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Adsorption and biodegradation of dye in wastewater with Fe_3O_4@MIL-100 (Fe) core–shell bio-nanocomposites

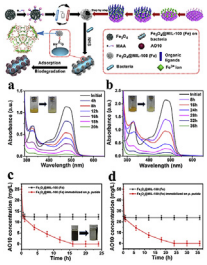
Jixiang Fan, Dongyun Chen**, Najun Li, Qingfeng Xu, Hua Li, Jinghui He, Jianmei Lu*

College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou, 215123, China

HIGHLIGHTS

- Surface-engineered bacteria for simultaneous adsorption and biodegradation (SAB).
- The Fe_3O_4@MIL-100 (Fe) nanocomposite had excellent adsorption properties.
- The synergistic effect could highly enhance the efficiency of dye degradation.
- The nanocomposite could be easily magnetic separated using an external field.

GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption and improved biodegradation of dyes in wastewater was achieved with Fe_3O_4@MIL-100 core-shell bio-nanocomposites, which were prepared by a step-by-step strategy and attached to the surface of bacteria via zero-length carbodiimide chemistry. The Fe_3O_4@MIL-100 (Fe) nano-composite showed excellent dye adsorption properties and the overall dye removal process followed second-order kinetics. The dye AO10 was completely eliminated from solution by the combined effects of adsorption and biodegradation within 15 and 25 h from initial dye concentrations of 25 and 50 mg/L, respectively. The time to degrade the dye decreased from 11 h for the free microorganisms to 5 h for the bio-nanocomposite. The procedure was non-toxic, allowed for magnetic separation of the bio-nanocomposite from solution, and showed good cycling performance for the removal of dye. Hence, the strategy of surface-engineering bacteria shows great potential for the treatment of dyes from industrial effluents.

1. Introduction

With rapid developments in printing technologies, dyes are widely applied in various industries, including the textile, food, leather, paper, pharmaceutical, and cosmetic industries (Ambashta and Sillanpää, 2010; Ghaedi et al., 2016). Approximately 100 tons of dyes are discharged each year in effluents from factories, which could lead to environmental pollution and threaten human health (Singh et al., 2012; Sonar et al., 2014; Asfaram et al., 2015). Consequently, the elimination of dyestuffs from wastewater samples is an important issue in the field of water pollution and has

* Corresponding author.
** Corresponding author.
E-mail addresses: dychen@suda.edu.cn (D. Chen), lujm@suda.edu.cn (J. Lu).

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attracted considerable attention in recent years (Sen et al., 2011; Xu et al., 2014). The most widely used traditional technologies for eliminating dyes include reverse osmosis and filtration, traditional coagulation and flocculation, and adsorption procedures (Saratale et al., 2011). Filtration and reverse osmosis have been widely applied to wastewater samples. However, there are strict requirements for the class and porosity of filters used in these procedures, which depend on the chemical structure and temperature of the filtrate (Dos Santos et al., 2007). Furthermore, membranes used for reverse osmosis are expensive and contaminated membranes require special treatments for their recovery (Robinson et al., 2001). Coagulation and flocculation methods have also been used to remove dyes from waste water; however, the low capacity and formation of large amounts of sludge have limited the development of these methods (Vandevivere et al., 1998). Among the above strategies, adsorption shows a number of inherent benefits: namely, adsorption methods are stable to anti-oxidizing environments, and are not heat or light sensitive. Furthermore, there is no need for extra pretreatment steps for adsorption techniques (C et al., 2005; Santhi et al., 2010; Han et al., 2010; Atun et al., 2011). Although traditional adsorbents have been extensively applied for the elimination of dyes, their adsorption capacity is limited (Hameed and El-Khaiary, 2008). Therefore, it is important to find novel materials that can be used for dye removal. In recent years, nanomaterials have attracted extensive research interest for environmental applications because of their differing behaviors compared with bulk materials, such as adsorption of molecules and promotion of redox and photocatalytic reactions (Khan et al., 2012; Walcarius and Mercier, 2010; Gao and Wang, 2014). Metal-organic frameworks (MOFs) are a particularly interesting type of porous crystalline material constructed from metal ions and organic ligands (Fan et al., 2014; Dhakshinamoorthy and Garcia, 2014; Yang et al., 2012; Ma et al., 2010; Wang et al., 2017; Ding et al., 2011). MOFs have attracted considerable interest owing to their applications in catalysis, selective adsorption, gas storage, and drug delivery (Mohamed et al., 2001; Yang et al., 2012). Because of their unique properties, MOFs have recently been shown to be suitable adsorption materials (Khan et al., 2012; Huang et al., 2011). The MOF MIL-100 (Fe), which consists of Fe (III) and trimesic acid, have been extensively studied because of its chemical robustness, thermal stability, presence of unsaturated metal sites, high surface area, and good biocompatibility compared with those properties of conventional adsorption materials and other MOFs (Burtch et al., 2016; Canivet et al., 2014; Qadir et al., 2015). Li and co-workers have reported the removal of different types of dyes with MIL-100 (Fe) (Jia et al., 2014).

