

Review

Review on the application of modified iron oxides as heterogeneous catalysts in Fenton reactions

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ABSTRACT

Heterogeneous Fenton reaction is an advanced oxidation process which has gained wide spread acceptance for higher removal efficiency of recalcitrant organic contaminants under wide range of pH compared to homogeneous reactions. Conventionally, iron oxides are used as heterogeneous catalysts for Fenton oxidation system because of their abundance, easy separation and lower cost. This paper reviews the substitution of iron in an iron oxide with other transition metals as a mean to improve the properties of the iron oxide towards higher performance for contaminant degradation. Several studies have reported enhanced performance resulted from this substitution based on two possible mechanisms. First is the conjugation of redox pairs of iron species and imported active ion in hydroxyl radical production cycle. Second: the generation of oxygen vacancies as active sites on the surface of catalyst via adjustments for unequal charge substitutions. This class of catalysts is anticipated to work effectively for treatment of various recalcitrant wastewaters using Fenton oxidation system. Subsequently, the stability of the produced catalyst needs to be examined under various experimental conditions to prevent the adverse effects of transition metals on the receiving environment.

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1. Introduction

Water pollution abatement and treatment of wastewaters carrying recalcitrant contaminants have been major issues for decades. Recalcitrant compounds are generally of high molecular weight and hydrophobic in nature. It poses high resistance to microbiological degradation (Alexander, 1975) and may not be degraded readily by biological treatment methods. Large number of pharmaceutical and agrochemical compounds are recalcitrant. Discharge of these recalcitrant compounds to the environment even in small quantities may eventually lead to accumulate in ecosystem (Knapp and Bromley-Challoner, 2003). Many of recalcitrant compounds are

capable to directly or indirectly affect living organisms including human being. Some examples are revelation of antibiotic-resistant bacteria (Walter and Vennes, 1985), interfering the human endocrine system (Bredhult et al., 2007) and oxidative stress on fish (Laville et al., 2004). To prevent their adverse effects, the attempt should encompass minimisation of recalcitrant wastewaters from industries (Klemeš et al., 2012) as well as enhancement in treatment technologies such as advanced oxidation processes (AOPs). AOPs have been applied for degradation and mineralisation of organic pollutants such as phenolic compounds (Babuponnusami and Muthukumar, 2011; Ortiz de la Plata et al., 2010), pharmaceuticals (Valcárcel et al., 2012), agrochemicals (Silva et al., 2012) landfill leachate (Rocha et al., 2011) and also for feasible and enhanced treatment of decentralised wastewaters (Chong et al., 2012). These processes were found to be environmentally sustainable if the process energy consumption was low (Chatzisyneon et al., 2013). Fenton process is a strong oxidation system amongst advanced oxidation processes and has been successfully put into use for removal of recalcitrant organic contaminants (Ortiz de la Plata et al., 2010; Rocha et al., 2011). This process is known as the reaction between hydrogen peroxide as an oxidant and iron ions as a catalyst to produce highly active species, mainly non-selective $\cdot\text{OH}$ radicals with oxidation potential of 2.8 V (Haber and Weiss, 1934), as shown in Equations (1) and (2) (Pignatello et al., 2006):

Abbreviations: AOPs, advanced oxidation processes; AV⁻, anion vacancies; BET, Brunauer-Emmett-Teller; C, Carbon; CA, chelating agents; CMCD, carboxymethyl- β -cyclodextrin; DMP, dimethyl phthalate; EDTA, Ethylene diamine tetraacetic acid; MB, methylene blue; MIMS, membrane introduction mass spectrometry; $\cdot\text{OH}$, hydroxyl radical; PCP, pentachlorophenol; SSA, surface area per unit mass; $t_{1/2}$, half-lives; T, tesla; TMSIO, transition metal substituted iron oxide; TNT, 2,4,6-trinitrotoluene; TOC, Total organic carbon; UV-Vis, Ultraviolet-visible light region.

