Degradation of refractory dibutyl phthalate by peroxymonosulfate activated with novel catalysts cobalt metal-organic frameworks: Mechanism, performance, and stability

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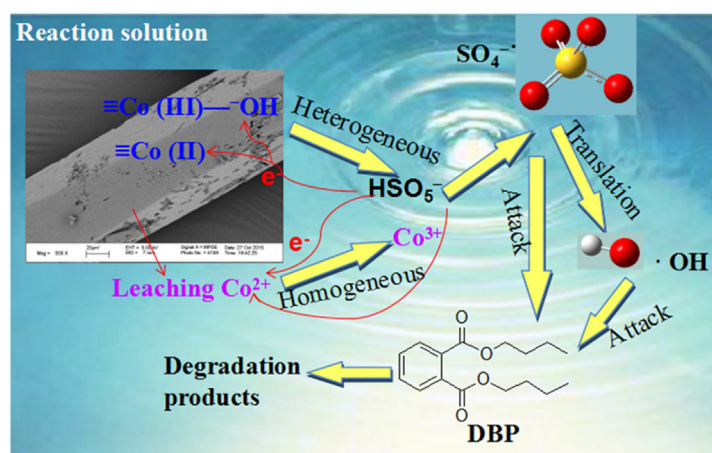[a] School of Environment and Energy, South China University of Technology, Guangzhou 510006, PR China
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HIGHLIGHTS

- $Co_3(BTC)_2 \cdot 12H_2O$ (Co-MOFs) has been tested for the first time to activate PMS.
- The pH showed DBP degradation rate with rank of 5.0 > 2.75 > 9.0 > 7.0 > 11.0.
- Co-MOFs displayed excellent reusability on PMS activation and DBP removal.
- The activation mechanism involved in homogeneous and heterogeneous reactions.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

In this work, a new effective and relatively stable heterogeneous catalyst of Metal-Organic Framework $Co_3(BTC)_2 \cdot 12H_2O$ (Co-BTC) has been synthesized and tested to activate peroxymonosulfate (PMS) for removal of refractory dibutyl phthalate (DBP). Co-BTC(A) and Co-BTC(B) were synthesized by different methods, which resulted in different activity towards PMS. The results indicated that Co-BTC(A) showed better performance on DBP degradation. The highest degradation rate of 100% was obtained within 30 min. The initial pH showed respective level on DBP degradation with a rank of 5.0 > 2.75 > 9.0 > 7.0 > 11.0 in PMS/Co-BTC(A) system. No remarkable reduction of DBP was observed in the catalytic activity of Co-BTC(A) at 2nd run as demonstrated by recycling. However, the DBP degradation efficiency decreased by 8.26%, 10.9% and 25.6% in the 3rd, 4th, and 5th runs, respectively. The loss of active catalytic sites of Co(II) from Co-BTC(A) is responsible for the activity decay. Sulfate radicals ($SO_4^{\bullet-}$) and hydroxyl radicals ($^{\bullet}OH$) were found at pH 2.75. Here,

we propose the possible mechanism for activation of PMS by Co-BTC(A), which is involved in homogeneous and heterogeneous reactions in the solutions and the surface of Co-BTC(A), respectively.

1. Introduction

In recent years, sulfate radical ($SO_4^{•-}$)-based oxidation processes have evoked more general interest in the field of wastewater treatment. The redox potential of $SO_4^{•-}$ is 2.5–3.1 V vs. normal hydrogen electrode (NHE), slightly higher than that of hydroxyl radical ($^•OH$) (1.9–2.7 V vs. NHE) [1]. As a result, $SO_4^{•-}$ could degrade a lot of refractory organic contaminants into innocuous or marginally toxic small compounds, or even thoroughly mineralize into carbon dioxide and water [2,3]. In general, $SO_4^{•-}$ reacts with organic pollutants via a one-electron transfer mechanism while $^•OH$ has a preference for hydrogen abstraction or addition reaction [4], which gives $SO_4^{•-}$ a longer half-time [5]. Additionally, $SO_4^{•-}$ is relatively stable and often less influenced by the operating pH relative to $^•OH$ [6,7], rendering $SO_4^{•-}$ more efficient for usage. Most often, $SO_4^{•-}$ can be produced by activation of persulfate (PS) or peroxymonosulfate (PMS) with extra energy and/or catalysts [8–10]. PS and PMS are two widely used oxidizing reagents to generate $SO_4^{•-}$, and both of them are commercially available. Of the two, PMS is more reactive to generate $SO_4^{•-}$ due to its asymmetric structure. In addition, PMS has been reported to decompose rapidly and yield O_2 (Eq. (1)) when the solution pH is about 10 [11], then Fenton reaction would occur and result in

$$HSO_5^- + SO_5^{2-} \rightarrow 2SO_4^{2-} + O_2 + H^+ \qquad (1)$$
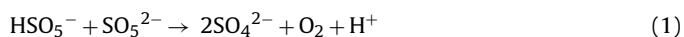
organic pollutants removal, illustrating that PMS is suitable for use in a wide pH and also could automatically adjust the solution pH with the production of H^+ (Eq. (1)).

