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Synthetic magnetite, maghemite, and haematite activation of persulphate for orange G degradation

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ABSTRACT

Due to the widespread application of persulphate (PS) for in-situ chemical oxidation (ISCO), the PS activating role of naturally occurring minerals, such as iron oxides, has been the subject of a number of studies. However, major discrepancies remain as to the effectiveness, mode, and factors that influence iron oxides activation of PS. In this study, an attempt has been made to bridge this important knowledge gaps by a systematic study of PS activation, measured by orange G degradation, using commercial and self-synthesised magnetite, maghemite, and haematite particles. The results showed that the activation of PS by iron oxides does not depend on mineralogy, surface area or concentration of surface OH groups, but on crystalline inhomogeneities or structural irregularities. Significant dissolution of iron oxides accompanied PS activation, in a mainly homogeneous process, requiring a low pH environment to be effective. The activation of PS by iron oxides at neutral pH was found to be no better than dissolved iron activation contrary to some earlier publications. The results also suggest that under alkaline conditions, PS alone was more effective in degrading orange G than with iron oxides or dissolved iron activation. Phosphate buffer significantly retarded orange G degradation by iron-activated or unactivated PS with negative implication for ISCO in non-acidic, buffering environments. The results of this study contribute to enhancing the fundamental understanding of ISCO processes.

1. Introduction

Within the last two decades, the application of persulphate (PS) for in-situ chemical oxidation (ISCO) of pollutants in subsurface environments has attracted significant practical and research attention. This is due to the ability of PS to oxidise a variety of contaminants (Tsitonaki et al., 2010; Devi et al., 2016; Zhang et al., 2015; Liu et al., 2016). Consequently, the role of naturally occurring minerals, such as iron oxides, in activating PS to produce the reactive sulphate radical ($\text{SO}_4^{\cdot-}$) has been the subject of a number of experimental investigations. These investigations were aimed at improving the efficiency of PS ISCO for the remediation of subsurface contaminations (Wu et al., 2017; Usman et al., 2012; Ahmad et al., 2010; Teel et al., 2011). The higher selectivity and the limited reaction with the natural organic matter of $\text{SO}_4^{\cdot-}$ compared to the hydroxyl radical (HO^{\cdot}), commonly produced from H_2O_2 , is one reason for the increasing interest in PS ISCO (Ahmed et al., 2012; Ike et al., 2018a; Avetta et al., 2015). However, under certain conditions, $\text{SO}_4^{\cdot-}$ may be substantially converted to HO^{\cdot} (Lutze et al., 2015; Liang and Su, 2009). Iron oxides have also been advanced as substitutes for soluble ferrous ion (Fe^{2+}) in the

activation of PS. Reduced consumption of PS and circumneutral activation are cited as advantages of iron oxides over dissolved Fe (Wu et al., 2017; Usman et al., 2012; Ike et al., 2017a).

Despite the progress made in understanding the mechanisms of iron oxides activation of PS, Ding et al. (Ding et al., 2017) maintained that there are still important unresolved questions. One of which is whether the activation of PS by iron oxides is mainly heterogeneous or homogeneous. In homogeneous activation, soluble Fe derived from the dissolution of the original iron oxide is principally responsible for PS activation. Where PS activation arises primarily from the interaction between the oxidant and the surfaces of the oxide particles, with or without some iron dissolution, the activation process is described as heterogeneous. Homogeneous processes are limited to conditions where soluble Fe is stable (i.e. conditions in which substantial dissolved Fe precipitation does not occur – typically acidic conditions), while heterogeneous processes are not dependent on dissolved Fe stability in solution. Consequently, homogeneous processes are effective only in acidic environments while the effectiveness of heterogeneous processes is less dependent on pH. As the pH in subsurface environments may not always be acidic, a knowledge of whether iron oxide activation of

Abbreviations: ISCO, in-situ chemical oxidation; Ms., saturation magnetisation; OG, orange G; PS, persulphate; SSA, specific surface area

