Scientific Research Publishing

The Role of Metal-Doped into Magnetite Catalysts for the Photo-Fenton Degradation of Organic Pollutants

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Abstract

Recently, the incorporation of transition metals into magnetite increasing the heterogeneous Fenton catalytic activity of magnetite with high efficiency and interesting magnetic properties applied for degradation of organic pollutants in water purification and wastewater treatment have attracted more and more researchers. In this review, using of one or some metal doped magnetite based systems in heterogeneous Fenton, or photo-Fenton processes are discussed. Then, the role of metal doped species for the enhanced efficiency of degradation process is presented. Finally, possible reaction mechanism for the photo-Fenton degradation pollutants in the present of metal doped magnetite is also given.

Keywords

Transition Doped Metal, Metal Doped Magnetite, Photo-Fenton, Role of Doped Metal

1. Introduction

The rapid global economic growth has resulted in clean water crisis and environmental pollution since industrial revolution. Literature indicates an increasing trend in generation of wastewaters with recalcitrant characteristics from the many activities of industrial societies [1]. A large number of these pollutants are toxic in nature even at micro quantities [2]. Wastewaters containing these compounds are known to be high in chemical oxygen demand (COD) and low in biological oxygen demand (BOD). These non-biodegradable molecules enter the environment predominantly from mainly industrial activities [3].

Currently, there are various of methods to deal with these issues such as:

bio-method, chemical-physical method and so on. However, traditional biological methods can effectively treat wastewaters with high biodegradability ratio ($BOD_5/COD \geq 0.4$). In many industries, conventional treatment technologies cannot even produce effluents that meet water quality criteria and effluent limitation guidelines for recalcitrant pollutants [4]. In addition, traditional treatment techniques only succeed in contaminants transfer from liquid phase to solid phase which can cause second pollution. To effectively treat recalcitrant effluent, the scope should encompass degradation as well as mineralization of organic contaminants. That is conversion of probe molecule to its highest stable oxidation state: water, carbon dioxide, and the oxidized inorganic anions of any heteroatoms present, mainly to inorganic acids; or to more easily degradable molecules, that can be easily removed biologically.
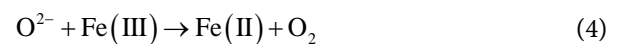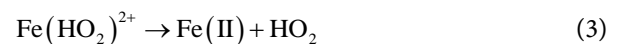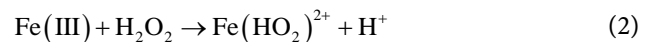
Accordingly, advanced oxidation processes (AOPs) are considered as powerful methods for degradation of these pollutants due to their ability for removing almost any organic contaminant [5]. AOPs are considered as water treatment processes at near ambient temperature and pressure that produce very active radicals for degradation of pollutants [6]. In water/wastewater treatment, AOPs generally refer to a group of processes that cover O_3 and H_2O_2 as oxidants with assistance of light, catalyst (e.g. Fe^{2+}, Fe^{3+} and TiO_2), ultrasonic insertion and/or thermal input and there are several combinations such as Fenton (H_2O_2/Fe^{2+}), photo-Fenton ($H_2O_2/UV/Fe^{2+}$), peroxidation combined with Ultraviolet light (H_2O_2/UV), Peroxone (O_3/H_2O_2). These oxidation processes are cost effective technologies and give rise to non-selective active species that oxidize a wide variety of non-biodegradable compounds [7]. AOPs have been used at various scales for overall organic content (COD) reduction, specific pollutant destruction, sludge treatment, increase of bioavailability of recalcitrant organics, destruction of micropollutants and color and odour removal [8] [9]. However, there are some disadvantages for the application of the traditional homogeneous Fenton and photo-Fenton process, including the requirement of low pH, a significant amount of ferric hydroxide sludge formed in the course of homogeneous Fenton treatment, high leaching ion iron in solution and difficult to separate catalyst after reaction [10]. The heterogeneous photo-Fenton reaction can solve the problem of eliminating and reusing e from the reaction system at the end of the process, but the separation of the solid phase is still a remaining issue [11]. The separation problem is even more important in the case of oxide nanoparticles, which are potentially more reactive because of the favorable surface-to-volume ratio. From this point of view, the fact that magnetite undergoes very easy magnetic separation from aqueous systems makes it a very interesting material to be tested for photo-Fenton reactivity. Recent studies demonstrate that magnetite is the most effective heterogeneous Fenton, photo-Fenton catalyst as compared to other iron oxides, possibly because it is the only one that has Fe^{2+} in its structure to enhance the production rate of OH radical [12]. Moreover, its interesting magnetism leads it easy to be separated from the reaction system

[13]. More recently, it is reported that the introduction of Mn, Zn, Ni [14], Cr [15], Ti [16] into magnetite structure may strongly promote the Fenton, photo-Fenton degradation of organic contaminants due to a significant promotion of H_2O_2 decomposition.

