Journal of Environmental Management 213 (2018) 392–399

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

A novel system of MnO_2-mullite-cordierite composite particle with NaClO for Methylene blue decolorization

Suli Zhi [a], Liang Tian [b], Nan Li [c, **], Keqiang Zhang [a, *]

[a] Agro-Environmental Protection Institute, Ministry of Agriculture, Tianjin, 300191, China
[b] Hebei University of Technology, Tianjin, 300132, China
[c] Wuhan Environmental Monitoring Center, Wuhan, 430000, China

A R T I C L E I N F O

Article history:
Received 30 November 2017
Received in revised form
20 February 2018
Accepted 23 February 2018

Keywords:
Commercial NaClO
MnO_2-mullite-cordierite composite
Fenton-like reaction
Methylene blue
Decolorization

A B S T R A C T

The MnO_2-mullite-cordierite composite particle (MnO_2-MCP) was prepared and firstly was applied as catalyst with sodium hypochlorite (NaOCl) as oxidant in heterogeneous Fenton-like system for methylene blue (MB) decolorization. The MnO_2-MCP was characterized by XRD, SEM, EDS and BET analysis. The decolorization efficiencies of MB/MnO_2-MCP, MB/NaClO, (MB after filtrating MnO_2-MCP)/NaClO and MB/MnO_2-MCP/NaClO were compared, which confirmed the interaction ability between MnO_2-MCP and NaClO. After evaluating the role of adsorption of MB by MnO_2-MCP, the catalytic oxidation effects of MnO_2-MCP with NaClO on MB were exploited. The adsorption results showed that the new porous catalyst had certain adsorption capacity for MB and the adsorption fit best with Langmuir model. The central composite rotatable design (CCD) of response surface methodology (RSM) was used to design catalytic oxidation experiments of MB/MnO_2-MCP/NaClO system, with influencing factors of catalyst dose, NaClO concentration, pH and initial MB concentration. The optimum conditions were 5.97 mM of NaClO, 37.9 g/L of catalyst dose, 5.74 of pH value and 100.71 mg/L of initial MB concentration, which could ensure nearly 100% MB decolorization. The effect of radical scavengers elucidated that superoxide anion (O_2^-) was the main species to decolorize MB. Then the possible degradation mechanism and pathway of MB were proposed in this MnO_2-MCP/NaClO system.

1. Introduction

Catalytic oxidation, such as Fenton or Fenton-like process, has become an increasingly attractive and important method for degrading organic pollutants in aqueous solution. In recent years, research efforts in this field have been focused on developing new catalyst materials with high activity, low costs and large applicable range (Ramesh et al., 2016; Bhuyan et al., 2015; Shayesteh et al., 2017). In another side, the concern on optimizing oxidant utilizing are also increasing, for lower dosage, higher efficacy and so on (Sohrabi and Ghavami, 2008; Abbasi and Razzaghi-Asl, 2008). Among all the catalysts and oxidants, this study will focus on the MnO_2-mullite-cordierite composite particle (MnO_2-MCP) and NaClO to decolorize methylene blue (MB) wastewater. The details of introduction and explanations are as following.

1.1. Cordierite and cordierite-mullite materials

Cordierite, expressed as $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$, usually has low thermal expansion coefficient, excellent thermal shock resistance, low dielectric constant, high volume resistivity, high chemical durability, relatively high refractoriness and high mechanical strength (Ramezani et al., 2017). In the past years, cordierite ceramics has been mainly applied in heat exchanger, gas turbines, porous membranes and so on (Thomaidisn and Kostakis, 2015; Wu et al., 2013; Chowdhury et al., 2007). Recently, cordierite materials are increasingly used as catalyst support (Li et al., 2016; Azalim et al., 2013), for its low cost, low pressure drop, good resistance and so on (El-Shobaky et al., 2012). Mullite is the secondary phase of cordierite, which is usually formed for the un-controlled reactions. In cordierite-mullite materials, cordierite usually supplies thermal resistance, while mullite provides the strength needed (Ibrahim et al., 1995). Cordierite-mullite composites can be made by different methods, as many researchers reported (Ibrahim et al.,

* Corresponding author.
** Corresponding author.
E-mail addresses: zhisuli87@163.com (S. Zhi), tianliangg@sina.com (L. Tian), 13720301564@163.com (N. Li), keqiangzhang68@163.com (K. Zhang).

https://doi.org/10.1016/j.jenvman.2018.02.082
0301-4797/

1995; Albhilil et al., 2013; Khattab et al., 2012).

For the excellent properties, cordierite, mullite or cordierite-mullite materials are widely used. They are abundant and easy to obtain. Especially, the used or non-used materials can be reused as catalyst support, after modified or activated. Up to now, cordierite, mullite or cordierite-mullite materials have been successfully used as a catalyst support for CuO-Mn_2O_3, Ce-Zr-Mn mixed oxides, MgO, Co_3O_4, Mn_2O_3, CuO, Fe_2O_3 and NiO (Li et al., 2016; Azalim et al., 2013; El-Shobaky et al., 2012; Dong et al., 2011; El-Shobaky and Fahmy, 2006a; Radwan et al., 2004; El-Shobaky and Fahmy, 2006b). However, most of these studies focused on the gaseous substances catalytic oxidation process (unburned hydrocarbons, carbon monoxide and nitric oxides etc.), few on catalytic oxidation of contaminants in wastewater. In this study, we will present a new insight of used cordierite-mullite composites as support for MnO_2 in wastewater purification.