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persulphate is principally heterogeneous or principally homogeneous is important in evaluating iron oxide contribution to the effectiveness of PS ISCO processes. Another unresolved question is whether the PS activation ability of a particular iron oxide is influenced more by the synthesis route and local crystalline defects than by mineralogy (Ding et al., 2017). To illustrate, Usman et al. (Usman et al., 2012) suggested that Fe^{II}-bearing iron oxides such as magnetite may be more effective in activating PS compared to Fe^{III} oxides such as haematite, an assertion that may be supported by Fe²⁺ faster activation of PS compared to Fe³⁺ (Rodriguez et al., 2014). However, the results published by Do et al. (Do et al., 2010) showed that haematite was more effective in activating PS, measured by a target pollutant degradation, compared to magnetite under the same condition (particle concentration, 8.3 g/L; pH 3; PS concentration, 500 mM). On the one hand, Ahmad et al. (Ahmad et al., 2010) reported < 60% degradation of nitrobenzene and hexachloroethane after 3 days (3 d) by PS activated by haematite (particle specific surface area (SSA), 28 m²/g; particle concentration, 400 g/L; pH = 6–3 or 13–12; PS concentration, 500 mM). On the other, an almost complete degradation of fluorenone was reported by Usman et al. (Usman et al., 2012) after only 50 h due to oxidation by PS under magnetite activation (particle concentration, 10 g/L; pH = circumneutral; PS concentration, 130 mM; see Section S.1 in the Supplementary material for the computation of the concentrations). A still more rapid degradation was reported by Yan et al. (Yan et al., 2011). According to the report, sulfamonomethoxine was almost completely degraded in < 2 min by PS activated by magnetite nanoparticles (computed SSA using particle size (Ike et al., 2017b), 78 m²/g; particle concentration, 0.6 g/L; pH = 6.4; PS concentration, 1.8 mM). It may be appreciated from the SSA values and the concentrations supplied that, for instance, surface area cannot explain the difference in the degradation periods reported by Ahmad et al. (Ahmad et al., 2010) and Yan et al. (Yan et al., 2011), even when consideration is made for the difference in experimental conditions.

Borggaard O. K. (Borggaard, 1983) demonstrated that mineralogy does not seem to affect certain physical and chemical properties of iron oxides such as surface charge, hydroxyl buffering, fluoride and phosphate adsorption capacities. It is therefore important to carry out controlled experiments to determine the impact of mineralogy and other properties of iron oxides such as SSA on PS activation. Understanding the factors that influence the effectiveness and duration of pollutant degradation under iron-oxide-activated-PS oxidation is crucial for the development of a better description of PS ISCO processes as well as a more complete explanation of wastewater treatment schemes.

This study is a first-pass, qualitative assessment of the effects of crystalline phase, Fe^{II} content, particle size, the degree of sintering/hydroxyl group concentration, and surface coating by co-existing minerals on PS activation by iron oxides. The specific aims embrace the advancement of a greater understanding of the modes (homogeneous or heterogeneous) and effectiveness of PS activation by the three common iron oxides, magnetite, maghemite, and haematite. For this purpose, both commercial and self-synthesised iron oxide particles were evaluated with respect to their effectiveness in activating PS. The extent of PS activation was measured by the degree of orange G (OG) degradation (decolourisation and mineralisation). The particle synthesis involved a stepwise modification of a base material to limit the effects of synthesis variability. OG, a typical azo dye, although not a common groundwater contaminant, was chosen for this study as its degradation behaviour under the influence of activated PS is fairly established (Ike et al., 2017a; Rodriguez et al., 2014; Xu and Li, 2010) and its colour provides for a convenient analysis. This is to focus the research on the effects of the iron oxides and the reaction environment. Nevertheless, OG, as an azo dye, still remains an important environmental contaminant in its own right due largely to the popularity of azo dyes in the textile industry, and because OG is structurally similar to more toxic azo dyes such as o-aminoazotoluene (Ike et al., 2017a; Drumond Chequer et al., 2013).