In this work, we give a mini review about using of some currently metal doped magnetite based systems in heterogeneous Fenton, or photo-Fenton processes for degradation of pollutants. Then, the role of metal doped species for the enhanced efficiency of degradation process is discussed. Finally, possible reaction mechanism for the photo-Fenton degradation pollutants in the present of metal doped magnetite is also given.
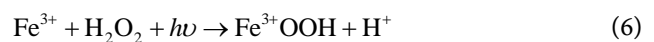
2. Fenton Process

In 1894, French scientist J. H. Fenton found that the oxidation ability of H_2O_2 has been greatly increased when Fe^{2+} catalyse H_2O_2 given the acid conditions (pH: 2 - 5). It is called Fenton reaction and the acid solution is called Fenton reagent [17]. It is clear nowadays that the hydroxyl radical ($\bullet OH$) which has strong oxidation ability is caused by the compound of Fe^{2+} and H_2O_2 [18]. The oxidation potential of hydroxyl radical ($\bullet OH$) is well known with 2.80V which is merely lower than that of F_2. The hydroxyl radical ($\bullet OH$) can destroy structure of organic synthesis because of strong oxidation. The fact make it possible that environmental pollutants can be degradated which can't often be done by other general methods. The mechanisms of generating $\bullet OH$ in Fenton reaction are as follows [12]:
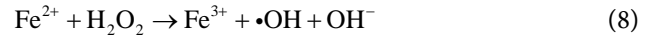
$$Fe(II) + H_2O_2 \rightarrow Fe(III) + \bullet OH + OH^- \tag{1}$$

$$Fe(III) + H_2O_2 \rightarrow Fe(HO_2)^{2+} + H^+ \tag{2}$$

$$Fe(HO_2)^{2+} \rightarrow Fe(II) + HO_2 \tag{3}$$

$$O^{2-} + Fe(III) \rightarrow Fe(II) + O_2 \tag{4}$$

$$\bullet OH + H_2O_2 \rightarrow HO_2 + H_2O \tag{5}$$

Thus $\bullet OH$ is formed from hydrogen peroxide when either Fe(II) or Fe(III) is present. The existence of $\bullet OH$ radicals in Fenton reaction has been proven by monitoring the fluorescence intensity changes [19].

3. Photo-Fenton Process

Heterogeneous photo-Fenton process is combination of Fenton reagents (H_2O_2 and Fe^{2+}) and UV-Vis radiation ($\lambda < 600$ nm) that gives rise to extra $\bullet OH$ radicals by two additional reactions. One is the photoreduction of Fe^{3+} to Fe^{2+} ions as shown and another is the peroxide photolysis via shorter wavelengths as the following equations [20]:

$$Fe^{3+} + H_2O_2 + h\upsilon \rightarrow Fe^{3+}OOH + H^+ \tag{6}$$

$$Fe^{3+}OOH \rightarrow Fe^{2+} + OOH \tag{7}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \tag{8}$$

$$Fe(OH)^{2+} + h\upsilon \rightarrow Fe^{2+} + \cdot OH \tag{9}$$

$$H_2O_2 + h\upsilon \rightarrow 2\cdot OH \tag{10}$$

The photo-Fenton process was reported as more efficient than Fenton treatment. In some cases, use of sunlight instead of UV irradiation reduced the costs [21]. However, this offers a lower degradation rate of pollutants. Acidic conditions (about pH 3) were also reported to be favorable and this may be mainly due to the conversion of carbonate and bicarbonate species into carbonic acid, which has a low reactivity with hydroxyl radicals [22].

In the case of conductor catalyst, the reaction mechanism can be proposed as following:

$$Catalyst + h\upsilon \rightarrow Catalyst\left(e_{cb}^-, h_{vb}^+\right) \tag{11}$$

$$e^- + H_2O_2 \rightarrow \cdot OH + OH^- \tag{12}$$

$$e^- + Fe^{3+} \rightarrow Fe^{2+} \tag{13}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \tag{14}$$
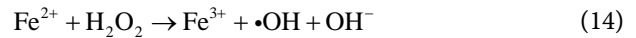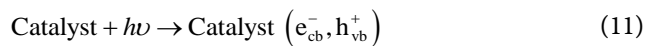
Regenerated Fe^{3+} will take place the reaction to form Fenton reagents leading to more •OH can be produced [23] as showed in **Figure 1**.