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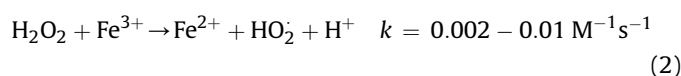
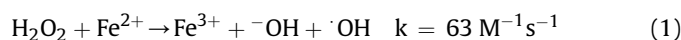


Photo-Fenton reaction is a combination of Fenton reagents and UV–Vis light that brings about additional $\cdot\text{OH}$ radicals via (i) photo-reduction of ferric ions to ferrous ions and (ii) hydrogen peroxide photolysis (Pignatello et al., 2006). The optimal pH value of 3 is accepted for Fenton process in which the quantum yield of $\cdot\text{OH}$ radical generation at this value is the most (Benkelberg and Warneck, 1995). At higher pH values than optimal value and/or at higher concentrations of H_2O_2 (>1%), other non-hydroxyl radicals that are less active in oxidation of contaminants when compared to $\cdot\text{OH}$ radicals are also formed (Pignatello et al., 2006; Watts and Teel, 2006). The Fenton reaction in which iron salts are used as catalyst is defined as homogeneous Fenton process. In homogeneous Fenton oxidation systems, mass transfer limitations are negligible and the readily available iron ion in the reaction medium reacts effectively in the degradation process. However, there are some drawbacks encountered by this process that are mainly (i) pH-dependence of the system (2.5–4.0), (Katsumata et al., 2005) (ii) formation of ferric hydroxide sludge at pH values above 4.0 (Tamimi et al., 2008) and its removal issue (iii) the generated sludge may prevent UV radiation penetration in photo-Fenton process (Faust and Hoigne, 1990) which will affect treatment process (iv) difficulty in catalyst recovery (Pariente et al., 2008) and (v) the cost associated with acidification and subsequent neutralization that may limit the application of homogeneous Fenton oxidation system at industrial scale. Therefore, the application of heterogeneous Fenton reactions as a possible solution to overcome the shortcomings of homogeneous catalysis has been put into perspectives by many researchers. This will enable pollutant mineralisation under non-controlled pH conditions and also for contaminated sites with pH adjustment limitations (Usman et al., 2012b). In heterogeneous catalysis, iron is stabilised within the interlayer space of the catalyst's structure and can effectively produce hydroxyl radicals from oxidation of hydrogen peroxide, under non-controlled pH conditions and without iron hydroxide precipitation (Garrido-Ramírez et al., 2010). Several heterogeneous catalysts have been employed in Fenton reactions such as mesoporous materials (Chun et al., 2012; Xia et al., 2011), iron pillared clays (Chen et al., 2010), iron containing zeolites (Dükkancı et al., 2010; Hassan and Hameed, 2011) and iron minerals (Lan et al., 2010; Magalhães et al., 2007; Ortiz de la Plata et al., 2010). There have been extensive studies on application of iron oxides in pure or structurally modified forms. At present time, several important reviews have been reported in the literature on the basic facets and applications of iron bearing minerals as active catalyst or support (Garrido-Ramírez et al., 2010) and also iron oxide nanomaterials in heterogeneous catalytic reactions for organic contaminant degradation (Soon and Hameed, 2011; Xu et al., 2012) and heavy metal removal from polluted sites and wastewaters (Hua et al., 2012). However, the recent reported findings on modified iron minerals and their structural changes toward effective contaminant removal have not been discussed in detail in any of past reviews reported in the literature. Therefore, this review aims at giving an account of fundamental aspects of different iron oxides as follows: Section 2 discusses the merits of different iron oxides and their applications as heterogeneous catalysts in Fenton treatment system. Section 3 introduces transition metal substituted iron oxides (TMSIOs) as a catalyst with higher performance in degradation of organic pollutants. In terms of TMSIOs, valence and occupied sites, changes in physico-chemical properties, adsorption capacity and catalytic activity are discussed in detail in the next sections. Section 4 provides a summary and

conclusion of the review and subsequently, suggestions are given for plausible research directions.

