



Prussian blue analogue derived magnetic carbon/cobalt/iron nanocomposite as an efficient and recyclable catalyst for activation of peroxymonosulfate



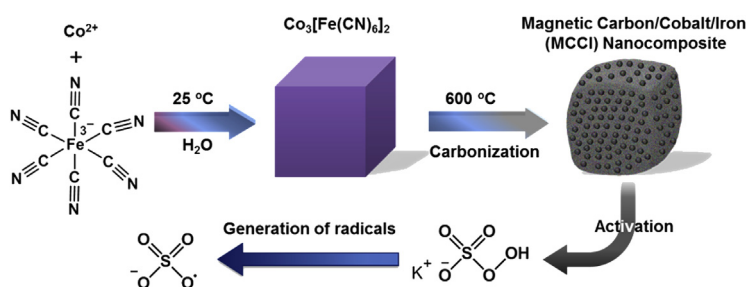
Kun-Yi Andrew Lin*, Bo-Jau Chen

Department of Environmental Engineering, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung, Taiwan

HIGHLIGHTS

- A magnetic carbon/cobalt/iron (MCCI) nanocomposite is prepared from PB analogue.
- MCCI contains cobalt and cobalt ferrite species dispersed in a porous carbon matrix.
- Factors affecting PMS activation by MCCI are studied via degradation of Rhodamine B.
- MCCI shows a higher catalytic activity than Co_3O_4 for activating PMS to degrade RhB.
- MCCI is reused multiple times without loss of catalytic activity for activating PMS.

GRAPHICAL ABSTRACT



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ABSTRACT

A Prussian blue analogue, cobalt hexacyanoferrate $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$, was used for the first time to prepare a magnetic carbon/cobalt/iron (MCCI) nanocomposite via one-step carbonization of $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$. The resulting MCCI consisted of evenly-distributed cobalt and cobalt ferrite in a porous carbonaceous matrix, making it an attractive magnetic heterogeneous catalyst for activating peroxymonosulfate (PMS). As Rhodamine B (RhB) degradation was adopted as a model test for evaluating activation capability of MCCI, factors influencing RhB degradation were thoroughly examined, including MCCI and PMS dosages, temperature, pH, salt and radical scavengers. A higher MCCI dosage noticeably facilitated the degradation kinetics, whereas insufficient PMS dosage led to ineffective degradation. RhB degradation by MCCI-activated PMS was much more favorable at high temperatures and under neutral conditions. The presence of high concentration of salt slightly interfered with RhB degradation by MCCI-activated PMS. Through examining effects of radical scavengers, RhB degradation by MCCI-activated PMS can be primarily attributed to sulfate radicals instead of a combination of sulfate and hydroxyl radicals. Compared to Co_3O_4 , a typical catalyst for PMS activation, MCCI also exhibited a higher catalytic activity for activating PMS. In addition, MCCI was proven as a durable and recyclable catalyst for activating PMS over multiple cycles without efficiency loss and significant changes of chemical characteristics. These features demonstrate that MCCI, simply prepared from a one-step carbonization of $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$ is a promising heterogeneous catalyst for activating PMS to degrade organic pollutants.

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* Corresponding author.

E-mail address: linky@nchu.edu.tw (K.-Y.A. Lin).

1. Introduction

Advanced oxidation processes (AOPs) represent one of the most important reactions for environmental pollution control (Oturán and Aaron, 2014; Ikehata et al., 2006; Klavarioti et al., 2009). AOPs typically involve using high oxidation potential radicals (e.g., hydroxyl (OH[•]) and sulfate (SO₄^{•-}) radicals (Glaze and Kang, 1989; Tsitonaki et al., 2010)) to degrade organic contaminants. While hydroxyl radicals-generating processes have been well developed (e.g., Fenton reaction), recently sulfate radicals-generating processes also gain enormous attention because of the following merits (Hu and Long, 2016). Sulfate radicals can possess comparable or even higher oxidation potentials (i.e., 2.5–3.1 V vs the normal hydrogen electrode (NHE)) than hydroxyl radicals (i.e., 2.8 V) (Neta et al., 1988). Sulfate radicals also exhibit a higher selectivity for attacking unsaturated and aromatic electrons (Neta et al., 1988; Antoniou et al., 2010); the half-life of sulfate radicals is longer than that of hydroxyl radicals (Olmez-Hanci and Arslan-Alaton, 2013; Janzen et al., 1992).

To obtain sulfate radicals, peroxymonosulfate (PMS) is usually used as an environmentally-friendly and easy-to-access reagent (Hu and Long, 2016); however, the generation of sulfate radicals from PMS in water is impractically slow. Thus, many approaches have been developed in order to facilitate decomposition of PMS for generation of sulfate radicals (so-called PMS activation). These approaches include heating (Yang et al., 2010; Huang et al., 2002), light irradiation (Yang et al., 2010; Gao et al., 2012), acoustics (Li et al., 2013; Kurukutla et al., 2014), as well as addition of catalysts (Anipsitakis et al., 2005; Wei et al., 2015; Lin et al., 2015a, 2015b). Since heating, light irradiation and acoustics require intensive and constant energy consumption, addition of catalysts appears as a more practical approach for activating PMS (Yang et al., 2009).