Table 1
Summary description of particles studied.

Particle	Description	Colour
S1	Magnetite aged in air for 1 min	Black
S2	Magnetite aged in air for 2 h	Black
S3	Magnetite aged in air for 10 h	Black
S4	S2 oxidised in air at 250 °C for 5 h (maghemite)	Brownish red
S5	S2 oxidised in air at 500 °C for 5 h (haematite)	Red
S6	S5 dehydroxylated by sintering in air at 800 °C for 5 h	Red
S7	S5 hydroxylated by boiling in MilliQ water for 5 h	Red
S8	S2 coated with silica	Brown
S9	S2 coated with calcium carbonate	Brown
S10	Aldrich magnetite nanopowder (50–100 nm)	Black
S11	Aldrich magnetite powder (< 5 µm)	Black
S12	Aldrich maghemite nanopowder (< 50 nm)	Brownish red

2. Methods

Milli-Q water and analytical grade chemicals were used throughout the study. The iron oxide particles and their modifications used in this study are summarised in Table 1. Magnetite nanoparticles were synthesised according to a method already published (Ike et al., 2017b). Three sets of black powders hereafter referred to as S1, S2, and S3, were produced by varying the ageing time of the nanoparticles, under atmospheric conditions, for 1 min, 2 h, and 10 h, respectively. The ageing was done to produce magnetite powders with varying degrees of surface oxidation. The aim was to evaluate the effect of surface oxidation/Fe^{II} content on the effectiveness of magnetite activation of PS. To compare the activation potential of magnetite to the other common iron oxides, maghemite and haematite, S2 was oxidised according to a literature procedure (Cornell and Schwertmann, 2003). A portion of the black S2 powder was subjected to air oxidation at 250 °C, for 5 h in a muffle furnace, which resulted in the production of a brownish-red maghemite powder (Cornell and Schwertmann, 2003). The maghemite powder is hereafter referred to as S4. An oxidation of a portion of the S2 sample at 500 °C for 5 h produced a red haematite powder (Cornell and Schwertmann, 2003), which is hereafter referred to as S5.

To determine whether the concentration of the hydroxyl groups on the surface of an iron oxide play a role in PS activation, a portion of S5 was subjected to a further thermal treatment at 800 °C for 5 h. The heat-treated powder is hereafter referred to as S6. Such heat-treatment results in irreversible sintering of particles and removal of surface hydroxyl groups (Cornell and Schwertmann, 2003). An attempt was also made to increase the concentration of the surface hydroxyl groups on a portion of S5 by boiling in Milli-Q water. The boiling lasted for 5 h. The aim of the boiling was to hydroxylate some oxo bonds that may have been formed during the initial production of S5 at a temperature of 500 °C (Cornell and Schwertmann, 2003). The tentatively hydroxylated powder is referred to as S7, hereafter. To assess the potential effect of iron oxide particles being coated by soil minerals, a portion of the S2 sample was coated with silica according to a published procedure (Ike et al., 2017b). The silica-coated S2 sample is referred to as S8 subsequently in this paper. Calcium carbonate coating was also applied on a portion of the S2 sample because carbonate minerals abound in the environment. To apply the carbonate coating, a wet portion of the S2 sample was placed in a flask to which 100 mM NaHCO₃ and 180 mM NaCl solutions were added. A solution of 300 mM NaOH was gently added to the mixture. Under rapid stirring, a solution of 100 mM CaCl₂ was added dropwise to precipitate CaCO₃ on S2 as S9 (Babou-Kammoe et al., 2012; Sanciolo et al., 2008). Three commercial iron oxide samples were also evaluated in this study. A commercial magnetite nanopowder from Aldrich (637106), with a specified size range of 50–100 nm, was designated as S10. S11 represents another commercial magnetite powder from Aldrich (310069), with a manufacturer's specified size of < 5 µm. A commercial maghemite nanopowder from Aldrich (544884), with a specified particle size of < 50 nm, will hereafter

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