4. Metal Doped Fe₃O₄ Based Catalysts

It is recently reported that Fe_3O_4 is the effective heterogeneous Fenton, photo Fenton catalyst for removal contaminants in wastewater treatment [24]. The magnetite ability to promote photo-Fenton reactions even under circum neutral pH conditions, the limited iron leaching and its easy magnetic separation makes magnetite a promising catalyst in wastewater treatment applications. In addition, magnetite can be synthesized in the laboratory by various biotic and abiotic
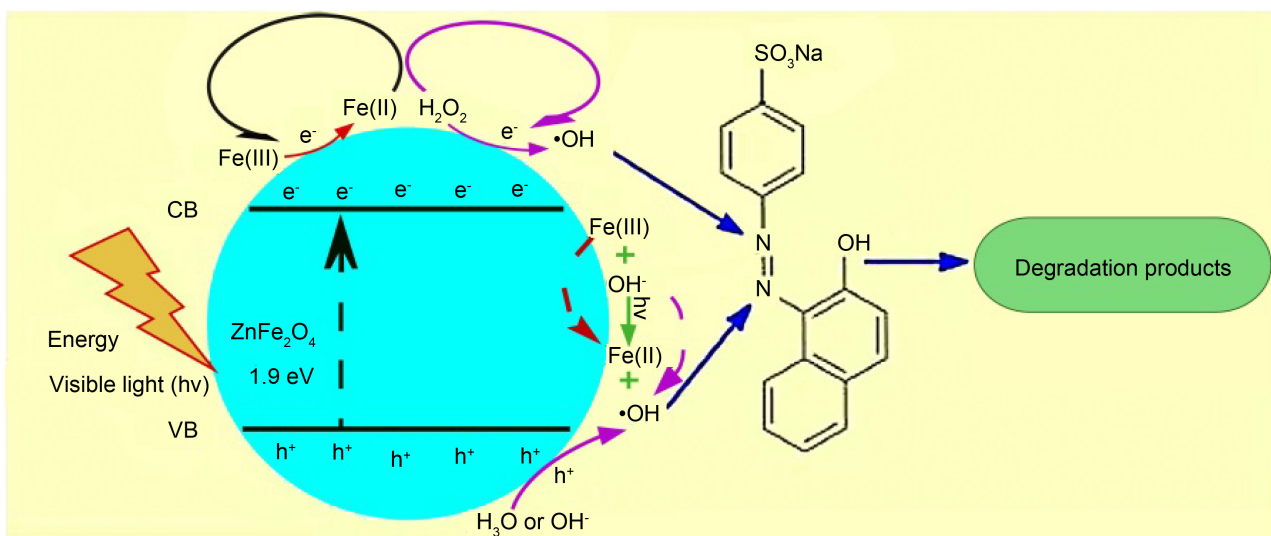

Figure 1. Proposed mechanism of Vis/ZnFe₂O₄/H₂O₂ system [23].

pathways. Abiotic procedures to form magnetite include co-precipitation of soluble Fe (II) and Fe (III) species, oxidation of hydroxylated Fe (II) species and ferric oxides trans-formation. The morphology, crystallography and specific surface area of natural or synthetic magnetite can be controllable synthesized with vary widely route. There are many ways for fabrication of magnetite nanoparticles, such as the hydrothermal route [25], ball mill method [26], polydiallyl-dimethylamonium chloride method [27], co-precipitation, emulsion method [28], solvothermal [29], etc. For example, iron oxide nanoparticles, with size ranging from 50 to 100 nm, were synthesized by a solvothermal method [11]. The samples with magnetic properties consisting of magnetite (Fe_3O_4), or by a mixture of magnetite and maghemite (γ-Fe_2O_3), and samples with no magnetism consisting of hematite (α-Fe_2O_3) can be obtained by a simple route of adjusting precursor materials. The catalytic activity of the materials was studied for the degradation of diphenhydramine using the photo-Fenton process. The results showed that complete degradation of diphenhydramine with 78% of mineralization was achieved at relatively low leaching of iron species from the catalyst to the aqueous solution (1.9 mg·L^{-1}) with magnetite catalysts (**Figure 2**).

However, using magnetite in the Fenton, photo-Fenton processes are still limited due to its drawbacks such as a low relative magneticity, poor dispersibility, limited adsorption properties, and low catalytic activity [30] [31]. To come out some of disadvantages of pure magnetite, amount of routes has studied extremely as synthesis with controllable size, morphology, shaped or composite with other materials or non-metal or metal doping. In these routes, metal element doping is reported to be a promising approach due to interesting properties of products.