The chemical properties of PMS make it a potentially important oxidant in Advance Oxidation Processes (AOPs). Therefore, studies were initiated to obtain the data for the evaluation of the potentiality of PMS as an oxidant for generation of $SO_4^{•-}$ and removal of organic compounds [11–13]. It was reported that Co^{2+} was the best catalyst for decomposition of PMS to generate $SO_4^{•-}$ compared to the other transition metal ions, such as Cu^{2+}, Mn^{2+}, Fe^{2+}, and Ag^+ [12]. Fernandez et al. [14] also found that Co^{2+} possessed the best catalytic property under simulated sunlight and effectively destructed Orange II. Nevertheless, as one of the toxic heavy metals, the use of cobalt may not be conducive to human health and the quality of the environmental systems due to Co^{2+} leaching [10], which limits its use in application [15]. Thus, much effort has been made to discover an alternative catalyst to overcome this drawback and avoid secondary pollution. The efficient heterogeneous cobalt catalyst would be a good candidate for such a purpose, such as cobalt oxides [13], cobalt-SBA-15 [16] and cobalt complexes. Deng et al. [13] found that nano-sized magnetic catalyst $CoFe_2O_4$ showed high activity on activation of oxone for degradation of diclofenac. Chen et al. [17] observed that Co_3O_4 exhibited good heterogeneous activity and low dissolved cobalt ions especially at neutral conditions. Shi et al. [18] synthesized Co_3O_4/GO as the heterogeneous catalysts of PMS, which exhibited an unexpectedly high catalytic activity for degradation of Orange II.

Metal-organic frameworks (MOFs) are a relatively new class of microporous and crystalline materials that are composed of metal ions and organic ligands by acting as the "nodes" and the "bridges" respectively [19]. MOFs also exhibit promising characteristics such as controllable pore volume, high surface area, multiple functionalities, high catalytic activity, etc. These characteristics could be achieved through design and synthesis with various species of metals and organics [20], which has raised attention in recent years. It is well known that oxidants such as H_2O_2, PS and PMS can be activated by transition metal ions to generate free radicals and degrade organic pollutants. Some MOFs are expected to be potential heterogeneous activators of PMS because of their transition metal ion constituents. Lin et al. [21] investigated MIL-88A as heterogeneous photocatalysts of PS for removal of toxic pollutants in water. Du et al. [22] employed MIL-53(M) (M = Al, Fe, Cr) as photocatalysts to activate H_2O_2, $KBrO_3$ and $(NH4)_2S_2O_8$, and these MOFs displayed a good degradation efficiency on methylene blue dye. Wang et al. [23] also reported that a highly selective benzene hydroxylation to phenol could be achieved over MIL-100(Fe) and MIL-68(Fe) under visible light irradiation using H_2O_2 as the oxidant. Therefore, it is reasonable to deduce that cobalt MOFs would be very helpful for the advancement of PMS-based oxidation processes.

Herein, the purpose of the present work is to evaluate the catalytic activity of Co-based MOFs ($Co_3(BTC)_2 \cdot 12H_2O$ (Co-BTC)) as the activator of PMS for degradation of dibutyl phthalate (DBP) in water. DBP is preferentially chosen because it is one of the most widely used phthalic acid esters (PAEs) [24] and easily releases into the environment due to its volatility. Moreover, it is suspected to be toxic and carcinogenic, leading to serious health problems such as peripheral polyneuritis, myelo meningitis, and multiple neuritis [25,26]. In addition, DBP is difficult to destruct by conventional methods because of its stable chemical structure and long chains [27].

In this study, Co-BTC was synthesized by two different methods. The performance of catalysts was investigated. Factors influencing the performance were studied, as well as the possible catalytic mechanism of PMS over Co-BTC. The development of highly efficient and environmentally benign oxidation processes has proven to be a significant challenge. Hence, the findings of this study will highlight the potential of developing MOFs as heterogeneous catalysts for pollutants degradation.

2. Materials and methods

2.1. Materials

Details of all chemicals used in this study are included in the Supporting Information (Text S1).

2.2. Preparation of Co-BTC

Details of the preparation of Co-BTC by two methods are included in the Supporting Information (Text S2).

2.3. Characterization

Details of characterization of Co-BTC with the Field emission scanning electron microscope (FESEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR), Photoelectron spectroscopy (XPS), and Brunauer-Emmett-Teller (BET) surface areas are displayed in the Supporting Information (Text S3).