PERSULFATE ACTIVATION BY A NATURAL IRON OXIDE FOR THE REMEDIATION OF DYE CONTAMINATION

S. Belaidi, L. Mammeri, W. Lakehal, H. Bounemoura, T. Sehili

Laboratoire des Sciences et Technologies de l'Environnement
Faculté des Sciences Exactes, Université des frères Mentouri, 25000 Constantine, Algérie
E-mail : belaidi_sihem@yahoo.fr

Abstract

The objective of this work was to evaluate the removal of crystal violet (CV), a cationic dye, using sodium persulfate (PS) as an oxidant in presence of a natural iron oxide (NIO). Experimental results indicate that approximately 89 % and 98% of CV removal was achieved by PS alone and by (PS/NIO) system respectively after 1 hour of reaction. Persulfate oxidation activated with soluble Fe (II) enhanced the kinetic oxidation of CV. The increase in removal is due to the adsorption of CV onto NIO surface and to the increased formation of either $SO_4^{\bullet-}$ or $^{\bullet}OH$ radicals. The effect of pH on the degradation of CV by PS/NIO was studied. Persulfate degradation increases with a reduction in pH causing increased rate of degradation of organic contaminants. An additional factor in the NIO/PS/UV process may be the photolysis of PS which produce two sulfate radicals ($SO_4^{\bullet-}$). Results of this study suggest that NIO can be used as iron source to activate persulfate oxidation.

Keywords: Crystal violet, persulfate, natural iron oxide, degradation, sulfate radicals .

1. INTRODUCTION

Wastewater treatment by means of advanced oxidation processes (AOPs) has become one of the issues of major interest in modern environmental chemistry. These techniques which involve the generation of the highly reactive and non-selective hydroxyl radical ($^{\bullet}OH$) are of interest for the destruction of organic pollutants in wastewater **[1, 2]**. Among these AOPs, Fenton treatments are showing great potential as viable remediation technology for the removal of organic pollutants **[3, 4]**. Fenton treatments utilize the high reactivity of hydroxyl radical, a very reactive chemical species, which is generated through Fenton's reaction **[5]** (Eq.(1)):

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (1)$$

Iron minerals are used instead of soluble iron to produce hydroxyl radical for an efficient degradation of the organic molecules at circumneutral pH and the process is known as Fenton-like oxidation. Persulfate (PS) was also proven to be very useful for the elimination of contaminants such as diphenylamine, trichloroethylene, benzene, toluene, ethyl benzene and xylene in aqueous and soil slurries **[6, 7, 8]** and was used instead hydrogen peroxide. The PS anion can be chemically, thermally or under UV irradiation activated to generate the intermediate sulfate free radical ($SO_4^{\bullet-}$) which is stronger oxidant (E^0= 2.6 V) than the PS anion (E^0= 2.01 V). PS chemical activation occurs through reduction upon reaction of an adequate amount of a transition metal like Fe^{2+}, Co^{2+} **[9, 10]**. This will result in the production of sulfate radicals which are very reactive toward organic molecules (Eq. (2)):

$$Fe^{2+} + S_2O_8^{2-} \longrightarrow Fe^{3+} + SO_4^{\bullet-} + SO_4^{2-} \qquad (2)$$

Although the activation of PS by soluble iron to form a sulfate radical ($SO_4^{\bullet-}$) has been previously reported, the initiation of PS decomposition by iron oxide minerals has been scarcely investigated **[11, 12]**. Minerals like ferrihydrite, goethite, manganese oxide and clay were used to activate the oxidation reaction of organic compounds **[11]**.

The main objectives of this study were to evaluate the ability of a natural iron oxide (NIO) to activate persulfate and to determine the efficiency of oxidation of (NIO/PS) system to degrade crystal violet (CV) dye, taken as a model substrate, in dark and under UV irradiation.

2. MATERIALS AND METHODS

2.1. Reagents

All reagents used in this work were analytical grade and were used without any further purification. Crystal violet was purchased from Biochem, Sodium persulfate was provided from Sigma–Aldrich, Sodium hydroxide (98%) by Carlo Erba Reagenti. Sodium acetate (99%) and sulfuric acid (98%) by Panreac; silver sulfate and 1,10 O-phenanthroline (>99%) by Fluka. Perchloric acid (60 %) was from Merck. All solutions were prepared in Milli-Q water (Millipore).

