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Degradation of methyl orange by heterogeneous Fenton-like oxidation on a nano-organometallic compound in the presence of multi-walled carbon nanotubes

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ABSTRACT

In this study, heterogeneous Fenton-like processes using ferrocene groups immobilized on aluminum-silicate nanoparticles and multi-walled carbon nanotubes (Si/Al@Fe/MWCNT) show a high degradation and decolorization efficiency for methyl orange (MO). The effects of several parameters such as pH, initial H₂O₂ concentration, reaction time, catalyst loading, and temperature on the oxidative degradation and decolorization of MO have been studied. The seven cycles of the Fenton-like processes utilizing the aforementioned catalyst showed the steady removal of MO, thereby demonstrating the high stability of the Si/Al@Fe/MWCNT system over several Fenton oxidation processes. Scavenging of the HO• produced in the reaction media was assessed using n-butanol and KI and confirmed that this radical, which is generated upon decomposition of H₂O₂, is mainly responsible for the heterogeneous Fenton-like oxidation of MO. A feasible Fenton-like oxidation pathway for MO in the presence of the Si/Al@Fe/MWCNT nanocatalyst was proposed. Finally, the degradation of various dyes using the Si/Al@Fe/MWCNT system was compared.

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1. Introduction

Synthetic organic dyes are present in wastewaters from the textile, paper, plastics, leather, food, cosmetics and some other industries. These potential contaminants are very toxic and difficult to remove from contaminated waters using standard and conventional methods, especially when the wastewater contains high concentrations of contaminants (Crini, 2006; Robinson et al., 2001; Bhattacharya, 1992). As such, in order to address this issue, various processes such as precipitation, flocculation, ozonation, adsorption, biological degradation

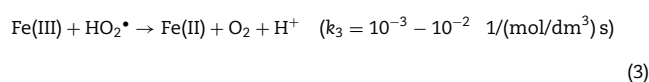
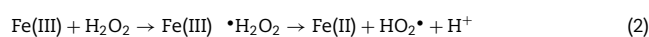
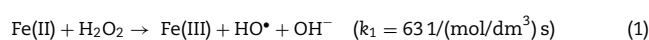
and coagulation have been investigated (Crini, 2006; Robinson et al., 2001; Bhattacharya, 1992; Arshadi et al., 2013, 2014, 2015a,b,c). Indeed, the implementation of advanced oxidation processes (AOPs), including photo-catalytic, electro-catalytic, or Fenton oxidation methods, has interested researchers for many years (Pignatello et al., 2006; Jeon et al., 2014). Of these AOPs, Fenton oxidation has been used for the treatment of various wastewaters as it can be applied at ambient temperature and atmospheric pressure with high oxidation efficiency and uses environmentally benign materials in the presence of dissimilar oxidizing agents, such as hydrogen peroxide, ozone, and oxygen, depending on

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process conditions. Among these, due to its non-toxic and colorless nature, hydrogen peroxide (H_2O_2) is an important oxidizing reagent that is easily converted into environmental friendly products such as water and oxygen. In fact, Fenton oxidation produces hydroxyl radicals that can oxidize a variety of organic pollutants when hydrogen peroxide reacts with transition metal compounds, especially several forms of Fe (see reaction (1)). However, the implementation of homogeneous Fenton oxidation based on ferrous or ferric salts has several limitations, including the conversion of $\text{Fe}(\text{OH})_3$ into sludge at a pH above 3.5. The residual $\text{Fe}(\text{III})$ is removed by increasing the pH and therefore generating a $\text{Fe}(\text{III})$ -oxyhydroxide precipitate after treatment, which deactivates the catalytic activity of the oxidation process by suppressing the rapid regeneration of reactive ferrous ion. In order to minimize the production of iron sludge, low concentrations of $\text{Fe}(\text{III})$ and high concentrations of H_2O_2 have been used to improve the traditional Fenton reagent ($\text{Fe}(\text{II})/\text{H}_2\text{O}_2$). This Fenton-like process ($\text{Fe}(\text{III})/\text{H}_2\text{O}_2$) has been designed based on the catalytic conversion of hydrogen peroxide into hydroxyl radical through reactions (2) and (3), which follow reaction (1).



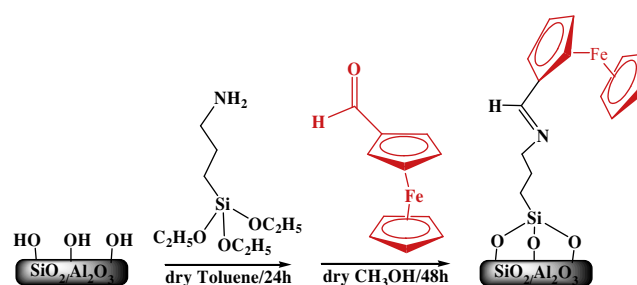
As the production of hydroxyl radical is controlled by reaction (3) (rate-determining step), its production is very slow, although this can be overcome by increasing the rate of reduction of $\text{Fe}(\text{III})$ into $\text{Fe}(\text{II})$ (De Laat and Gallard, 1999). To address the above-mentioned problems, heterogeneous Fenton-like systems in which $\text{Fe}(\text{II})$ or $\text{Fe}(\text{III})$ are grafted onto various organic and inorganic supports have been designed (Ersöz, 2014; Noorjahan et al., 2005).