While various catalysts have been proposed to activate PMS (Lin et al., 2015a, 2015b; Lin and Chen, 2016; Oh et al., 2016; Andrew Lin and Zhang, 2016), metallic catalysts (e.g., cobalt, copper, iron and manganese) are proven to activate PMS (Oh et al., 2016, 2014, 2015) effectively. Particularly, cobalt is considered as the most efficient non-noble metallic catalyst for PMS activation (Yang et al., 2009; Cai et al., 2015). Thus, a number of studies had demonstrated adding cobalt ions (i.e., Co²⁺) directly to solutions for activating PMS (Guo et al., 2015; Do et al., 2009; Wacławek et al., 2015; Chan and Chu, 2009). However, homogeneous cobalt ions added to solutions cannot be easily recovered, leading to secondary pollution. Thus, cobalt oxide (e.g., Co₃O₄) and related nanoparticles are proposed as a heterogeneous catalyst for activating PMS (Anipsitakis et al., 2005; Chen et al., 2008). Nevertheless, these cobalt-based nanoparticles tend to aggregate, diminishing the catalytic activity of cobalt (Anipsitakis et al., 2005; Chen et al., 2008; Guo et al., 2013). In view of this issue, a number of attempts have been made to anchor nanoscale cobalt and related particles to substrates. By anchoring nanoscale cobalt-based particles to supports, release of nanoparticles to the environment can be prevented (Yang et al., 2007), and nanoscale catalysts can be also evenly distributed on supports or within substrates to facilitate PMS activation (Yang et al., 2007).

Up to date, various substrates have been used to anchor cobalt/cobalt oxide nanoparticles, including SiO₂ (Yang et al., 2008), TiO₂ (Zhu et al., 2013; Du et al., 2016), Al₂O₃ (Yang et al., 2008), MnO₂ (Liang et al., 2012), fly ash (Muhammad et al., 2012) and carbonaceous materials (Lin et al., 2015b; Xu et al., 2015a; Yao et al., 2012; Wang et al., 2016; Shi et al., 2013; Zhou et al., 2015; Xu et al., 2015b). Among these supports, carbonaceous materials are particularly attractive because carbon is a non-metal and abundant element. Carbon materials also possess many advantageous properties, such as chemical inertness, and high electrical conductivity (Huang et al., 2016). In addition, carbon materials can be designed and prepared

to exhibit various morphologies, including spheres and sheets (Wang et al., 2014; Lin et al., 2015b), for anchoring cobalt oxide particles.

Even though carbon/cobalt composites are favorable heterogeneous catalysts for activating PMS, fabrication of these cobalt-containing carbonaceous composites is usually sophisticated, involving multiple-steps and long preparation time. Thus, development of an easy-to-prepare carbon/cobalt composite is still necessary. Moreover, recovery of catalysts is also an important aspect of using heterogeneous catalysts. Therefore, the desired carbon/cobalt composites should be also magnetic, allowing it to be easily recovered from solutions (Xu et al., 2015a; Wang et al., 2014). Typically, equipping substrates with magnetism involves post-modifications by decorating substrates with magnetic nanoparticles (Lin et al., 2015c; Lili et al., 2014). However, this method requires additional reagents and relatively long preparation time. A more convenient approach to enable catalysts to be magnetic should be developed. In view of these requirements, we propose to employ a cobalt-containing Prussian blue analogue (PBA) as a precursor for preparing such a magnetic carbon/cobalt nanocomposite. PBAs, represented as M^(II)₃[M^(III)(CN)₆]₂ frameworks, are easy-to-prepare but intriguing and versatile materials which have been widely employed in many areas, such as catalysis (Pintado et al., 2013), electronic (Itaya et al., 1986) and adsorption/separation applications (Torad et al., 2012; Kaye and Long, 2005). Nevertheless, to our best knowledge, PBAs have not been adopted as precursors to prepare carbon/cobalt nanocomposites for activating PMS.

Thus, in this study, we specifically select a cobalt-containing PBA, cobalt hexacyanoferrate (Co₃[Fe(CN)₆]₂), and convert it for the first time to obtain a magnetic carbon/cobalt/iron (MCCI) nanocomposite via a one-step carbonization. The as-prepared MCCI was characterized by electronic microscopies, X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), N₂ sorption/desorption isotherms, thermogravimetric (TG) analysis as well as saturation magnetization analysis. The resulting MCCI consisted of evenly-distributed cobalt/cobalt oxide and cobalt ferrite in a porous carbonaceous matrix, making it an attractive magnetic heterogeneous catalyst for activating PMS. To evaluate catalytic activity of MCCI for activating PMS, degradation of a toxic dye Rhodamine B (RhB) by MCCI-activated PMS was employed as a model test as dye-containing wastewater treatment has been intensively investigated using many approaches, including adsorption (Jiang et al., 2016; Gupta and Suhas, 2009), chemical oxidation (Arslan et al., 2000) and biological degradation (Banat et al., 1996).

Factors influencing RhB degradation by MCCI-activated PMS were examined, including MCCI and PMS dosages, temperature, pH, and salt. Effects of radical scavengers were also investigated to reveal the RhB degradation mechanism by MCCI-activated PMS. Recyclability of MCCI for activating PMS was also evaluated by reusing MCCI to activate PMS for multiple cycles.

2. Experimental

2.1. Materials

Chemicals involved in this study were commercially available and used directly without purification. Potassium hexacyanoferrate (K₃Fe(CN)₆) was purchased from J. T. Baker (Germany). Potassium peroxymonosulfate (PMS), Rhodamine B (RhB) and potassium iodide (KI) were obtained from Sigma-Aldrich (USA). Cobalt nitrate (Co(NO₃)₂) was obtained from Choneye Pure Chemicals (Taiwan). *tert*-butyl alcohol (TBA) was purchased from Alfa Aesar (USA). Methanol was obtained from Echo Pure Chemicals (Taiwan). Deionized (DI) water was prepared to less than 18 Megohm-cm.

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