2.2. Experimental procedures

The oxidation experiments were performed in a Pyrex cylindrical reactor with a double envelope was placed in the centre of a cylindrical aluminium container. The suspensions of CV (6 ppm) and 1 g L^{-1} of iron oxide were stirred in the dark for 30 min to establish adsorption/desorption equilibrium. After that the required volume of persulfate was then added. In the photo-oxidation experiments, the reactor was exposed to the radiation sources composed of a fluorescent lamp (Philips TLAD 15W/05), which dominantly emits radiation at 365 nm. Light intensity (I = 0.45 mW cm^{-2}) was measured using a radiometer type VLX 3W. The solution was continuous magnetically stirred during experiments to insure its homogeneity. The samples withdrawn at different reaction times were filtered with cellulose acetate filters (0.45 µm) to separate NIO particles. All experiments were performed at T = 293±1°K by cycling water. The solution pH was adjusted by 1.0 M of $HClO_4$ or NaOH and measured by means of an HANNA Instruments 8521 pH-meter

2.3. Analytical methods

The concentrations of the residual CV were determined by monitoring decrease in absorbance at the maximum wavelength (592 nm) employing a Thermo scientific spectrophotometer controlled by software « Thermo INSIGHT ».The Fe(II) leached from NIO into the reaction solution was determined by using the 1, 10-phenanthroline method. Low dissolved iron concentration was detected in the solution

3. RESULTS AND DISCUSSION

3.1. Properties of material

The NIO used in this study was obtained from the iron deposits which is located in North-East Algeria. The collected powder was washed and dried at 45°C before using for oxidation treatment. The characterization of NIO has been studied in a previous work **[13]**. The analyses showed that the mineral has a mixed crystal structure composed mainly of hematite.

3.2. Kinetics degradation of CV

In order to determine the role of NIO in presence of persulfate on the kinetics of CV removal, oxidation experiments were carried out in different systems (**Fig. 1a**). Adsorption experiment (conducted in the absence of the oxidant) revealed almost moderate degradation (47%). Significant reduction (89%) in presence of PS alone was obtained. NIO activation by PS resulted in degradation extent of CV of almost 98% after 1 hour of reaction. The acid medium causes the dissolution of the iron oxide, Fe (II) dissolved from NIO, was also measured by assaying with O-phenantroline (**Fig. 1b**). According to Eq. (2), sulfate radicals were produced and Fe (II) was oxidized to Fe(III) and gradually consumed. The reaction slowed down due to the low concentration of Fe(II). Since ferric oxides like ferrihydrite and goethite were shown to activate persulfate **[11]**, Fe^{III}-oxide surface could react with $S_2O_8^{2-}$ to generate sulfate radical but the interactions of persulfate anion with the iron mineral surface are not yet well argued.

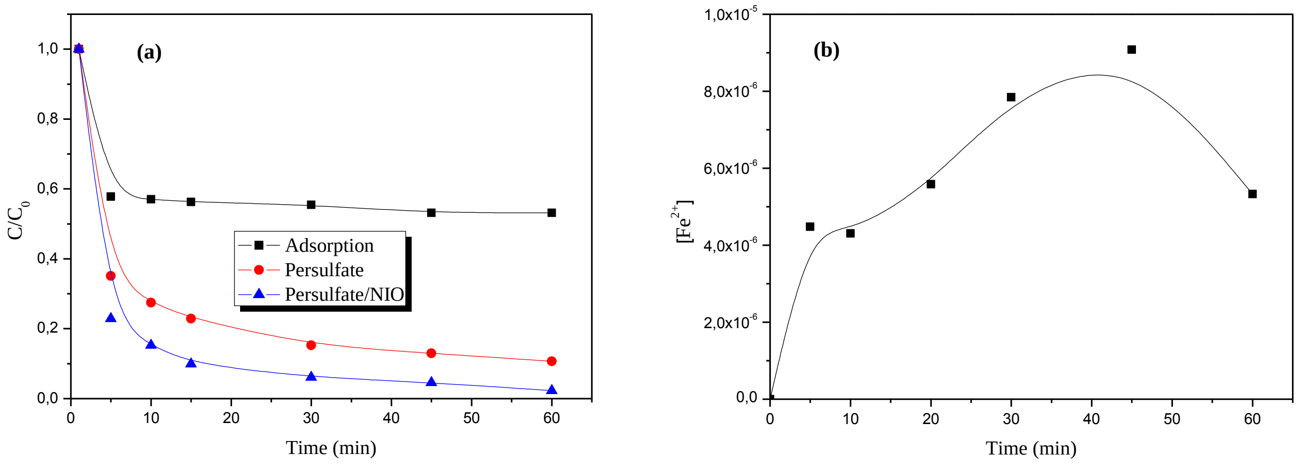

Fig.1: Effect of persulfate on the degradation of CV (6ppm) in presence of NIO (a), formation of Fe^{2+} in NIO/ $S_2O_8^{2-}$ system (b) ; $[S_2O_8^{2-}]$ = 5 mM, [NIO] = 1 $g.L^{-1}$, pH = 3.0.

