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Efficient activation of peroxymonosulfate by using ferroferric oxide supported on carbon/UV/US system: A new approach into catalytic degradation of bisphenol A

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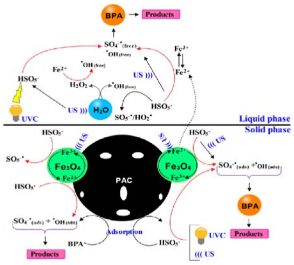
GRAPHICAL ABSTRACT



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ABSTRACT

In the present research, a new method of sulfate radical-based advanced oxidation process was developed for the degradation of bisphenol A (BPA). In this regard, magnetite nanoparticles supported on carbon (MNPs@C), as a heterostructure catalyst was combined with UV light and ultrasound (US) irradiation to efficient activate peroxymonosulfate (MNPs@C/UV/US/PMS). Several parameters affecting the degradation efficiency including pH, reaction time, different concentrations of catalyst, BPA and PMS, US power and water matrix components were studied. BPA degradation rate was considerably enhanced when US and UV irradiations were applied simultaneously with MNPs@C for activate PMS. A possible oxidation mechanism and reaction pathway for BPA degradation was proposed. Under optimized conditions, complete removal of BPA was obtained while the mineralization degree was only 56.4%. Toxicity tests with activated sludge demonstrate that MNPs@C/UV/US/PMS system could be improved the biodegradability of the solution. The quenching experiments proved that both $^{\cdot}OH$ and $SO_4^{\cdot -}$ radicals participate significantly during the degradation of BPA and sulfate radicals were dominant species. The MNPs@C also show a high synergistic effect (42.6%) on the BPA degradation in the presence of the other used agents during MNPs@C/UV/US/PMS system. I_{OUR} decreased substantially after 60 min treatment, confirming the toxicity of intermediates eliminated by process. The catalytic performance in degrade BPA was decreased at the presence of anions follows the order of $HCO_3^- > H_2PO_4^- > NO_3^- > SO_4^{2-} > Cl^-$. Cycling tests indicate the MNPs@C was reusable to activate PMS for degrade BPA for six consecutive cycles and the removal efficiency still remains at 95.2%. Overall, these

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results reveal that the activation of PMS by MNPs@C/UV/US system is an efficient and promising advances oxidation technology for the treatment of BPA-contaminated waters and wastewaters.

1. Introduction

In recent decades, advanced oxidation processes (AOPs) have attracted great interest among environmental researchers in the field of water and wastewater purification. High efficiency for destruction of persistent organics, enhancing biodegradability potential, reduction of the toxicity and high capability in mineralization are known as the most essential benefits of AOPs. They are apparently more beneficial than the conventional wastewater treatment methods, due to their non-selectivity and high redox potential of the free radicals on degradation of recalcitrant contaminants [1,2]. Among AOPs, heterogeneous catalytic processes (HCPs) using metal-containing solids have been proven to be the most effective remediation approach for degradation of recalcitrant hazardous compounds in water owing to their advantages such as lack of sludge production, no requirement to neutralization of treated water, recyclability and stability of transition metals, and cost-effectiveness [2,3]. HCPs have also been introduced as green environmental technologies, due to low leaching transition metals, which not generate secondary pollution in water [4,5]. In this regards, magnetic catalysts containing metal oxides (Fe_2O_3 and Fe_3O_4, etc.) have been widely applied, because of having high reusability potential and ability of easily and quickly separation from aquatic environments [6–9].

On the other hand, $SO_4^{-\cdot}$ radical-based AOPs shows promising results for degradation of non-biodegradable organics, due to not only slow application of precursor oxidant, but also high redox potential of $SO_4^{-\cdot}$ radicals. $SO_4^{-\cdot}$ radicals, compared to $^{\cdot}OH$ radicals ($E^0 = 1.8–2.7$ v), are more selective for destruction of aromatic molecules, higher oxidation potential ($E^0 = 2.5–3.1$ v), and also possesses a longer half-life [2,7]. They are mainly generated via activation of either persulfate (PS, $S_2O_8^{2-}$) or peroxymonosulfate (PMS, HSO_5^-). Since the degradation process of organic compounds has been carried out in a more efficient way compared to PS as well as favorable performances in destruction of pollutants, lots of researchers have focused their attentions on the application of PMS in HCPs, as a green and promising oxidant [10]. Over the last decades, the activation of PMS has been performed by UV and ultrasound (US) irradiation, thermal, electrochemistry method, non-metal or carbon-based catalysts and with transition metal ions, and satisfactorily applied by researchers for the treatment of water pollutants [5–7]. The reactions related to the decomposition of PMS into $SO_4^{-\cdot}$ radicals can be described by the equations below (Eqs. 1–8):