4.1. Metal Doped Fe_3O_4 Based Catalysts for Fenton, Photo-Fenton Degradation

Recently, studying on metal doped magnetite based catalyst has paid more and
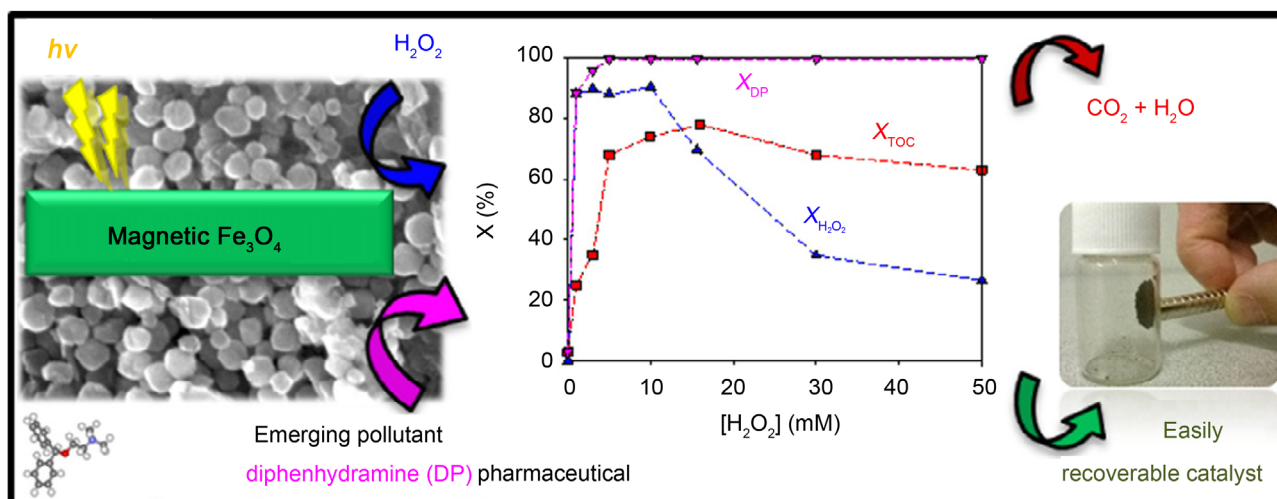

Figure 2. Using magnetite in the photo-Fenton degradation of diphenhydramine [11].

more attention of researchers. Based on the previous reports in this filed, it is can be seen that the introduction of Co, Cr [32], Ti, Zn and Mn into magnetite structure may strongly promote the Fenton, photo-Fenton degradation of organic contaminants due to a significant promotion of H_2O_2 decomposition. Our previous report showed Zn doped magnetite has higher capacity in the photo-Fenton degradation of cephalexin and rhodamine B compared to pure magnetite. Hongping Hea *et al.* have prepared substituted magnetite with chromium via a simple precipitation-oxidation method. The applicability of series of substituted magnetite as Fenton catalyst in the degradation of cationic (MB) and anionic (acid orange II) model dyes was investigated [33]. Cr incorporation significantly improved the catalytic activity of magnetite in heterogeneous Fenton reaction. After 200 min of degradation, the MB removal rate was 59.3%, 71.3%, 87.0% and 95.2% in the presence of $Fe_{2.82}Cr_{0.18}O_4$, $Fe_{2.67}Cr_{0.33}O_4$, $Fe_{2.53}Cr_{0.47}O_4$ and $Fe_{2.33}Cr_{0.67}O_4$, respectively (as shown in **Figure 3**). A series of Mn doped magnetite was showed the enhanced efficiency in photo-Fenton degradation of MB compared to non-doped magnetite (**Figure 4**). It is noted that magnetite doping 1% Mn has higher catalytic capability than that of 10% [34].

