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Short Communication

Catalytic decolorization of methyl orange by the rectorite–sulfite system

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ABSTRACT

The simple rectorite–sulfite system has been found to decolorize methyl orange efficiently with dioxygen as the oxidant under mild conditions. The rectorite was also stable during the reaction without significant metal ions leaching. The iron impurity, mainly presented as highly dispersed hematite, probably acted as the active centers. Suggested by the electron spin resonance spin-trapping technologies and radical scavenger measurements, the produced sulfate radicals were to be responsible for the dye decolorization. This study can provide us a simple, effective and economic system ideal for the treatment of toxic and nonbiodegradable azo dye.

1. Introduction

Color removal in effluents generated by the textile industry is a main issue in wastewater treatment, as it has been estimated that over 15% of the total world production of dyes is lost in their synthesis and dyeing process [1]. Various oxidants, such as dioxygen, hydrogen peroxide, ozone, and peroxymonosulfate salts, have been used in organic dyes decolorization by combining with catalysts [2–5]. Among them, dioxygen from air is the cleanest and the most abundant oxidative agent, the catalytic activation of dioxygen to reactive oxygen species (ROS) for organic dye removal from aquatic environments has become a major public concern in almost all parts of the world [6–8]. For instance, the Mo–Zn–Al–O catalyst has been synthesized by Sun's group and successfully applied for cationic red GTL removal under room temperature and atmospheric pressure, to overcome the drawback of catalytic wet air oxidation with high temperature and high pressure. The possible reaction mechanism was that the Mo–Zn–Al–O catalyst can efficiently react with adsorbed oxygen/H_2O to produce hydroxyl radicals (HO•) and singlet oxygen (${}^1O_2$) and finally induce the degradation of the dye [9]. However, finding the more efficient and cheap catalysts for application in industrial processes is still the main issue in the area.

Sulfite is the main by-products from flue gas desulfurization. The catalytic-oxidation and non-catalytic oxidation of sulfite to sulfate by dioxygen is an important chemical processes [10,11]. Many kinetics and mechanisms have been proposed and free radicals have been demonstrated to be produced during the oxidation of sulfite [12]. For example, the enzymatic oxidation of sulfite proceeds via a two-electron oxidation with the formation of $SO_3^{-\bullet}$ anion radicals, which can react rapidly with dioxygen and give rise to the formation of $SO_5^{-\bullet}$, $SO_4^{-\bullet}$ and HO• radicals [13]. As the high active species can be produced during sulfite oxidation, it has a great potential value in wastewater treatment. In fact, the homogeneous iron–sulfite system has been demonstrated as efficient system for organic pollutants degradation [14–16]. But until now, no heterogeneous catalysts have been used in the reaction.

Rectorite is a regular clay mineral and occurs in large deposits in Hubei, China. As it can adsorb organic substance both on its external surface and within its interlaminar space by interaction or substitution, numerous research projects have been focused on rectorite and pillared rectorite in the past decades as absorbent, solid acid catalyst and catalyst supports [17–19]. Rectorite intergrowths with pyrrhotite, so before purification, the clay usually contains some iron as the main impurity. Several years ago, the raw rectority with 4.21% iron was found exhibiting high efficiency or catalytic wet air oxidation of phenol [20]. Herein, we report the catalytic behavior of the rectorite for sulfite oxidation and organic dyes decolorization in wastewater.

2. Experimental

2.1. Chemicals and reagents

Sodium sulfite, ferrous sulfate, ferric nitrate, tert-butanol (TBA), ethanol (EtOH) and other chemicals were of analytical grade if not noticed otherwise. The spin trap reagent 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) was purchased from Sigma Chemical Co. Methanol orange (MO) was from Sinopharm Chemical Reagent. Sodium rectorite (Na-Rec) was refined from clay from Zhongxiang, Hubei province, China.

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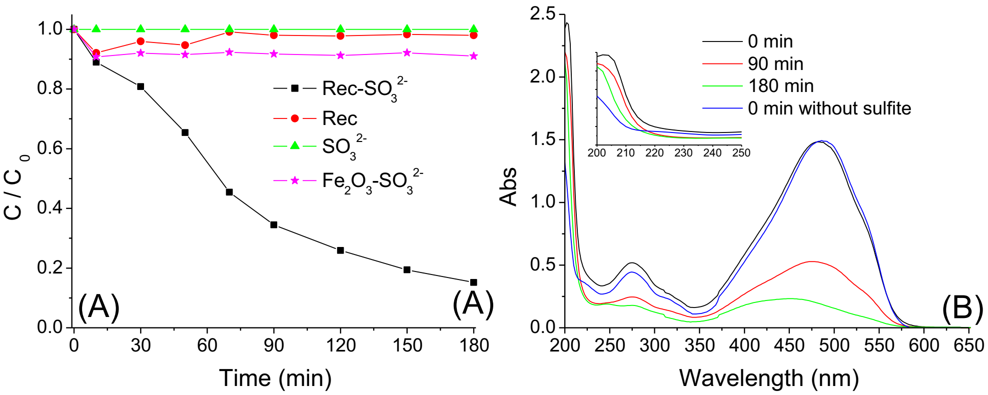

Fig. 1. (A) MO decolorization under different reaction conditions and (B) UV–Vis spectra for MO decolorization by the rectorite-sulfite system. Inset: the enlargement of panel (B) from 200 nm to 250 nm. Conditions: rectorite 2 g/L, a-Fe_2O_3 2 g/L, SO_3^{2-} 5 mmol/L, MO 20 mg/L, pH 3.5, 25 °C.

