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 the worthy reviewer for providing a comprehensive review on my PhD dissertation/thesis, which helped me a lot in the compilation of the final version. The analytical techniques were performed by the concerned laboratory experts. Although, I was present at the time of SEM, EDS, XRD and DRS investigations. Moreover, the results from all these techniques were evaluated by the candidate. The responses to the specific questions are given below point by point.

Specific questions

Question 1: You have used mainly "relative degradation efficiencies" to characterize the efficiency of the catalysts. Although, in this way, if the selected reference catalyst has inferior performance, then the performance increment can reach more than 1000% (but, in reality, can degrade just e.g. 10% of the contaminant vs. the 1% efficiency of the control). In extreme cases, if the control has an efficiency of ≈0%, the enhancement will be close to infinite. Why have you used this way to characterize these efficiencies instead of the classic definition/presentation of yields?

Answer: I would like to clarify that the relative degradation efficiency was calculated by dividing the initial reaction rate constant of the sample experiment by that of control experiment.

For example, the efficiency of the control experiment at the optimum conditions using methylene blue was calculated as follows;

% efficiency = initial rate constant of the control / initial rate constant of the control

= $(1.06 \times 10^{-4}\ s^{-1}) / (1.06 \times 10^{-4}\ s^{-1})$ = **100%**

The efficiency of the control experiment can never be 0% in this method because it is the ratio of two similar numbers, as we can see in the case of MB in Figure 25 {Spectral change during Methylene Blue degradation in photocatalytic system containing NP-3 (x = 0.4). The inset shows the absorbance vs. time plot at λ_{max}=665 nm. Concentrations: MB = 1.5×10^{-5} mol/L, NP-3 = 22.73 mg/L, initial pH = 7.5, H_2O_2 = 1.01×10^{-2} mol/L, temperature = 25±2 °C and irradiation time = 140 min.} and in Table 5 {Control experiments for MB degradation. Concentrations: MB = 1.5×10^{-5} mol/L, NP-3 = 22.73 mg/L, H_2O_2 = 1.01×10^{-2} mol/L, temperature = 25±2 °C and irradiation time = 140 min.}. Moreover, in the case of RhB in Figure 38 {Spectral change during Rhodamine B degradation in photocatalytic system containing NP-3 (x = 0.4). The inset shows the absorbance vs. time plot at λ_{max}=554 nm. Concentrations: RhB = 1.75×10^{-5} mol/L, NP-3 = 400 mg/L, initial pH = 7.5, H_2O_2 = 1.76×10^{-1} mol/L, temperature = 25±2 °C and irradiation time =140 min.} and in Table 6 {Control experiments for RhB degradation. Concentrations: RhB = 1.75×10^{-5} mol/L, NP-3 = 400 mg/L, H_2O_2 = 1.76×10^{-1} mol/L, pH = 7.5, temperature = 25±2 °C, and irradiation time = 140 min.}

Similarly, the catalytic efficiency for sample NP-3 at optimum conditions, using methylene blue, was calculated as follows;

% efficiency = initial rate constant obtained in NP-3 experiment / initial rate constant of the control without catalyst

= $(5.19 \times 10^{-4}\ s^{-1}) / (1.06 \times 10^{-4}\ s^{-1})$ = **489%**

The addition of catalysts to the system will always give you a % value either higher or lower than the control values.

This way of the characterization of the catalysts in the heterogeneous system is much easier to implement and investigate the performance of each reaction condition. That's why this technique was applied in this study instead of the presentation of yields.

Question 2: Regarding the BET results: you say that the catalyst consisting primarily of spherical and small needle-like structures have a lower surface area compared to the samples

with larger needles. Was there any evaluation about the ratio of spherical/needle-like structures of the NP1-3 samples?

Answer: NP-1 (Figure 1) was mainly composed of spherical-like structure and no other morphology was observed. From NP-2 onwards, as the consequence of addition of Cu^{2+}, the morphology changed to needle-like structures. NP-2 (Figure 2) and NP-3 (Figure 3) were totally needle-like, which can be confirmed from the SEM images, where no other morphology was observed. The brightness in the images was observed due to the potential charging while SEM investigations.