From the fact that in most natural cases, more than two kinds of metals are simultaneously introduced into magnetites in geological processes so studies on the influence of co-substituting metals on the structure and properties of magnetite, especially the surface reactivity and catalytic activity have been conducted widely [35]. The application of V-Ti co-doped magnetite in heterogeneous Fenton reaction showed that the incorporation of Ti^{4+} and V^{3+} can greatly enhance UV-Fenton catalytic activity of magnetite during the MB decolorizaition [36]. **Figure 5** revealed that Ti or V doped magnetite exhibited the higher catalyst in
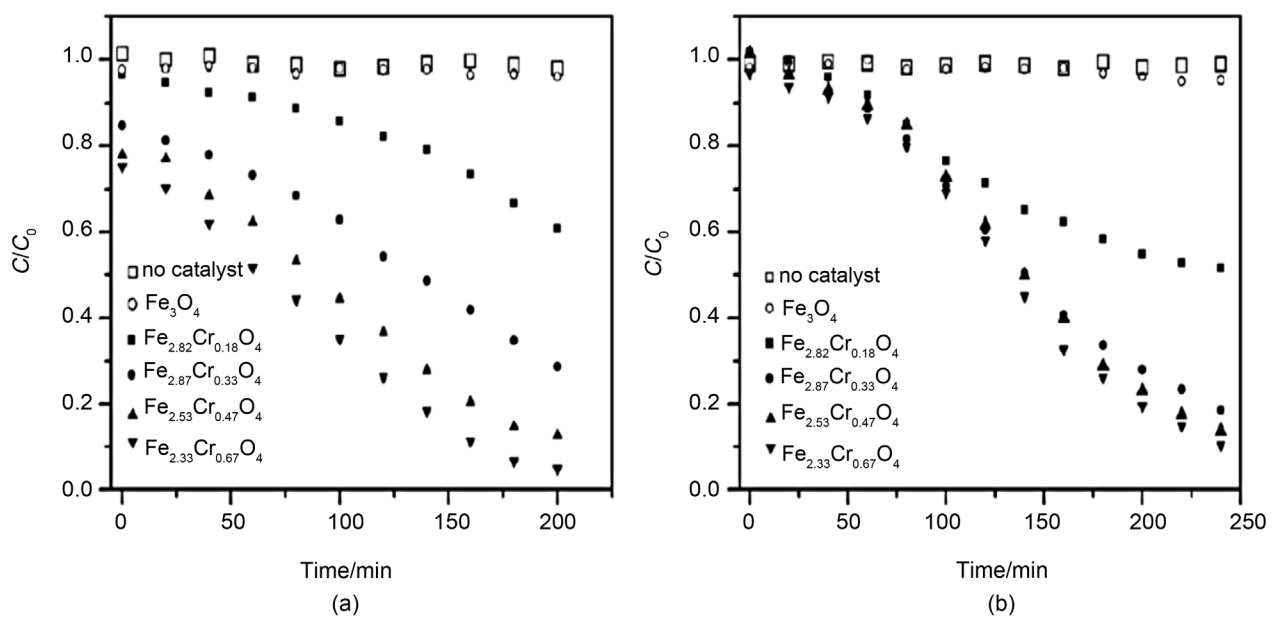

Figure 3. (a) Decolorization of methylene blue; (b) acid orange II through heterogeneous Fenton reaction catalyzed by $Fe_{3-x}Cr_xO_4$ (C_0 = 0.2 mmol·L^{-1}, 80 mmol·L^{-1} of H_2O_2, 1.0 g·L^{-1} of catalyst, 250 mL, pH 7.0, 25°C) [33].
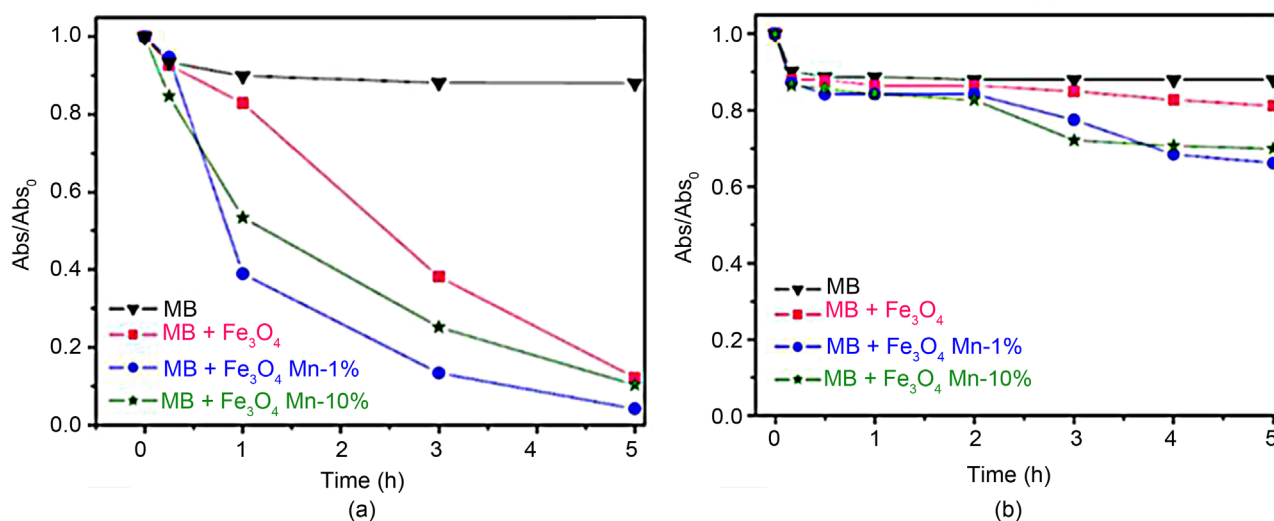
Figure 4. Influence of Mn incorporation level of magnetite on the photocatalytic dis-coloration of methylene blue in presence of H_2O_2: (a) irradiated by UV-A and (b) in the dark [34].
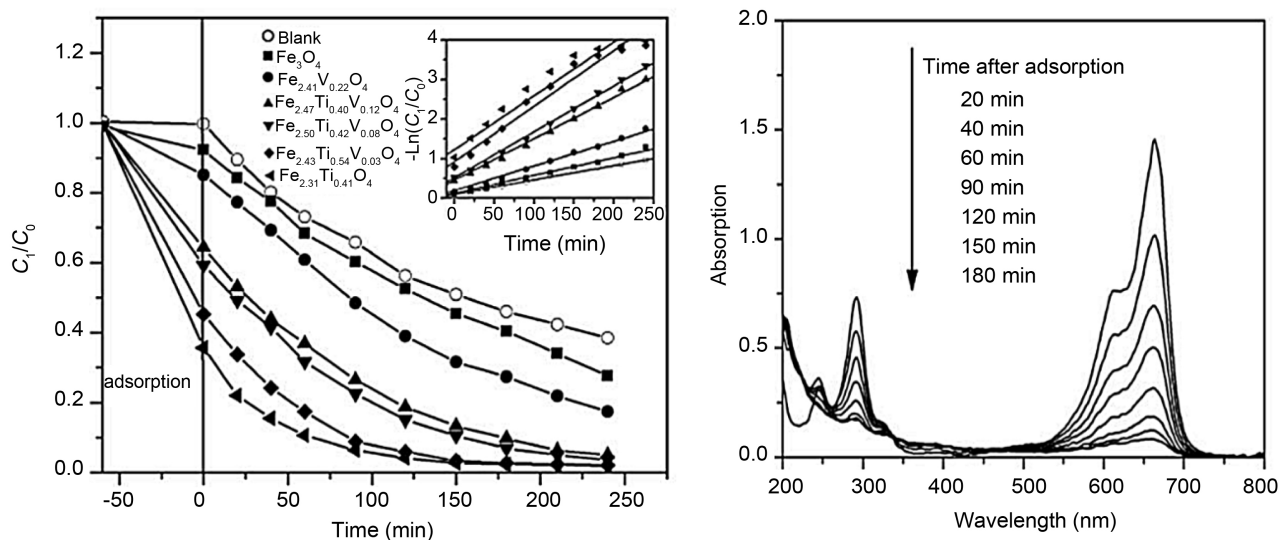