3.2.1 Effect of pH

The effect of pH on the degradation rate of CV (6 ppm) in presence of NIO/ $S_2O_8^{2-}$system (1 $g.L^{-1}$, 5 mM) at acidic and alkaline pH was studied. The effect of varying the solution pH value on the adsorption of CV is illustrated in **Fig. 2.** The absorption rate of the CV, at pH = 9.7 and pH = 3, are 65.8% % and 47 % respectively. The observed sorption behavior can be attributed to a combination of pH-dependent speciation of CV (pK_a= 1) and surface charge characteristics of the NIO (pH_{pzc}= 8,3). Based upon surface charging, adsorption is high at high pH values and then decreases when pH decreases. After adding PS, we note that the pH does not affect much the disappearance of the CV high degradation rates were recorded after one hour of reaction, 94.2% and 89.2% in acidic pH and alkaline pH, respectively. Persulfate degradation increases with a reduction in pH causing increased rate of degradation of organic contaminants **[14]**. In systems containing PS, hydroxyl radical can also be formed via following reactions (Eqs. (3), (4)), and may participate in contaminants oxidation **[15]**.

All pH:

$$SO_4^{\bullet -} + H_2O \longrightarrow {}^{\bullet}OH + H^+ + SO_4^{2-} \qquad (3)$$

Alkaline pH:

$$SO_4^{\bullet -} + OH^- \longrightarrow SO_4^{2-} + {}^{\bullet}OH \qquad (4)$$

Liang et al. (2007) **[16]** suggested that the sulfate radical predominates under acidic conditions and the hydroxyl radical under alkaline conditions. Both hydroxyl and sulfate radicals could attack the target contaminants.

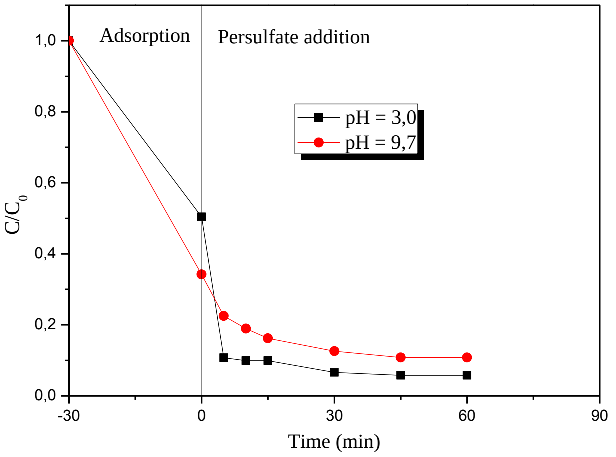

Fig.2: Effect of initial pH on the degradation of CV in NIO/ $S_2O_8^{2-}{}_2$ system.
$[CV]_0$ = 6 ppm; [NIO] = 1 g L^{-1}; $[S_2O_8^{2-}]$ = 5 Mm.

3.2.2. Effect of UV- light

The process PS/NIO was experienced by using UV light irradiation where mixture of CV/NIO/PS (6 ppm, 1 g L^{-1}, 5 mM) was exposed to irradiation at 365 nm. **Tab.1** shows the pseudo-first-order kinetic constants for the removal of CV, after adsorption, by the oxidizing species in NIO/ $S_2O_8^{2-}$ system, in the presence and absence of UV light. The moderate improvement of CV degradation under UV irradiation is due to additional sulfate radicals derived from photolysis of $S_2O_8^{2-}$. Under UV irradiation, the persulfate ion degrades giving two sulfate radicals **[17, 18]**.

Tab.1: Pseudo-first-order kinetic constants for the removal of CV in NIO/ $S_2O_8^{2-}$ system in the presence and absence of UV light.

Process	**k (min^{-1})**	**R^2**
NIO/ $S_2O_8^{2-}$	$3.08x10^{-2}$	0.957
NIO/ $S_2O_8^{2-}$ /UV	$3.38x10^{-2}$	0.979

4. Conclusion

The aim of this study was to test ability of a natural iron oxide (NIO) to activate persulfate oxidation for the degradation of CV in aqueous solution. Results of this study suggest that NIO can be used as iron source to activate persulfate oxidation of CV through the possible formation of reactive species such as $SO_4^{\bullet-}$ and •OH. The acidic pH favored the generation of oxidant radicals, which resulted in an increase of the degradation efficiency of CV. however CV degradation at alkaline pH remains significant. Under UV irradiation additional sulfate radicals derived from photolysis of $S_2O_8^{2-}$ enhanced the degradation of CV. This study provides new insights into the mechanism of heterogeneous catalysis based on Fe^{III}-oxide in presence of persulfate toward environmental contaminants.

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