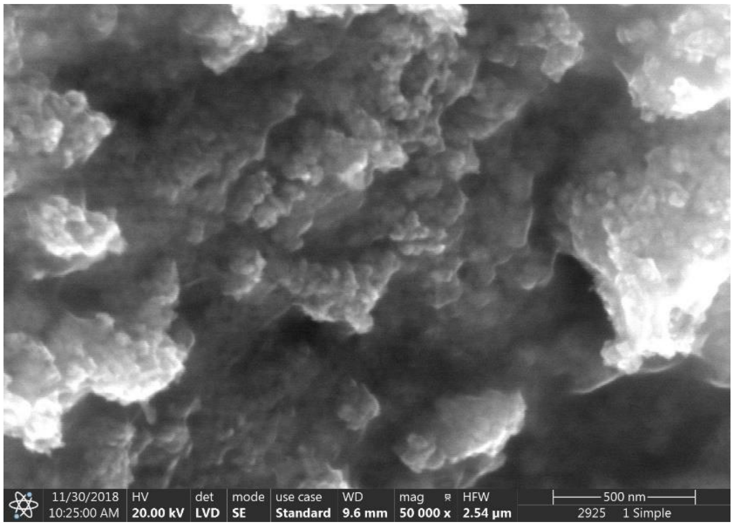

Figure 1. NP-1 showing spherical-like morphological structure

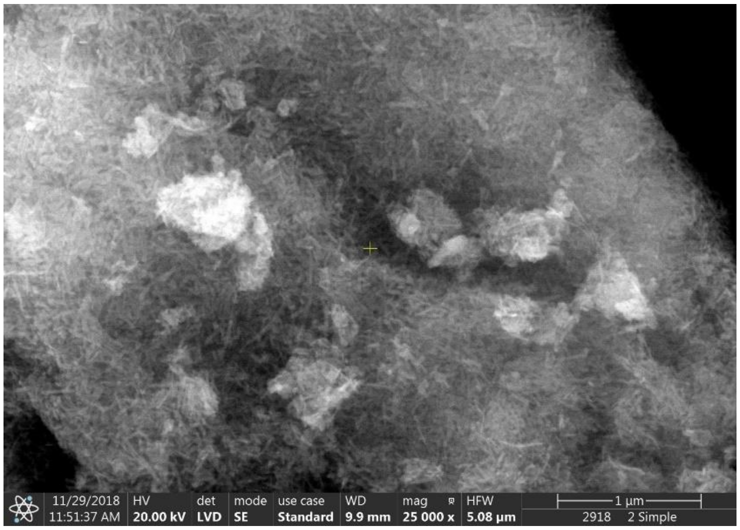

Figure 2. SEM image of NP-2 showing needle-like morphological structure

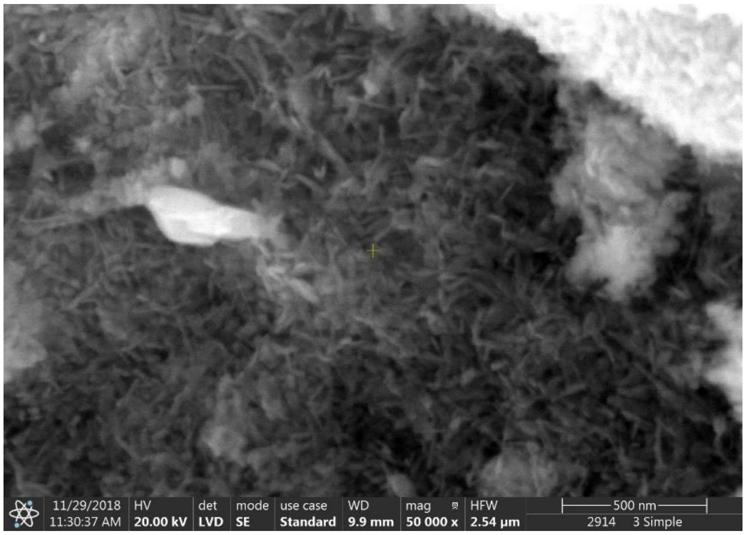

Figure 3. SEM image of NP-3 showing needle-like morphological structure

Question 3: The specific surface area values and the band gap values have a “linear” enhancement in the range of samples NP1-NP6 (the value of SSA increases from NP1 to NP5/6, while the band gap values are decreasing). Although, in term of relative degradation efficiencies (fig 32), the samples NP2-3 were proved to be the best photocatalyst. How can you explain this (apparent) contradiction between these results? (as usually it is said, that the high SSA and low band gap values are benefic for high photocatalytic efficiencies).

Answer: This is true that specific surface area and band-gap energy are directly related to the photocatalytic efficiency of the catalysts. In this study, NP-2 and NP-3 showed best results, which can be attributed to their special and smaller needle-like morphology. In addition, their band-gap energies were enough to absorb visible light irradiation in this heterogeneous photo-Fenton system. In the conclusion of all photocatalytic results, it is clear that this special needle-like morphological feature of NP-2 and NP-3 is the determining factor of their higher efficiencies.

Question 4: How can you explain that compared to the conventional Fenton systems (which are usually performing better at lower pH), your system showed better performance at high pH values?

Answer: The conventional photo-Fenton system produces hydroxyl radicals (Equation (1) and (2)) in the pH range of 2.8 – 3.5, which proceeds the degradation of contaminants present in the reaction mixture [1].

$$Fe^{3+} + H_2O + h\nu \longrightarrow Fe^{2+} + {}^{\bullet}OH + H^{+} \tag{1}$$

$$Fe^{2+} + H_2O_2 \xrightarrow{\qquad} Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (2)$$

When the pH is increased towards neutral, the Fe(III) produced in Equation (2) forms Fe(III)-complexes, which precipitates and settle down in the reaction mixture in the form of inactive sludge [2]. For pH values above 4 the degradation strongly decreases as Fe(III)-complexes rapidly precipitate and thus, the regeneration of Fe(II) is reduced [3]. Thus, the cyclic reaction between Fe(II) and Fe(III) is hindered and the efficiency of the Fenton system is diminished.