Figure 5. UV-Fenton degradation and the changes of absorption spectra of MB catalyzed by synthetic magnetite samples ($C_0 = 0.2$ mmol·L^{-1}, 10 mmol·L^{-1} of H_2O_2, 1.0 g·L^{-1} of catalyst, UV (6 W, 365 nm), 500 mL, pH 7.0, 25°C). Inset: UV-Fenton degradation processes fitted by pseudo first-order kinetics [38].
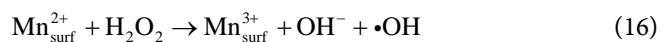
the Fenton-degradation of MB. Through a series of experiments about the degradation and mineralization of two dyes (MO and MB) in heterogeneous Fenton using modified magnetite nanoparticles ($Fe_{3-x-y}Nb_xMo_yO_4$), Shima Rahim Pouran *et al.* found out that co-doped Nb-Mo-magnetite nanoparticles showed highest activity in comparison to single Nb- and Mo-substituted magnetite samples [37].

The results from previous reports have indicated that metal doping with magnetite can be a promising approach for improving the efficient degradation of contaminants in the Fenton and photo-Fenton due to high degradation efficiency around neutral pH, easy recycle of catalyst in practical wastewater purifi-

cation. It is also because that metal doping magnetite can be easy to controllable synthesis. The obtained products have many interesting catalytic and magnetic properties. The different characterization of these obtained products depends tightly on not only the prepared route but also the metal doping.