Because of the difficulty of separating adsorbent materials from reaction solution, MOFs that can be easily separated from solution have received attention. Fe_3O_4 is a magnetic material that had been widely investigated owing to its properties including a high saturation magnetization, biocompatibility, and low toxicity to microorganisms (Lee et al., 2015). The combination of MOFs and Fe_3O_4 has been used in applications including water research, drug delivery, and catalysis. Chen et al. investigated magnetic materials based on Fe_3O_4@MIL-100 (Fe) for the elimination of Cr (VI) (Yang Q. et al., 2016). A layer-by-layer growth approach was used to prepare a core–shell structure of Fe_3O_4–MOF by Qiu and co-workers (Ke et al., 2012). However, the above strategies could only be used to adsorb dyestuffs rather than completely degrade them.

Chemical approaches have also been widely used for the treatment of effluents because these strategies can thoroughly degrade dyes. Chemical oxidation by O_3 and H_2O_2 has been used for the decomposition of dyestuffs (Jerič et al., 2013). This approach to chemical oxidation is effective because of its high reactivity; however, the associated high-costs and low capacity have limited the development of this technique. Advanced photocatalytic oxidation processes have been developed for the decomposition of dye effluents by catalysts. (Wang et al., 2009; Mousavinia et al., 2016). Photochemical oxidation processes are considered to be harmless to the environment and human beings and do not produce hazardous byproducts; however, the efficiency of decolorization is typically low for dyes. Photocatalytic oxidation processes are economically unfeasible, and the facilities required are expensive and the procedures time-consuming (Rosenfeldt et al., 2006). Therefore, treatment systems based on the use of bacteria to degrade dyes have attracted considerable research interest in recent years. Govindwar and co-workers reported on the degradation of dyes by bacterium (Saratale et al., 2011). In particular, microbial degradation was found to be an environmentally friendly and low-cost alternative to physicochemical treatment approaches. However, the efficiency of microbial treatment processes is much lower than that of physical and chemical adsorption processes (Meehan et al., 2001; Bras et al., 2001). Furthermore, bacteria are inefficient at catching dye molecules at low concentrations in aqueous solution. Therefore, combinations of technologies have been the subject of extensive studies (Yang S. et al., 2016). The advantages of biological treatments combined with the high adsorption capacity of MOFs could increase the efficiency of biological treatments.

In this work, we combined biodegradation and physical adsorption using a zero-length carbodiimide linker to prepare Fe_3O_4@MIL-100 (Fe) immobilized on P. putida (Fig. 1) (Taherkhani et al., 2014). We studied the cycling efficiency of dye adsorption and degradation by Fe_3O_4@MIL-100 (Fe) immobilized on P. putida. Our results showed that the combination of physical adsorption and biodegradation enhanced the efficiency of dye degradation compared with the performances of the free microorganism and adsorbent alone. Furthermore, the overall degradation/absorption process followed a pseudo-second-order kinetic model, and the materials could be easily separated under a magnetic field, making this a suitable method for degradation of dyes in wastewater.

2. Materials and methods

2.1. Materials

All chemicals and reagents were at least of analytical grade and used without further purification. $FeCl_3$ (Lingfeng, Shanghai, China), trisodium citrate, NaAc (Sinopharm, Shanghai, China) were used to prepare Fe_3O_4. Nitric acid, hydrofluoric acid, iron powder, and trimesic acid (Macklin, Shanghai, China) were used to synthesize MIL-100 (Fe). Tryptone and yeast extract were supplied from Suzhou Biogene Biotechnology Co., Ltd. Acid orange 10 (AO10) and inorganic salts were achieved from Sinopharm Chemical Reagent Co., Ltd. 1-ethyl-3-[3-(dimethylamino)propyl]-carbodiimide (EDC), *N*-hydroxysuccinimide (NHS) were used for the immobilization of microorganism.

2.2. Preparation of Fe_3O_4 magnetite nanoparticles

Fe_3O_4 magnetite nanoparticles were synthesized by a solvothermal method based on a reported procedure with a slight modification (Liu et al., 2009). Briefly, $FeCl_3$ (0.1625 g), trisodium citrate (0.2 g) and NaAc (1.2 g) were dissolved in ethylene glycol (20 mL) with the condition of stirring. The composites were stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclave was heated at 200 °C and kept for 10 h, and then allowed to cool to RT. The precipitation was washed with ultra-pure water and ethanol for three times.