Response to Referee Report on PhD Thesis

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

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I heartily appreciate and thank the reviewer for his worthy comments during the first review, which helped me a lot in the preparation of the final version of the PhD dissertation for public defense. My responses to the current questions of the official referee report are discussed here point by point.

Question 1: Is there a standardized photochemical degradation experiment? What are the proper controls of these experiments? Is there any way to compare the results from different photodegradation experiments? How do you think your photo-Fenton system performed as compared to other heterogeneous systems?

Answer: There is **no** standardized photochemical degradation experiment reported in the literature up to date. However, in most of the heterogeneous systems, various sets of experiments have been made to investigate the individual effects of several **important parameters**, which are:

I) Photo-induced degradation of model compound
II) Adsorption of the model compound on the catalyst surface
III) Addition of oxidant to the system (for Fenton type systems)
IV) Combined effect of catalyst and oxidant on the degradation of model compound
V) Combined effect of light and oxidant on the degradation of model compound
VI) Finally, the combined effect of light, catalyst, and oxidant on the degradation of the model compound. The results of step (V) and step (VI) are compared, which reveals the potential efficiency of the catalyst in these systems.

In this study, all these important parameters were explored in the start of the research work using both model dyes.

Besides this, the **proper controls** during these experiments are the type and intensity of irradiation source, temperature, irradiation time, pH, initial concentration of the pollutant, catalyst dosage, and the dosage of Fenton reagent [1, 2]. A powerful irradiation source, temperature range of 20 – 80 °C, and lower initial concentration of the pollutant are favored to complete the photocatalytic degradation in a shorter time. However, the pH of the system depends on the type of catalyst and pollutant because it influences the surface-charge-properties of the photocatalyst and affects the ionic species in the solution [3, 4]. In the heterogeneous systems, using ferrites as the catalysts, various pH ranges were investigated and several studies revealed better efficiencies at neutral and alkaline pH, similar to this research work. The catalyst dosage in the range of 100 to 1000 mg/L was studied and various optimum dosages were concluded.

In the literature, researchers concluded that the catalyst dosage, pH of the reaction mixture, and oxidant dosage are the **three major determinants** in such heterogeneous Fenton type systems [5]. Thus, in this research work, these three determinants were deeply established.

The results from different photodegradation experiments **can be compared when the same experimental assembly and reaction conditions are applied**, only changing the type of catalyst. Each individual reaction condition has a significant effect on photocatalysis and small changes can influence the reaction. I compared the photocatalytic results of different catalysts, i.e., doped copper ferrites (NP-3) and metal oxides, by keeping other reaction conditions constant.

This photo-Fenton system performed very well and resulted in the 100% degradation of both model compounds in almost half of the allocated experimental time (140 min). The results are **comparable and even better** than those of several studies, e.g., the methylene blue degradation under visible light irradiation using aluminum-doped cobalt ferrite (500 mg/L) [1] and cobalt substituted zinc ferrite [6]. The oxidation of a mixture of methylene blue + rose bengal (>95%) by applying zinc ferrite nanoparticle (500 mg/L) [7] under visible light irradiation was also published. In addition, the results of this photo-Fenton type system are also comparable to the study reported by Soltani and Entezari [8], where they observed the complete degradation of methylene blue by applying bismuth ferrites nanoparticle (500 mg/L) under visible light induced irradiation (90 min). Also, our rhodamine b degradation results obtained at optimum conditions were comparable to nickel ferrites [9] and Ce-doped copper ferrites [10] under heterogeneous photo-Fenton systems.

Moreover, the optimized reaction conditions in this research work are more efficient and resulted in faster degradation of both model dyes.

Question 2: Discuss the applicability of your photo-Fenton system in industry. How can the presented photo-Fenton system be scaled up to industrial application? One aspect to practical use of such heterogeneous photo-Fenton process is the amount of catalyst. In my view, the working range of absorbance (in spectrophotometry) set a limit to the concentration of the photocatalyst during the model experiments presented in the thesis. How would you discuss the useful concentration values of the catalyst or other important parameters in real applications?

Answer: This type of photo-Fenton system should be highly applicable in the industry because of the following pros.

I) The synthesis of the catalyst using co-precipitation and calcination technique is very easy, cheap, and facile even for large-scale industrial applications.

II) Next, the pH control during photocatalysis will also be very easy because of the natural alkaline pH of the textile industry wastewaters. Most of the textile industries use reactive, direct, and basic dyes which need alkaline pH for the application on textile substrates. In such conditions, the wastewater is alkaline and doesn’t need the addition of extra alkali for pH control. Thus, it would be a cost-effective process in comparison to the lab-scale experimental design, where NaOH was added to adjust the pH.

III) Visible light irradiation is cheap and easily applicable for industrial use. Also, this type of reactions can be performed in the open air under solar light-induced reactors.

IV) These magnetic catalysts can also be easily separated by sedimentation and filtration, and reused for several photodegradation cycles. Also, they are stable in such reaction conditions with less than 1% leaching of metal ions into the solution.

The presented photo-Fenton system can be easily scaled up to the industrial application, especially in the wastewater of the textile industry. Dyeing and printing is usually the last step involved in the chemical processing of textile substrates and the wastewaters are full of toxic species at this stage. So, the liquor containing the toxic species can be sent to the next plant, where the catalyst, oxidant and irradiation source are provided. The complete degradation of dyes may need more time due to its slightly higher concentration and the presence of other auxiliaries during dyeing.

The model experiments presented in this dissertation and thesis are lab scale. For instance, the earlier published results confirmed these optimized reaction conditions may be applicable on the industrial scale too. Jaafarzadeh *et al.* [11] reported that the catalytic efficiencies of magnetite nanoparticles prepared by co-precipitation technique in the lab-scale and real textile wastewaters were comparable. They observed a slightly lower efficiency of the catalysts in the treatment of real textile wastewater. In addition, their lab-scale reaction conditions, such as catalyst dosage, oxidant concentration, and pH, were applicable for the treatment of real textile wastewater.

Therefore, the important parameters investigated in this research work should be usable in real industrial applications.

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