4.2. Role of Metal Doped Species and Compare Enhanced Efficiency of Degradation Process

So far, several single-metal cations, such as Ti^{4+}, V^{3+}, Mn^{2+}, Co^{2+}, Cr^{3+}, Zn^{2+}, and co-substituting metals have been reported as active components to increase the Fenton, photo-Fenton catalytic activity of magnetite. It has been widely acknowledged that the catalytic activity of magnetite is greatly dependent on the species, valence and occupancy of substituting metals. Substituting metals exhibiting thermo-dynamically favorable redox pairs can improve the catalytic activity of magnetite by accelerating the electronic transfer to produce the active species Fe^{2+} for the Fenton reaction [33]. Effect of metal doped that exhibiting thermo-dynamically favorable redox pairs has proved via experiments reported by Rochel M. Lago *et al.* [39]. The experiments results showed that a low activity for methylene blue or chlorobenzen oxidation in the presence of $Fe_{2.46}Ni_{0.54}O_4$, with only 10% color reduction after 50 min but Mn and Co substituted magnetites showed very high oxidation activity with complete discoloration of the solution in 5 and 10 min, respectively. This constraint efficiency can be explained by the different role of substituted metal. For nickel it can be considered that only the Ni^{2+} species is stable and for this reason cannot initiate the reaction like Fe^{2+} and Mn^{2+}. Another reason for low efficiency of Ni doped magnetite is that Ni^{2+} can replace mainly Fe^{2+} in the magnetite structure leading to the reaction inhibited since Fe^{2+} is responsible for the initial step. On the other hand, cobalt and manganese exhibit the redox pairs Co^{2+}/Co^{3+} and Mn^{2+}/Mn^{3+}, which could also produce radicals according to the reactions:

$$Co^{2+}_{surf} + H_2O_2 \rightarrow Co^{3+}_{surf} + OH^- + \bullet OH \tag{15}$$

$$Mn^{2+}_{surf} + H_2O_2 \rightarrow Mn^{3+}_{surf} + OH^- + \bullet OH \tag{16}$$
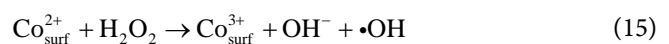
The strong effect of Co and Mn substitution it could also be considered a thermodynamically favorable electron transfer during the reaction shown by the following equations:

$$Fe^{2+} + Co^{3+} \rightarrow Fe^{3+} + Co^{2+} \tag{17}$$

$$Fe^{2+} + Mn^{3+} \rightarrow Fe^{3+} + Mn^{2+} \tag{18}$$

The efficient regeneration of the surface Co^{2+} or Mn^{2+} species by this process would be responsible for the remarkable increase an activity of H_2O_2 decomposition and organic oxidation observed for these materials. Radicalar mechanism proposal for the activation of H_2O_2 by Fe^{2+} or meal doping of magnetite can be shown in Figure 6.

Magnetite is a semiconductor with a narrow band gap (0.1 eV) and shows a very high conductivity with almost metallic character which is important for
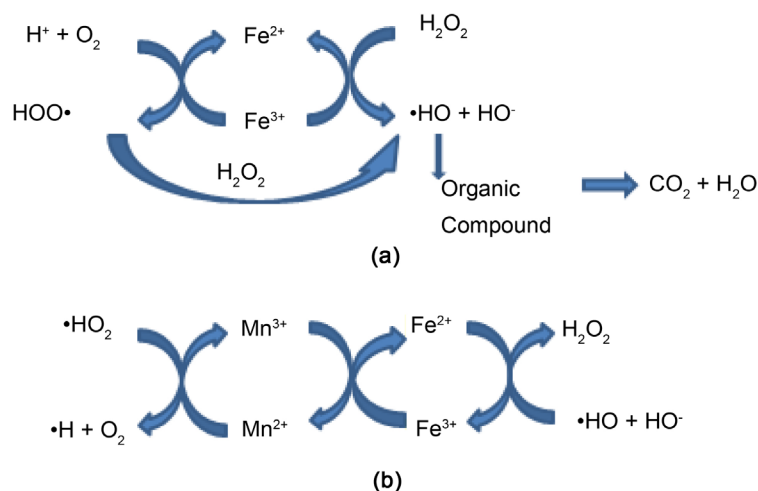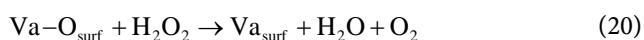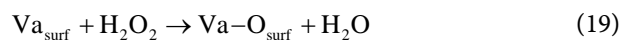
Figure 6. (a) Radicalar mechanism proposal for the activation of H_2O_2 by Fe^{2+} of Magnetite [32]; (b) Proposed mechanism for the participation of Mn^{2+} in the Fenton reaction.

electron transport. Metal doping in magnetite is also expected as reactor for controllable synthesis of magnetite which the metal doped present can be change chemical and physical properties of initial magnetic leading to enhance catalytic activity. Our previous showed that diffusion of Zn into crystal Fe_3O_4 can form new magnetite exposing interesting properties as optical absorption spectra, area surface and unique structure, resulting in higher capacity of photo-Fenton degradation of pollutants [40]. Recently, Hongping He reported that Cr substitution greatly increases the catalytic activity of magnetite in the heterogeneous Fenton reaction, but its enhancement extent depends on the chromium substitution level [33]. The catalytic activity relies on the octahedral cations rather than the tetrahedral ones, as the octahedral sites are almost exclusively exposed at the surface of the spinel structure (as **Figure 7**).

