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Magnetic biochar catalyst derived from biological sludge and ferric sludge using hydrothermal carbonization: Preparation, characterization and its circulation in Fenton process for dyeing wastewater treatment

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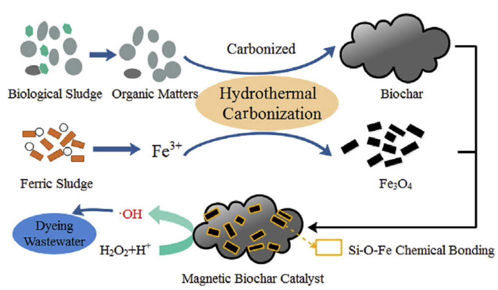
HIGHLIGHTS

- Sludge derived from the dyeing wastewater treatment process were converted into a magnetic biochar catalyst under hydrothermal conditions.
- The optimal catalyst preparation conditions were evaluated.
- The nano-level magnetic biochar catalyst showed excellent characteristics to promote a heterogeneous Fenton reaction to treat dyeing wastewater.
- Biochar and Fe_3O_4 in the magnetic biochar catalyst were found to be tightly combined through chemical bonding.
- A methodology is described that resource sludge and enables it internal recycling in a dyeing wastewater treatment plant.

GRAPHICAL ABSTRACT



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ABSTRACT

To solve sludge disposal and management problems during dyeing wastewater treatment, the produced excess biological sludge and ferric sludge were fabricated into a magnetic biochar composite (MBC) under the optimal hydrothermal carbonization (HTC) conditions. With ferric sludge mixing, the generated MBC contained paramagnetic Fe_3O_4, showed a smaller diameter of approximately 200 nm, a smaller pore size, a larger specific surface area and a higher carbonization degree than BC prepared using a single biological sludge process under the same HTC conditions. Additionally, biochar and Fe_3O_4 in the MBC were found to be tightly combined through chemical bonding, imparting MBC with its own property of magnetic recycling. The stable high Methylene Blue (MB) degradation performance in a Fenton reaction after recycling designated it as a good catalyst. The MB degradation pathway was proposed based on GC–MS results. When the MBC was used to treat actual dyeing wastewater through a Fenton process, the chemical oxygen demand (COD) and total organic carbon (TOC) removal efficiencies reached 47 ± 3.3%

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and 49 ± 2.7%, respectively. Therefore, MBC could be recycled as a catalyst in dyeing wastewater treatment. And a methodology is described that minimizes the produced sludge and enables sludge internal recycling in a dyeing wastewater treatment plant.

1. Introduction

Dyeing wastewater is a typical refractory industrial wastewater because of its complex composition, deep color and high risk to the environment and ecosystems when improperly discharged to the surroundings. In recent years, the Chinese discharge standards for textile dyeing wastewater have gradually become more stringent because of the deterioration of environment quality. New *Discharge standards of water pollutants for dyeing and finishing of textile industry* (GB 4287-2012) have replaced the previous standards (GB 4287-92). The water quality of dyeing wastewater after traditional biological process treatment does not always meet the current standard. Therefore, combined processes, i.e., Fenton or Fenton-like processes for textile dyeing wastewater as pretreatment, followed by biological oxidation, have been extensively applied (Blanco et al., 2012). Additionally, the discharge volume of textile dyeing wastewater was approximately 1.84 billion tons in 2015, making it the third largest source of Chinese industrial wastewater (China Environmental Statistical Yearbook in 2014). Therefore, a huge volume of ferric sludge from the Fenton process and excess biological sludge from biological oxidation is produced by the combined process.

The cost of sludge disposal is almost one-third of the total operation cost and is a bottleneck in Chinese low-margin textile enterprise development (Kalderis et al., 2010). In China, incineration and sanitary landfill are the main disposal methods for dyeing sludge (Lin et al., 2014). However, territorial resources are becoming increasingly scarce because of accelerating urbanization in China. Incineration is not a valid alternative because of its secondary pollution (Lin et al., 2014; Hu et al., 2015). For these reasons, the development of a green and sustainable sludge disposal technology is needed. Thermal conversion provides an alternative approach for the reutilization of sludge and comprises pyrolysis, gasification and hydrothermal carbonization (HTC) (Bien and Wystalska, 2015; Wiedner et al., 2013a,b). As an effective sludge resourcing method, it can be used to valorize sludge and convert it into a valuable solid product called biochar (BC) (Khan et al., 2013; Liu et al., 2016; Van et al., 2014; Wu et al., 2016). However, technologies such as pyrolysis and gasification require pretreatment to reduce the sludge moisture content and have disadvantages of high energy consumption, high pollution and complex operation (Funke and Ziegler, 2010; He et al., 2013; Monte et al., 2009).

