites may be able to harvest the energy of near infrared light in a photocatalytic system, too.

B) After successful structure elucidation of NPs, I investigated the photocatalytic performance of doped and simple metal oxide NPs, using two organic model compounds; Methylene blue (MB) and Rhodamine B (RhB) in photo-Fenton systems.

I) In the case of MB, the efficiency of six doped copper ferrites were analyzed at various reaction conditions. NP-3 proved to be the most efficient photocatalyst in the series studied. On the basis of the experiment, the optimized values for the reaction conditions such as catalyst dosage, hydrogen peroxide concentration, and pH were determined to be 400 mg/L, 1.76×10^{-1} mol/L, and 7.5, respectively. The total disappearance of the UV-visible spectra of MB confirmed the complete removal of the dye from the aqueous medium.

II) Also, in the case of RhB, NP-3 proved to be the most efficient photocatalyst in the series studied. The optimized values of the reaction conditions such as catalyst dosage, hydrogen peroxide concentration, and pH were determined to be 500 mg/L, 8.88×10^{-2} mol/L, and 7.5, respectively.

C) To confirm the reusability and stability of catalysts at optimized reaction conditions, I checked NP-3 from the series of doped metal ferrites and simple metal oxide composite ($Fe^{II}O$, $Cu^{II}O$, $Fe^{III}_2O_3$) for reusability in photocatalytic applications.

I) Under five cycles of reusability experimental series, NP-3 and the composite ($Fe^{II}O$, $Cu^{II}O$, $Fe^{III}_2O_3$) showed an increase in the reaction rate up to the third cycle, as the consequence of the potential degradation of initial impurities on the active sites of photocatalysts. A slight decrease in the fourth and fifth cycles could be attributed to the loss of the catalyst between the cycles.

II) The leaching of metal ions into the solution was lower than 1%, confirmed by ICP and spectrophotometric measurements.

D) To compare the photocatalytic performance of simple metal oxides, doped (NP-3) and the composite of the metal oxides ($Fe^{II}O$, $Cu^{II}O$, $Fe^{III}_2O_3$), all these catalysts were applied in photo-Fenton system under similar reaction conditions, using MB and RhB as model compounds.

I) Using MB as model compound, the following sequence for reaction rate was observed: NP-3 > ($Fe^{II}O$, $Cu^{II}O$, $Fe^{III}_2O_3$) > $Cu^{II}O$ > $Fe^{III}_2O_3$ > $Fe^{II}O$. This decreasing tendency may be attributed to higher degree of agglomeration and comparatively larger crystallite sizes.

II) A similar sequence was observed for the use of RhB as model compound: $Cu^{II}O$ > ($Fe^{II}O$, $Cu^{II}O$, $Fe^{III}_2O_3$) > NP-3 > $Fe^{III}_2O_3$ > $Fe^{II}O$. The small differences may originate from the lower band-gap energy and highly crystalline structure.

III) On the basis of comparison studies, it can be confidently concluded that NP-3, composite of metal oxides ($Fe^{II}O$, $Cu^{II}O$, $Fe^{III}_2O_3$) and $Cu^{II}O$ alone have strong degradation potential for organic compounds.

E) The antimicrobial activity of doped copper ferrites and simple metal oxides were investigated in a bioluminescence inhibition assay. It was proved that all simple metal oxides and all doped copper ferrites exhibited more than 60% antimicrobial property against the gram negative bacterium *Vibrio fischeri* in the bioluminescence inhibition assay.

Scientific publications and presentations related to the dissertation

A) Publications

I) **Khan, A.,** Valicsek, Z., and Horváth, O., "Synthesis, characterization and application of iron (II)-doped copper ferrites ($Cu^{II}_{(x)}Fe^{II}_{(1-x)}Fe^{III}_2O_4$) as novel heterogeneous photo-Fenton catalysts". Nanomaterials. 2020, 10, 921. (IF = 4.32)

II) **Khan, A.,** Valicsek, Z., and Horváth, O., "Comparing the degradation potential of copper(II), iron(II), iron(III) oxides, and their composite nanoparticles in heterogeneous photo-Fenton system ". Nanomaterials. 2021, 11, 225. (IF = 4.32)

III) **Khan, A.,** Valicsek, Z., and Horváth, O., "Photocatalytic degradation of Rhodamine B under heterogeneous and homogeneous systems" 2021. (Accepted for publication in the Hungarian Journal of Industry and Chemistry).

B) Publications from other research works

I) Jiang, H., Hu, X., **Khan, A.,** Yao, J., and Tahir Hussain, M. (2020). "Dyeing mechanism and photodegradation kinetics of gardenia yellow natural colorant," Textile Research Journal, vol. 91(7-8), pp. 839-850, 2021. (IF = 1.90)

II) K. Iqbal, **Khan A.,** Sun D., Ashraf M., Rehman A., Safdar F., *et al*., "Phase change materials, their synthesis and application in textiles – a review," The Journal of The Textile Institute, vol. 110, pp. 625-638, 2019. (IF = 1.26)

III) **Khan, A.,** Nazir, A., Rehman, A., Naveed, M., Ashraf, M., Iqbal, K., *et al.*, "A review of UV radiation protection on humans by textiles and clothing," International Journal of Clothing Science and Technology, vol. 32(6), pp. 869-890, 2020. (IF = 0.90)

C) Scientific conferences/posters

I) **Khan, A.,** Valicsek, Z., and Horváth, O., Photochemical degradation of Methylene blue and Rhodamine B under heterogeneous photo-Fenton system using $Cu^{II}_xFe^{II}_{1-x}Fe^{III}_2O_4$ ferrites, 6th International Conference on Photocatalytic and Advanced Oxidation Technologies for the Treatment of Water, Air, Soil and Surfaces (NPM-5/PAOT-6), Szeged – Hungary, May 24-27, 2021.

II) **Khan, A.,** Valicsek, Z., and Horváth, O., Synthesis and photochemical reactions of iron(II) doped copper ferrites as heterogeneous catalysts, Proceedings of the 4th World Congress on Civil, Structural, and Environmental Engineering (CSEE'19), Rome, Italy – April, 2019.

III) **Khan, A.,** Valicsek, Z., and Horváth, O., An approach towards synthesis of novel heterogeneous catalysts and their application for degradation of hazardous dyes, The Chemical Engineering Conference, University of Pannonia, Hungary – April, 2019.

IV) **Khan, A.,** Valicsek, Z., and Horváth, O., Photochemical degradation of Rhodamine B under heterogeneous photo-Fenton system, PhD students day, University of Pannonia, Hungary – December, 2019.

V) **Khan, A.,** Valicsek, Z., and Horváth, O., Synthesis of novel $Cu^{II}O$, $Fe^{III}_2O_3$, and $Fe^{II}O$ nanoparticles via co-precipitation method and comparison of their photocatalytic properties, International scientific conference on water and wastewater treatment in the industry, Zalakaros – Hungary, October 10, 2019. Organized by University of Pannonia Soós Ernő Water Technology Research and Development Center.

VI) **Khan, A.,** Valicsek, Z., and Horváth, O., Photochemical degradation of methylene blue under heterogeneous photo-Fenton system, Central European Conference on Photochemistry, CECP Bad-Hofgastein, Austria – February, 2020.