The obtained novel insights on role of metal doped species are of high importance for the designed synthesis as well as the utilization of substituted magnetite in the field of wastewater treatment.

5. Reaction Mechanism

From recent reports in literature on the transition metal oxide promoted H_2O_2 decomposition in the absent of light, a possible reaction mechanism can be proposed. The H_2O_2 decomposition in participate of doped metal is take place by two possible reaction pathways [41]: 1) the surface oxygen vacancies (Va_{surf}) mechanism and 2) the radicalar mechanism. In the first route, a H_2O_2 molecule will be actived by oxygen vacancy on the oxide surface participates to form O_2 (Equations (19) and (20)):

$$Va_{surf} + H_2O_2 \rightarrow Va-O_{surf} + H_2O \qquad (19)$$

$$Va-O_{surf} + H_2O_2 \rightarrow Va_{surf} + H_2O + O_2 \qquad (20)$$

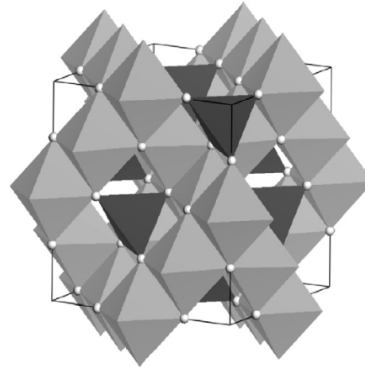The radical mechanism will be initiated by a reaction of H_2O_2 with a partially
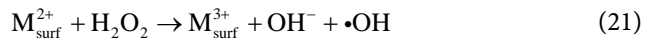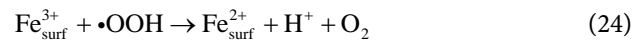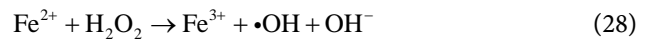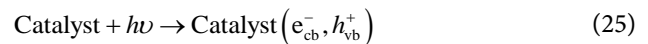
Figure 7. A unit cell of magnetite [33].

reduced surface pieces according to a Fenton like reaction or conduct reduce-oxidation reactions between redox pairs:

$$M_{surf}^{2+} + H_2O_2 \rightarrow M_{surf}^{3+} + OH^- + \cdot OH \tag{21}$$

$$Fe^{2+} + M^{3+} \rightarrow Fe^{3+} + M^{2+} \tag{22}$$

In the radical route, O_2 can be form and the formation of O_2 can be proposed simply via the hydroperoxide radical:

$$H_2O_2 + \cdot OH \rightarrow H_2O + \cdot OOH \tag{23}$$

$$Fe_{surf}^{3+} + \cdot OOH \rightarrow Fe_{surf}^{2+} + H^+ + O_2 \tag{24}$$

Due to magnetite, Fe_3O_4, is a semiconductor with a narrow band gap (0.1 eV) so in the present of light (UV/visible light), a following reaction mechanism suggested for understanding photo-Fenton reaction in the present of Zn doped Fe_3O_4 HSMSs catalyst [42]. Under visible light irradiation, electron/hole pairs can be photogenerated in the catalyst. Then, photogenerated electrons can be trapped by H_2O_2 leading to $\cdot OH$. Simultaneously, they can be trapped by Fe^{3+} on surface of catalyst forming Fe^{2+}. Then more $\cdot OH$ can be produced that resulting in reaction between formed Fe^{2+} with H_2O_2.

$$\text{Catalyst} + h\upsilon \rightarrow \text{Catalyst}\left(e_{cb}^-, h_{vb}^+\right) \tag{25}$$

$$e^- + H_2O_2 \rightarrow \cdot OH + OH^- \tag{26}$$

$$e^- + Fe^{3+} \rightarrow Fe^{2+} \tag{27}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \tag{28}$$

6. Conclusion

Based on the reports on magnetite increasing intensity in the literature recently, it can be seen that the introduction of Co, Cr, Ti, Zn and Mn into magnetite structure may strongly promote the Fenton, photo-Fenton degradation of organic contaminants due to a significant promotion of H_2O_2 decomposition. Moreover, role of metal doping in the most case have been proposed. A possible reaction mechanism suggested for understanding photo-Fenton reaction in the present of metal doped magnetite have discussed in this work. However, reac-

tion mechanism with participation of transition metal doping need make clearer by more studies. In particular, how to synthesis metal doped magnetite based materials to meet designed requirements plays a very important role in this field. These new insights are important direction for the controllable synthesis and the environmental application of metal substituted magnetites in the purification of organic contaminant textile wastewater.

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