$$HSO_5^- + h\nu \rightarrow SO_4^{\cdot -} + \cdot OH \qquad (1)$$

$$HSO_5^- +))) \rightarrow SO_4^{\cdot -} + {}^{\cdot}OH \qquad (2)$$

$$HSO_5^- + \text{heat} \rightarrow SO_4^{\cdot -} + {}^{\cdot}OH \qquad (3)$$

$$HSO_5^- + AC \rightarrow SO_4^{\cdot -} + HO^- + AC^+ \qquad (4)$$

$$HSO_5^- + AC \rightarrow {}^{\cdot}OH + SO_4^{2-} + AC^+ \qquad (5)$$

$$M^{n+} + HSO_5^- \rightarrow SO_4^{-\cdot} + M^{n+} + OH^- \qquad (6)$$

$$M^{n+1} + HSO_5^- \rightarrow SO_5^{-\cdot} + M^{n+} + H^+ \qquad (7)$$

$$HSO_5^- + e_{CB-} \rightarrow SO_4^{\cdot -}{}_{(ads)} + OH^- \text{or} {}^{\cdot}OH + SO_4^{2-} \qquad (8)$$

Recently, various combinations, in form of hybrid systems, have been applied for enhancing decomposition rate of PMS molecules as convenient approaches in the degradation of organic substances. In previous research, PMS have been activated via some these agents either single or simultaneous. Heterogeneous transition metals (Fe-Co/SBA-15 along with US [11], Fe_3O_4 and US [7], $CuFeO_2$ [12], $CuFe_2O_4$ [13], CuO-Co_3O_4@MnO_2 [14], magnetic Mn-MGO [15]), metal-free heterogeneous catalysts (sulfur-doped carbon nitride (CNS) [5]), UV/photolysis only [16,17], Fe^{2+} with UV [18], carbon-based materials [19–23], Co^{2+} coupled with US [24], samarium doped ZnO (Sm/ZnO) with US [25], heat/thermolysis [26] are some PMS activators employed in the literature to produce $SO_4^{-\cdot}$ radicals. According to the performed studies, it can be concluded that the decomposition rate of PMS and consequently generation of $SO_4^{-\cdot}$ radicals have enhanced considerably when over one activator applied simultaneously. In this way, the additional production of $SO_4^{-\cdot}$ in system could improve effectively catalytic performance. Although integration of some of these activators has been presented promising findings, the simultaneous utilization of several activators might be an effective approach for achieving the maximum mineralization degree.

For this purpose, this research studied the combination of several agents (i.e., heterogeneous catalyst (activated carbon (AC) and Fe_3O_4 nanoparticles), UV and US) simultaneous for the efficient activation of PMS, as first report for the degradation of refractory organic matters. Herein, magnetite nanoparticles (Fe_3O_4, MNPs) supported on AC was prepared and employed as a heterogeneous catalyst for some convincing reasons. First, both AC and MNPs have a remarkable potential in the activation of PMS, so their integration would be a very effective approach. Second, the removal performance of process enhanced significantly via adsorption of both target pollutant and oxidant, due to high surface area and adsorption capacity of AC. Third, uniformly deposition of MNPs on AC surface may overcome some MNPs drawbacks such as strong tendency to agglomerate, slow degradation rate, low catalytic capability, and low surface/volume ratio. In addition, MNPs possesses octahedral sites containing Fe^{2+} ions which can react with PMS to produce $SO_4^{-\cdot}$. Also, it is well known that MNPs are non-toxic, inexpensive, stable physiochemical structure and easily recyclable. Meanwhile, coupling US and UV with AOP's systems result in additional formation of strong oxidizing radicals and subsequently increase the catalytic degradation reaction rate. Removal efficiency may be significantly improved by UV irradiation, due to the regeneration of Fe^{2+}, which promotes the production of additional strong oxidizing radicals efficiently. US in solution phase is not only capable of decreasing mass transfer limitations, but also can provide a clean and reactive surface for catalyst thereby removing the products from the catalyst surface.

Nevertheless, up to know, no research has been reported on UV/US-assisted heterogeneous activation of PMS for degradation of organic matters. Hence, the most principal objective of this work is integration of magnetic heterogeneous catalyst (MNPs@C) with UV and US irradiations as PMS activators in order to enhance the degradation of bisphenol A (BPA) as a model organic pollutant. To the best of our knowledge, this is the first study on BPA degradation by this system. The BPA degradation efficiency by means of MNPs@C/UV/US/PMS was evaluated affected by different key operational parameters including the catalyst loading, PMS and BPA concentrations, ultrasonic power and co-exiting ions. The recyclability, durability and mineralization degree were also examined. A possible mechanism for activate PMS and BPA degradation was also proposed to deepen the understanding of system.

2. Materials and methods

2.1. Synthesize and characterization of catalysts

In this study, both MNPs and MNPs@C catalysts were prepared using in-situ chemical co-precipitation of Fe^{2+} and Fe^{3+} under an