The solution pH was adjusted by H_2SO_4 and NaOH. The sample solutions were prepared using deionized water throughout the experiments.

2.2. Degradation experiments and analysis

Oxidation reactions were performed in a 250 mL open flask at ambient temperature and under normal laboratory light. The flask was putted in a shaker at a stirring speed of 50 rpm. After the desired amounts of sulfite and MO in 100 mL of the aqueous solution were added into the reactor, pH of the solution was adjusted with diluted H_2SO_4 (0.1 M) and it was not controlled during the reaction. Then the reaction was initialized by adding 0.2 g rectorite. To monitor the organic pollutant degradation process, solution samples were taken out at given time intervals and measured immediately at 464 nm on a Varian Cary 50 Scan UV–Vis spectrophotometer. Total organic carbon (TOC) of the initial and treated samples was determined by an Apollo 9000 TOC analyzer. Electron spin resonance (ESR) spectra were recorded at room temperature using a Bruker ESR A-300 spectrometer with the following parameters: center field 3516 G, sweep width 100 G, microwave frequency 9.86 G, modulation frequency 100 kHz, microwave power 1 mW.

3. Results and discussion

3.1. Characterization of rectorite

Raw rectorite usually coexists with illite, halloysite, gypsum, pyrite and rutile. The sample used in this study contains 70% rectorite and 4.21% Fe expressed as Fe_2O_3 as the main impurity. The catalyst has been extensively characterized by XRF, BET, XRD, FT-IR, TPR and SEM in our previous work [20]. In general, the BET surface area of the sample is 8.2 m^2/g, and the analyses from XRD, FT-IR and TPR imply that Fe in the rectorite mainly presents as the highly dispersed α-Fe_2O_3 clusters.

3.2. Catalytic activity for MO decolorization

The catalytic performance of rectorite–sulfite system with dioxygen as the oxidant at a pH of 3.5 is shown in Fig. 1. From Fig. 1(A) one can see that the system shows high efficiency for MO removal with 85% decolorization after 180 min, while for the experiment with only rectorite, nearly no decolorization occurs, implying that the contribution of adsorption is minor. One can also see that the MO concentration does not decrease exponentially during 180 min for the two systems. This may be attributed to that the adsorption ability of rectorite for MO depends on solution pH (the lower the solution pH, the higher the adsorptivity), but the solution pH is not constant for these experiments. For example, during the adsorption experiment, the solution pH slightly increases due to the adsorption of H^+ by rectorite; while during the decolorization reaction, the solution pH first increases to 4.6, for the simultaneous decrease of H^+, and then decreases to 3.2, due to the oxidation of sulfite and increasing of H^+ concentration. The catalytic or noncatalytic oxidation of sulfite are usually considered as a radical reaction with the production of many species such as $SO_3^{-\bullet}$, $SO_5^{-\bullet}$, $SO_4^{-\bullet}$ and HO• [13]. For the experiment with only sulfite, no decrease of MO concentration was observed, implying that the high reactive radicals such as $SO_4^{-\bullet}$ and HO• can only be produced by the catalytic oxidation. When rectorite is replaced by α-Fe_2O_3 powder the activity also decreases dramatically only with 10% MO removal within 180 min, suggesting that the highly dispersed α-Fe_2O_3 clusters in rectorite are the active species for the reaction. The result is consistent with other

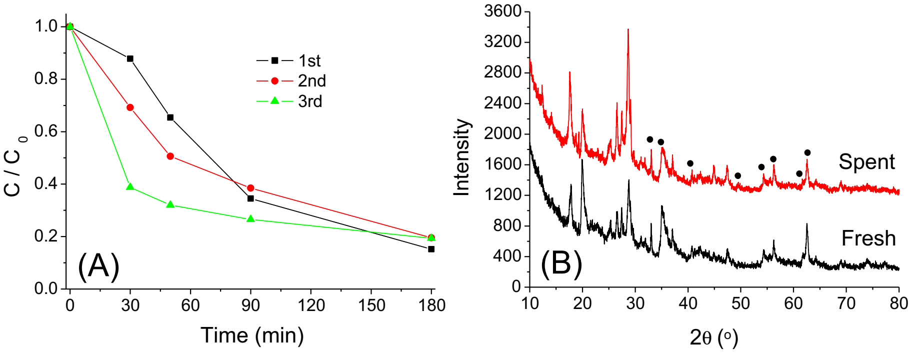

Fig. 2. (A) MO decolorization with the recycled rectorite catalyst and (B) XRD patterns of fresh and spent rectorites. Conditions: Rectorite 2 g/L, SO_3^{2-} 5 mmol/L, MO 20 mg/L, pH 3.5, 25 °C.