2. Iron oxides in wastewater treatment

Iron oxides are abundantly available minerals present in the earth crust. Out of the sixteen known iron oxides and hydroxides (Cornell and Schwertmann, 2003), magnetite (Fe_3O_4), goethite (αFeOOH), maghemite ($\gamma\text{Fe}_2\text{O}_3$) and hematite ($\alpha\text{Fe}_2\text{O}_3$) are widely used in heterogeneous catalysis processes and have been attractive alternatives for remediation of polluted soil, groundwater (Aredes et al., 2012) and wastewater. Different physico-chemical characteristics of these oxides make them more or less favourable for oxidative reactions. From these features, surface area, pore size/volume and the crystalline structure have principal effects on their activities (Huang et al., 2001; Xue et al., 2009a). Moreover, because the rate constant of Equation (1) is much higher than Equation (2) ($63 \text{ M}^{-1} \text{ s}^{-1}$ vs. $0.002\text{--}0.01 \text{ M}^{-1} \text{ s}^{-1}$), structural Fe^{II} content is influential in Fenton oxidation systems (Xue et al., 2009a). These solid catalysts present powerful potential for degradation of recalcitrant pollutants such as dyes and phenolic compounds (Table 1).

Magnetite is a spinel iron oxide with chemical formula of $(\text{Fe}^{3+})_{\text{tet}}[\text{Fe}^{2+}\text{Fe}^{3+}]_{\text{oct}}\text{O}_4$ where Fe^{3+} cations occupy equally both octahedral and tetrahedral sites and Fe^{2+} cations are placed only in octahedral sites. In Fenton process, magnetite has gained considerable attention than other iron oxides due to its unique characteristics: (i) It is the only most abundant iron oxide with Fe^{II} in its structure that improves hydroxyl radical production through Fenton reaction, Eq. (1) (Kwan and Voelker, 2003; Moura et al., 2005), (ii) The presence of octahedral sites in its structure that are mostly at the surface of the crystal and the catalytic activity is chiefly on account of the octahedral cations (Ramankutty and Sugunan, 2001), (iii) The magnetically easy separation of magnetite catalysts from the reaction system as a result of its magnetic property (Ai et al., 2011; Chun et al., 2012), (iv) Production of more active systems by modification in the physico-chemical properties of the magnetite through isostructural substitution of iron by different transition metals (Moura et al., 2005) and (v) Higher dissolution rate of magnetite compared to other iron oxides (Matta et al., 2008) and accordingly, higher electron mobility in its spinel structure (Litter and Blesa, 1992). As a consequence, magnetite has been used frequently in contaminant oxidation systems (Ai et al., 2011; Usman et al., 2012b; Xue et al., 2009a; Yang et al., 2009a; Zhong et al., 2012). Usman et al. (2012a) conducted six set of oxidative degradation systems using soluble Fe^{2+} with H_2O_2 (homogeneous Fenton), H_2O_2 and magnetite rich sand (heterogeneous Fenton-like), singular H_2O_2 , magnetite and sodium persulfate, soluble Fe^{2+} and sodium persulfate and singular sodium persulfate to evaluate the efficacy of magnetite catalysed oxidation system to other combinations in degradation of oil hydrocarbons. The resulted degradation was above 80% by magnetite with both oxidants, ending to inconceivable by-products, while the oxidants represented minor degradation efficiency exclusively or even with homogeneous catalyst (10–15%).

The investigation to compare catalytic activity of amorphous iron (III) oxide, maghemite, magnetite and goethite mixed with quartz was carried out by Hanna et al. (2008) for methyl red degradation in presence of H_2O_2 . The authors believed that the oxidation state of iron in the oxides has been the key parameter as Fe^{II} is superior to Fe^{III} in Fenton processes. In the study reported by Hanna et al. (2008), magnetite exhibited the highest rate constant normalised to surface area per unit mass of oxide (SSA) at neutral pH value and the rate constant according to pseudo-first order kinetic model for goethite was the highest at pH 5. However, their

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