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Reuse of Fenton sludge as an iron source for $NiFe_2O_4$ synthesis and its application in the Fenton-based process

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ABSTRACT

The potentially hazardous iron-containing sludge from the Fenton process requires proper treatment and disposal, which often results in high treatment cost. In this study, a novel method for the reuse of Fenton sludge as an iron source for the synthesis of nickel ferrite particles ($NiFe_2O_4$) is proposed. Through a co-precipitation method followed by sintering at 800°C, magnetic $NiFe_2O_4$ particles were successfully synthesized, which was confirmed by powder X-ray diffraction (XRD), scanning electronic microscopy (SEM), energy dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy. The synthesized $NiFe_2O_4$ could be used as an efficient catalyst in the heterogeneous Fenton process. In phenol degradation with H_2O_2 or $NiFe_2O_4$ alone, the phenol removal efficiencies within the reaction time of 330 min were as low as 5.9% ± 0.1% and 13.5% ± 0.4%, respectively. However, in the presence of both $NiFe_2O_4$ and H_2O_2, phenol removal efficiency as high as 95% ± 3.4% could be achieved, indicating the excellent catalytic performance of $NiFe_2O_4$ in the heterogeneous Fenton process. Notably, a rapid electron exchange between ${=}Ni^{II}$ and $={Fe^{III}}$ ions in the $NiFe_2O_4$ structure could be beneficial for the Fenton reaction. In addition, the magnetic catalyst was relatively stable, highly active and recoverable, and has potential applications in the Fenton process for organic pollutant removal.

Introduction

The Fenton process, which is based on the generation of hydroxyl radicals (HO.) from hydrogen peroxide (H_2O_2) in the presence of Fe^{2+}, has been extensively studied and successfully applied for the effective treatment of various industrial wastewaters (Bautista et al., 2008; Pignatello et al., 2006). However, despite its simplicity, the main weakness of the Fenton process is the formation of sludge during neutralization after Fenton oxidation (Ma and Xia, 2009). The yield of Fenton sludge is dependent upon the ratio and volume of the added reagents. Due to the residual of toxic organics or heavy metals in it, sludge from the Fenton process treating recalcitrant industrial wastewater is often disposed as hazardous solid waste, which leads to high sludge disposal cost and the risk of secondary pollution. Therefore, Fenton sludge is the main obstacle preventing full scale application of the Fenton process in the field of industrial wastewater treatment (Bautista et al., 2008).

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To minimize the production of Fenton sludge, two approaches have been suggested, i.e., development of heterogeneous catalysts and reuse of iron in the sludge. Various heterogeneous catalysts have been developed, such as natural minerals (Garrido-Ramirez et al., 2010), iron-containing clays (Navalon et al., 2010), iron immobilized on solid support (Aleksić et al., 2010) and zero-valent iron (Shen et al., 2013; Liu et al., 2015). Heterogeneous catalysts are superior to the traditional homogeneous catalyst, i.e., Fe^{2+}, due to the easy separation of the catalysts from the treated wastewater by sedimentation or an external magnetic field (Liu et al., 2012). Therefore, generation of Fenton sludge in a heterogeneous Fenton system can be reduced to some extent. However, the catalytic activity is usually deteriorated after repetitive use due to the leaching of active iron (Ji et al., 2011) or the decay of active catalytic sites (Takbas et al., 2008). Recently, reuse of iron-containing Fenton sludge has been drawing increasing interest from researchers world-wide. Yoo et al. (2001) suggested the recycling of sludge generated from Fenton oxidation in a coagulation process. With the recycling of Fenton sludge, the sludge to be disposed could be reduced up to 50% and the coagulant could be reduced by 50%. Sheu and Weng (2001) developed a recycling system based on the reduction of Fe^{3+} by H_2O_2 to produce Fe^{2+}, which could be used as a Fenton reagent. Bolobajev et al. (2014) developed a sequential Fenton/Fenton-based system for the treatment of landfill leachate. Iron-containing sludge produced from the Fenton process could be reused as an iron source in the following Fenton-based system, thus production of hazardous ferric waste could be minimized. Cao et al. (2009) presented a simple method for recovering the iron catalyst from the iron hydroxide sludge for oxidative treatment of industrial wastewaters. The sludge was dewatered, dried and baked at 350–400°C, and then the residual solids were dissolved in sulfuric acid to form a reusable catalyst for Fenton and Fenton-like reactions. The reuse routines mentioned above are beneficial for the reduction and minimization of iron-containing sludge compared with traditional treatment processes. However, they increase the overall cost and operational difficulty because of the low utilization efficiency or additional sludge regeneration step. In addition, a feasible method for final and thorough disposal of Fenton sludge has not been suggested so far. Resourcization of Fenton sludge in order to achieve final and thorough disposal merits investigation.

