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MAGNETIC NANOPARTICLES FOR BISPHENOL A DEGRADATION**

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## PHOTO-ACTIVATION OF PERSULFATE AND HYDROGEN PEROXIDE BY HUMIC ACID COATED MAGNETIC NANOPARTICLES FOR BISPHENOL A DEGRADATION

N.P.F Gonçalves<sup>a</sup>, M. Minella<sup>a</sup>, D. Fabbri<sup>a</sup>, P. Calza<sup>a</sup>, G. Mailhot<sup>b</sup>, M. Brigante<sup>b</sup>, A. Bianco-Prevot<sup>a</sup>

<sup>a</sup>Department of Chemistry, Università di Torino, Torino, Italy

<sup>b</sup>Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-Ferrand, France

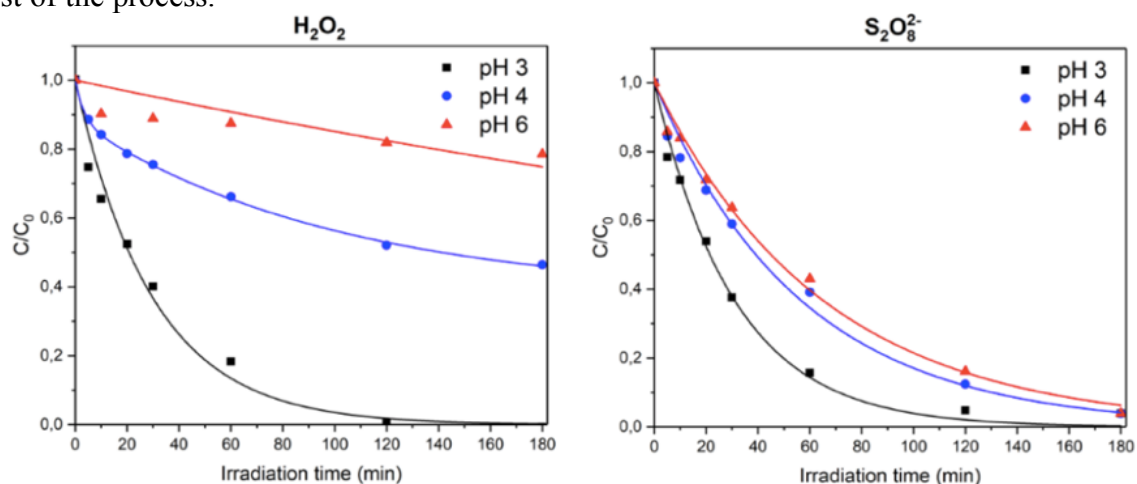
Among the advanced oxidation processes (AOPs), Fenton, photo-Fenton and Fenton-like have been attracting wide attention to degrade recalcitrant organic pollutants in water (Richardson and Ternes, 2018) for environmental remediation due to its ability to generate highly reactive species (Mirzaei et al, 2017). In the “classic” Fenton process, the highly reactive species, mainly hydroxyl radical ( $\bullet\text{OH}$ ), are generated by the reaction between Fe(II) ions and hydrogen peroxide. The reaction strongly depends on the pH: the pH has to be adjusted to the optimum of 3 and subsequently it has to be neutralized, with sludge formation and increase of the overall cost of the process (Minella et al., 2018). In the heterogenous Fenton and photo-Fenton reactions the  $\text{H}_2\text{O}_2$  is activated by iron supported in a solid matrix at acidic or even circumneutral pH. Due to its advantages on the catalyst recovery and reuse, avoiding the sludge formation and significantly simplifying the process, the heterogenous conditions have been exploited (Deng and Zhao, 2015; Minella et al, 2014).

Similarly to the hydroxyl radical, the sulfate radical ( $\text{SO}_4^{\bullet-}$ ) has a high oxidation potential, being investigated for oxidation of recalcitrant pollutants (Waclaweka et al, 2017). The activation of persulfate ( $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$ ) to generate the sulfate radical can be promoted by reaction with iron both in the dark or under irradiation. Additionally, the persulfate is described as less subject than hydroxy radical to constituents of the real water samples, presenting potential higher selectivity for organic molecules (Avetta et al, 2015). Considering its low cost and high reactivity, the activation of  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$  by heterogeneous iron-based catalysts is raising growing interest in water treatment for emerging contaminant abatement (Ike et al, 2018; Avetta et al, 2015). Due to the complex reaction system, the mechanism behind these heterogeneous processes has not been fully assessed yet, and it is worth to be studied in deeper details.  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles (MNPs) have been investigated as iron-source due to their advantages such as high catalytic activity, negligible toxicity, low-cost, facile recovery and recycling by means of a magnetic field (Fragoso et al, 2017).

Bare  $\text{Fe}_3\text{O}_4$  MNPs are susceptible to air oxidation and aggregation in aqueous systems. As previously reported, the stabilization with organic coating can reduce the oxidation of the magnetic phase (magnetite/maghemite) to hematite. Additionally, the introduction of humic-like substances, in both Fenton and photo-Fenton processes appears to significantly enhance the pollutant degradation capacity. Even though the effective role played by humic-like substances in the oxidation mechanism has not been already fully solved (Carlos et al, 2012).

In this study, humic acid coated  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles ( $\text{Fe}_3\text{O}_4/\text{HA}$ ) prepared by co-precipitation method under controlled conditions, were tested for  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$  activation under UVB irradiation in aqueous media using bisphenol A (BPA) as a model pollutant. Both processes, with  $\text{H}_2\text{O}_2$  and persulfate, are compared and the involvement of reactive species during the degradation pathways was determined through kinetic competition experiments using selective quenchers. The role of HA coating on the reactive species activation is also

explored comparing the BPA abatement obtained when using the pristine magnetite, at different pH. The obtained results clearly indicate that the humic coated nanoparticles give better results.  $\text{Fe}_3\text{O}_4/\text{HA}$  in the best experimental conditions allowed to achieve significant BPA abatement for both  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$  systems. Moreover, very promising results were obtained when treating real sewage treatment plant waters. The possibility of recovery the catalyst by means of a magnetic field and reuse it without losing efficiency for the BPA degradation rate was confirmed. Significant BPA degradations were observed with persulfate also at pH higher than 3 (up to pH 6) as shown in figure 1, allowing to envisage significant contraction of the overall cost of the process.



**Figure 1.** Bisphenol A degradation photo-catalyzed by  $\text{Fe}_3\text{O}_4/\text{HA}$  MNPs at different pH in the presence of  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$  under UVB irradiation.

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