1.2. MnO_2

As we know, precious metals as well as transition metal oxides are known to be active phase in oxidation of different pollutants (Barakat et al., 2011; Wyrwalski et al., 2010). Precious metals usually have higher activity compared to transition metal oxides; however, they are not only expensive but also susceptible to poisoning. Transition metal oxides now are acting as one of the most important and widely applied classes of solid catalyst, either as active phase or as support (Azalim et al., 2013). Up to now, different transition metal oxides have been exploited, such as Al_2O_3, La_2O_3, ZrO_2, TiO_2, CeO_2, CuO and Mn_2O_3 (Azalim et al., 2013; El-Shobaky et al., 2012; Azalim et al., 2011).

Among these different transition metal oxides, MnO_x has received the attention of many researchers. MnO_2 has been considered as a kind of promising material for its low toxicity, low volatility (Li et al., 2016; Azalim et al., 2013; El-Shobaky et al., 2012), high stability, relatively low cost, abundant source and environmental-compatibility (He et al., 2018). For wastewater treatment, He et al. (2018) synthesized MnO_2 nanosheets on montmorillonite for oxidative degradation and adsorption of methylene blue in wastewater. Fathy et al. (2013) used a novel nanocomposite catalyst, MnO_2 on multi-walled carbon nanotube, with H_2O_2, for catalytic oxidation of an anionic reactive blue 19 (RB19) dye solution. Bao et al. (2017) exploited gold nanoparticles on MnO_2 nanosheets with H_2O_2, for the enhanced oxidative degradation of basic dye. However, no one has shown the performance of the catalyst with MnO_2 on cordierite-mullite materials in wastewater treatment, especially with the oxidizing agent of NaClO.

1.3. Sodium hypochlorite

Fenton or Fenton-like processes are widely used for MB degradation due to the high redox potential radicals ($\cdot OH$ or $SO_4\cdot^-$) generated by H_2O_2 or persulfate (Liu et al., 2013; Shahwan et al., 2011; Yang et al., 2009; Liang et al., 2012; Noubactep, 2009). Sodium hypochlorite (NaClO) also has the potential of producing nascent oxygen species. Similar to the decomposition character of H_2O_2 (Bokare and Choi, 2014), NaClO is known to slowly self-decompose in solution but could rapidly decompose to chloride and oxygen in the presence of the metal ions such as nickel, cobalt, iron, manganese and copper (Kim et al., 2012), as shown in Eqs. (1) and (2). Meanwhile, it was also certificated that the metal ions could not accelerate the decomposition to chlorate and chloride (Lister, 1956).

$$H_2O_2 \xrightarrow{metals} H_2O + O_2 \tag{1}$$

$$NaClO \xrightarrow{metals} NaCl + O_2 \tag{2}$$

Being used widely in industry for surface purification, bleaching, water purification or chemicals synthesis, NaClO (~450 RMB/t, 10%) is much cheaper than H_2O_2 (~1600 RMB/t, 30%) and persulfate (~8500 RMB/t). In previous researches, commercial NaClO was once directly used as the oxidant to decolorize MB, and the chromophoric groups in MB molecule could be destroyed by NaClO through forming HClO or Cl_2 under certain pH values. However, the method turned out to be ineffective due to the pH regulation, large scale consumption of NaClO and the formation of organochlorides (Pizzolato et al., 2002). However, NaClO is never considered as the Fenton-like oxidant same to the analogic mode of H_2O_2 by researchers before. So this study will give a novel evidence of NaClO being oxidant in the Fenton-like process.

1.4. Methylene blue

Methylene blue (MB), a heterocyclic aromatic compound, is the most commonly used substance for cotton dying, chemical indicator or biological stain. However, it can result in permanent burns to the eyes of human and animals, nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia (El-Sharkawy et al., 2007). Besides, the stability of the dye molecule makes it difficult to decompose naturally. As a result, serious environmental problems may arise from the hazardous, pathogenic and hard-to-decolorized nature of MB. Therefore, MB degradation has attracted considerable attention in the environmental field.

In this study, commercial NaClO is firstly regarded as the Fenton oxidant to decolorize methylene blue (MB). The material of MnO_2-mullite-cordierite composite particle (MnO_2-MCP) is applied as the heterogeneous Fenton catalyst from the perspective of catalyzing NaClO decomposition and reducing NaClO consumption. In order to evaluate the role of adsorption by MnO_2-MCP, sorption experiments are firstly conducted under various chemical conditions. Then the decolorization ability of the Fenton-like system formed with commercial NaClO and MnO_2-MCP was investigated. Therefore, the main purpose of this study is focusing on the following aspects: (1) characterization of MnO_2-MCP; (2) adsorption of MB by MnO_2-MCP; (3) decolorization of MB by NaClO/MnO_2-MCP under different operational conditions; (4) durability of MnO_2-MCP and (5) possible reaction mechanisms and products.

2. Materials and methods

2.1. Materials

All chemicals used in the study are of analytical grade and purchased from Jiangtian industrial chemicals, Tianjin, China. Sodium hypochlorite (NaClO) was titrated by $Na_2S_2O_3$ before use in order to quantify the concentration of sodium hypochlorite. Mullite-cordierite composite (MCP) is obtained from Tohkemy Corporation, Japan.

2.2. Preparation of MnO_2-MCP

The preparation of MnO_2-MCP was according to the existing method in a report (Fathy et al., 2013). Simply, the obtained MCP can be acted as supporting materials with a high surface area for the formation of MnO_2 nanoflakes. Afterwards, about 0.2 g of the MCP was dispersed into 300 ml of 0.1 M $KMnO_4$ solution under