Hydrothermal carbonization is a mild thermal conversion process that requires short reaction times in a relatively low temperature range (453–523 K), with corresponding pressures less than 45 bar (Fakkaew et al., 2015). Due to its adaptability for high-moisture feedstock and economical operation, HTC is always used to convert biological sludge into BC without pretreatment (He et al., 2013). Nevertheless, a method to dispose of ferric sludge commonly produced after Fenton pretreatment followed by biological treatment unit (another fraction of waste mainly composed of inorganic matter) has not yet been developed. However, BC has been reported to be modified by the addition of metals such as iron to function as a magnetic biochar catalyst (MBC) in a Fenton-based oxidation process for dyeing wastewater treatment and as a bactericide in bodies of water (Zhou et al., 2015; Yuan and Dai, 2014; Zuo et al., 2016). For instance, Zhou et al. reported a thermal method to prepare paper mill sludge-derived catalyst by adding pure iron resource chemicals (Zhou et al., 2015). Yuan et al. found a pyrolysis way of converting sewage sludge into Fe_2O_3 catalyst for photo-Fenton reaction (Yuan and Dai, 2014). Meanwhile, Zuo et al. reported that using alpha-FeOOH hydrothermal biochar as photocatalyst to treat dyeing wastewater, which had excellent effects (Zuo et al., 2016). However, in all these reported iron-containing catalysts, the existing form of iron is ferric, thus they have poor catalytic performances in Fenton process and used in processes requiring photon-assisted or longer time. Meanwhile, their preparation methods were all pyrolysis, which required pretreatment to reduce the sludge moisture content.

At present, ferric iron has been reported to be reduced to ferrous iron by pure organic compounds such as ethylene glycol and glucose in the HTC process (Su et al., 2016; Zhu et al., 2011). Similarly, in the present study, the biological sludge contains considerable amounts of organic matter and the major constituent of ferric sludge is also ferric iron. Thus, two relevant issues are worthy of exploration: 1) whether ferric iron in ferric sludge can be reduced to ferrous iron by organic matter in biological sludge via HTC; and 2) whether the HTC product can catalyze the Fenton process if 1) is effectively achieved. As shown in Fig. 1, sludge from Fenton pretreatment and biological oxidation processes are used to fabricate MBC through HTC, minimizing the final sludge disposal quantity. Moreover, the ferrous salt dosage in the pretreatment unit can also be decreased because ferrous salt can be partially replaced by the HTC product. In general, this novel sludge disposal method can reduce the cost of dyeing wastewater treatment through decreased sludge production and lower agent dosage.

In this study, ferric sludge and biological sludge derived from the dyeing wastewater treatment process were converted into a Fenton catalyst under hydrothermal conditions. The optimal HTC conditions were determined by Methylene Blue (MB) degradation efficiency catalyzed by HTC products via a Fenton process. The HTC products' composition, morphology, stability and reusability were characterized. Finally, the feasibility of using MBC as a catalyst in a Fenton-like process for treating actual dyeing wastewater treatment was evaluated.

2. Materials and methods

2.1. Sludge, wastewater and chemicals

Biological sludge from the secondary settling tank in a textile and dyeing industrial park was collected for this study. Dewatered ferric sludge was collected from the Fenton pretreatment unit of the same industrial park. These two types of collected sludge were immediately transferred to the laboratory and stored in a plastic box within 24 h at 277 K prior to use. Table S1 (in Supporting Information (SI)) shows the characteristics of the biological sludge and the ferric sludge. Actual dyeing wastewater was collected from the raw water tank of the same industrial park. Methylene Blue (MB, $C_{16}H_{18}ClN_3S$, 82%, w/w) was purchased from Sinopharm Chemical Reagent Co. Ltd. China. The other chemicals used in this work are described in the SI.