Recently, ferrites, such as $NiFe_2O_4$, $CuFe_2O_4$ and $ZnFe_2O_4$, have drawn much more attention due to their potential application in the fields of catalysis (Rashad and Fouad, 2005), high sensitivity gas sensors (Rezlescu et al., 2006), magnetic fluids (Hasmonay et al., 2000) and microwave devices (Giannakopoulou et al., 2002). Sugimoto et al. (1998) suggested that ferrites could be synthesized by using ferric salts as raw material. Recently, ferrite has been used as the catalyst for heterogeneous photo-Fenton or Fenton-like processes (Liu et al., 2012; Marco et al., 2014). However, to the best of our knowledge, preparation of ferrite using Fenton sludge as an iron source and application of the obtained ferrite as a Fenton catalyst have not yet been reported.

In this work, a new reuse method for Fenton sludge was investigated. The iron-containing Fenton sludge was used as an iron source for the synthesis of nickel ferrite ($NiFe_2O_4$), which was used as a catalyst in the Fenton process. Thus, the objectives of this study were: (1) to synthesize and to characterize $NiFe_2O_4$, (2) to evaluate the catalytic properties and stability of the synthesized $NiFe_2O_4$, and (3) to propose a possible catalytic mechanism for the Fenton process using $NiFe_2O_4$ as catalyst.

1. Experimental

1.1. *Characterization of Fenton sludge*

The iron-containing sludge derived from the Fenton process was characterized as follows. The chemical oxygen demand (COD) value was found to be 6500 ± 500 mg/L. The total iron content of the sludge was as high as 7.67 ± 1.87 g/L, which provided a rich iron source for the synthesis of $NiFe_2O_4$. The ratio of volatile solids (VS) to total solids (TS) was 90.46% ± 2.43%, indicating the presence of abundant organics in the sludge. In addition, the iron-containing sludge was fluidized, with water content and total solid content of 89.65% ± 1.75% and 10.35% ± 1.75%, respectively.

1.2. *Synthesis of $NiFe_2O_4$ from Fenton sludge*

$NiFe_2O_4$ particles were synthesized according to the controlled co-precipitation method (Kulkarni et al., 2014). Before the synthesis process, the iron content in the Fenton sludge was determined. $Ni(NO_3)_2$ was dissolved into ultrapure water, and then $Ni(NO_3)_2$ solution was added and mixed into the Fenton sludge at Fe/Ni mole ratio of 2:1. Then 4 mol/L sodium hydroxide solution was added dropwise into the mixture of Fenton sludge and $Ni(NO_3)_2$ to adjust the pH value to 9.0–10.0. During this procedure, the mixture was continuously stirred using a magnetic agitator and kept at a temperature of 50°C. Six hours later, the resultant precipitate was filtered and washed with ultrapure water until the pH value of the filtrate reached 7.0. The solid product was dried in a vacuum oven at 100°C for 8 hr and then sintered at 800°C for 6 hr. The obtained particles were ground and stored for further characterization and application.

1.3. *Application of $NiFe_2O_4$ in heterogeneous Fenton process*

The heterogeneous Fenton reaction for phenol degradation was performed in 100 mL centrifuge tubes containing 50 mL phenol solution. The initial phenol concentration and the initial pH of the phenol solution were 250 mg/L and 3.0, respectively. Then H_2O_2 and the obtained $NiFe_2O_4$ powder were added at dosages of 120 mmol/L and 2.0 g/L to initiate the Fenton reaction. The Fenton reaction was carried out on a rotary shaker at 25°C and 200 r/min. After Fenton reaction, $NiFe_2O_4$ was collected by magnetic separation for possible reuse. The control reactions carried out with $NiFe_2O_4$ but without H_2O_2 or with H_2O_2 but without $NiFe_2O_4$ were performed in the same manner.

1.4. *The role of the leached iron ions in Fenton process*

To evaluate the contribution of homogeneous Fenton oxidation catalyzed by the leached iron ions in the phenol degradation process, the role of the leached iron ions was investigated. After

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