In contrast, under a heterogeneous photo-Fenton system, surface catalyzed reactions take place, which promote the degradation of model compounds. In the literature, Guo *et al.* [4] reported the application of sphere-like copper ferrites in the photo-Fenton degradation of methylene blue as a model compound. They investigated the pH of the system in the range of 1.1 to 13.0, and observed an increasing trend in the degradation efficiency (similar to this PhD study). They claimed that the surface of copper ferrites have a negative charge at alkaline pH [4]. Thus, the cationic dye, e.g., methylene blue, is attracted towards the catalyst surface, where it is subsequently degraded. Soltani and Entezari [5] also observed a higher photocatalytic activity of bismuth ferrite nanoparticles for the degradation methylene blue at pH value 11-12 [5].

In this PhD study, higher photocatalytic activities were observed in the case of both model compounds.

Question 5: Which is the equation for the trendline shown in Fig. 33? (if there is not a defined equation then you should not use this option).

Answer: The equation of the trendline shown in Figure 33 is polynomial of order 4. However, the equation was not added because the main purpose was to show the increasing trend for the ease of the readers. The polynomial equation is; $y = -1\times10^{-9}x^4 + 2\times10^{-6}x^3 - 1.5\times10^{-3}x^2 + 4.4\times10^{-1}x^1 - 35.327$ and the regression is $R^2 = 9.0\times10^{-1}$.

Question 6: How can you detail the mechanism proposed about the attachment of copper-based nanoparticles? How can this behaviour be compared to the literature?/are there any references investigating the antibacterial effect of similar nanomaterials?

Answer: A similar mechanism about the attachment of copper-substituted cobalt ferrite ($Cu_xCo_{1-x}Fe_2O_4$) nanoparticles on the surface of drug resistant *E. Coli* was reported in the literature by Samavati and Ismail [6]. The bactericidal potency of these nanoparticles was enhanced with increasing the Cu content. A similar mechanism was reported by Raffi *et al.* [7] using copper ferrite nanoparticles against *E. Coli*, where the catalysts adhere to the surface of bacteria and penetrate through the cell membrane. Thus, the bacterial cell wall is destroyed and the cytoplasm is degraded, which ultimately causes cell death [7, 8]. In addition, the antibacterial activity of copper ferrite hollow fibers and Ag–$CuFe_2O_4$ fibers explored against several bacteria, revealed the synergistic effect of the presence of silver on the activity [9].

In these studies, the presence of Cu content was proven to enhance the antibacterial property of the nanoparticle and a similar trend was observed in this PhD study.

Question 7: How can you explain the unusual behavior/effect of different concentrations of H_2O_2 on the degradation of MB, presented in Fig. 29?

Answer: This unusual behavior occurred due to the potential scavenging effect of $^{\bullet}OH$ radicals by the present excess of hydrogen peroxide. This effect was reported by Dutta et al. [10] using CI Reactive Red 2 dye. High concentration of H_2O_2 is known to act as self-scavenger for $^{\bullet}OH$ radicals to produce perhydroxyl radical $HO_2^{\bullet}$ which is less active than hydroxyl radical [11]. $HO_2^{\bullet}$ radical can be terminated into H_2O and O_2 via the interaction with the $^{\bullet}OH$ radical species [10, 12]. Another study focused on UV-assisted degradation of Reactive Yellow 14 azo dye also revealed a similar behavior of hydrogen peroxide [12].

In this PhD study, using MB, an increase in the reaction rate of degradation was observed by the increase of H_2O_2 concentration up to 3.9×10^{-2} mol/L. However, further increase in the H_2O_2 concentration inhibited the MB degradation reaction rate, which are in agreement with earlier published results.

Question 8: In Chapter 4.6, it is observed that the NP-3 has its best performance around 3-4 cycles. How can you explain this (the increase compared to the first cycle and the decrease after the 4th cycle)?

Answer: The increase in the photocatalytic activity in the first 3-4 cycles may be due to the increasing availability of the active sites for photodegradation. This may be attributed to the dissolution of some residues of materials which were used for the synthesis and remained on the surface of the catalyst particles, covering active sites. However, the decrease after 4th cycle may be attributed to the saturation of the available active sites by the adsorbed organic species (reactants and intermediates) in the mixture. The major causes of the decrease in the photocatalytic activity reported in literature are depositions onto the catalyst surface, poisoning of the catalyst by compounds formed during oxidation, accumulation of intermediates formed during various dye degradation process, and the leaching of catalysts into aqueous medium [13, 14].

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