The preparation of modified bis(η^5 -cyclopentadienyl)iron(II) (ferrocene) compounds continues to play a significant role in organometallic chemistry due to the ease of handling of ferrocene complexes, their non-toxicity, the known thermal and chemical resistance of these species and the ease of modification and flexibility of the cyclopentadienyl rings, all of which promote the formation of an $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ redox couple (Stepnicka, 2008). In 1978 Brynes (Fiorina et al., 1978) demonstrated the anticancer activity of ferrocenyl complexes against the lymphocytic leukemia P388 cell line. As ferrocene can be readily tailored in synthetic chemistry, numerous functionalizations have been incorporated for implementation in several areas, including adsorption, catalysis, sensor and biology (Arshadi et al., 2013; Habibi et al., 2013; Ensafi et al., 2013; Evans, 2010).

Since the discovery of carbon nanotubes (CNTs), scientists have begun to explore their applications due to their unique high electrical conductivity, high surface area and high mechanical, thermal and chemical stability. In this regard, as a filler in nanocomposites, CNTs have shown their potential to increase the mechanical, rheological and electrical properties of nanoparticles because of their high aspect ratio, electrical and thermal conductivity and mechanical strength (Ensafi et al., 2011, 2013; Arshadi et al., 2011, 2012). Indeed, it has been observed that in the presence of carbon materials, especially multi-walled carbon nanotubes (MWCNTs), iron redox cycling in the $\text{Fe}(\text{III})/\text{H}_2\text{O}_2$ system ($\text{Fe}(\text{III})$ into $\text{Fe}(\text{II})$) can be accelerated, thereby promoting the decomposition of H_2O_2 into HO^\bullet (see reaction (4)) (Seo et al., 2015).



The aim of this study is to assess the catalytic performance of ferrocene immobilized on a modified aluminum-silicate nanoparticle as a heterogeneous catalyst in the Fenton-like oxidation of methyl orange (MO), which is a typical azo dye present in textile industry wastewater. Our findings confirmed the preparation of a green, commercially available and low cost catalyst that can be used in the treatment of



Scheme 1 – Procedure for immobilizing ferrocene on modified aluminum-silicate nanoparticles.

non-biodegradable dye from wastewaters using advanced oxidation processes.

2. Experimental

2.1. Materials

All reagents were purchased from Merck or Aldrich and were used without further purification, except for solvents, which were treated according to standard methods. Carbon nanotubes [$>90\%$ MWCNT basis, $d \times l = (110\text{--}70 \text{ nm}) \times (5\text{--}9 \mu\text{m})$] were purchased from Fluka and used it after was washed with concentrated hydrochloric acid (100 cm^3) to remove its iron impurities.

2.2. Preparation of the organometallic functionalized nanosized $\text{SiO}_2\text{--Al}_2\text{O}_3$ mixed-oxides

Aluminum-silicate nanoparticles (ASNPs) were used as the support. The supported ferrocene was prepared using the sol-gel method according to the literature and was fully characterized (Arshadi et al., 2013, 2015d; Ensafi et al., 2013). ANSP-supported 3-aminopropyl was prepared by refluxing 5.2 g $\text{SiO}_2\text{--Al}_2\text{O}_3$ (1:1) that had been activated at 550°C for 6 h under air with 3.5 cm^3 (0.0195 mol) of 3-aminopropyltrimethoxysilane in dry dichloromethane (100 cm^3) for 24 h. The solid was filtered, washed with methanol and dichloromethane and dried at 100°C under vacuum for 6 h. The functionalized ASNPs are referred to hereafter as $\text{Si}/\text{Al}\text{-pr-NH}_2$. Subsequently, ferrocenecarbaldehyde (FCA) was added to a suspended solution of $\text{Si}/\text{Al}\text{-pr-NH}_2$ in dry methanol. The mixture was refluxed for 48 h to prepare an organometallic compound ($\text{Si}/\text{Al}\text{-pr-N} = \text{ferrocene}$, identified as $\text{Si}/\text{Al}@\text{Fe}$) (see Scheme 1) on the surface of the ASNPs. The resulting material (dirty red powder) was then filtered off, washed with copious amounts of ethanol and methanol, and finally dried under vacuum at 60°C .

2.3. Preparation of $\text{Si}/\text{Al}@\text{Fe}/\text{MWCNT}$

90 mg of $\text{Si}/\text{Al}@\text{Fe}$ was mixed with 10 mg of multi-walled carbon nanotubes in a mortar and pestle (see Fig. 1) and the resulting mixture mixed well for 40 min to obtain a uniform $\text{Si}/\text{Al}@\text{Fe}/\text{MWCNT}$, which was then kept in a glass tube before use.

2.4. Characterization

Transmission electron microscopy (TEM) was carried out on powdered samples using a Tecnai F30 TEM operating at an accelerating voltage of 300 kV. The H_2O_2 concentration was

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