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Article

Optimization of a digested sludge-derived mesoporous material as an efficient and stable heterogeneous catalyst for the photo-Fenton reaction

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ABSTRACT

The anaerobic digestion of sludge has recently received increased interest because of the potential to transform organic matter into methane-rich biogas. However, digested sludge, the residue produced in that process, still contains high levels of heavy metals and other harmful substances that might make traditional disposal difficult. We have devised a facile method of converting digested sludge into a mesoporous material that acts as an effective and stable heterogeneous catalyst for the photo-Fenton reaction. A comparison of the removal of rhodamine B under different conditions showed that FAS-1-350, which was synthesized by mixing the digested sludge with a 1 mol/L $(NH_4)_2Fe(SO_4)_2$ solution followed by calcination at 350 °C, exhibited the best catalytic activity owing to its faster reaction rate and lower degree of Fe leaching. The results indicate that Fe^{2+}-loaded catalysts have significant potential to act as stable and efficient heterogeneous promoters for the photo-Fenton reaction, with better performance than Fe^{3+}-loaded catalysts because the Fe(II)/Fe(III) compounds formed in the calcination process are necessary to sustain the Fenton reaction. This protocol provides an alternative, environmentally friendly method of reusing digested sludge and demonstrates an easily synthesized mesoporous material that effectively degrades azo dyes.

1. Introduction

Sewage sludge, the residue produced by wastewater treatment processes, is regarded as a significant risk to the environment and human health and has recently become a growing concern [1–3]. Most sludge is disposed of in landfills, by incineration or agricultural reuse, all of which have numerous associated hazards, such as the presence of pathogens or metals [4–7]. Recently, there has been renewed interest in anaerobic digestion, one of the most widely used sludge treatment methods, because of the ability of this technique to transform organic matter into methane-rich biogas (60–70 vol% CH_4). Compared with traditional anaerobic digestion of low-solids sewage sludge, high-solids anaerobic digestion, which is characterized by feedstocks having a high content of total solids (TS, typically greater than 15 wt%) [8], has several advantages. These include higher loadings, smaller reactor volumes, and lower energy consumption [9].

Biogas (a mixture of CH_4 and CO_2) is generated through the biodegradation of organic matter during anaerobic digestion.

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However, tyrosine and tryptophan and their analogues, along with humic substances, are difficult to biodegrade [10]. In addition, although the bioavailability of heavy metals is increased to some extent after high-solids anaerobic digestion, the concentration of these metals is also increased [11], which can make traditional sludge disposal methods, such as incineration and agricultural reuse, difficult. The product of the anaerobic digestion of sewage sludge is known as digested sludge (DS), and this material retains refractory organic compounds, dead bacterial cells, and inorganic components in the form of various oxides and salts, in addition to Fe-based compounds.

The Fenton reaction is based on the transfer of electrons between H_2O_2 and metal ions, such as ferrous ions (Fe^{2+}), that act as catalysts [12]. Although they exhibit high degradation efficiency, traditional Fenton systems have several defects, such as pH limitations and iron precipitation. Despite these disadvantages, Fenton and photo-Fenton systems have proven to be efficient at hazardous waste remediation and water disinfection. In recent years, a variety of heterogeneous Fenton catalysts, including Fe_2O_3, $FeVO_4$, and $BiFeO_3$, have been applied to the degradation of organic contaminants [13–15], and many studies have been performed using various supports (zeolite, graphene oxide sheets, clays, carbons and resin) to enhance the efficiency of the heterogeneous Fenton process [16–18]. Unfortunately, many of these catalysts present leaching concerns and tend to produce high concentrations of Fe ions [19,20] that are well above the European Union directives that allow only 0.0002% Fe in treated water transferred directly into the environment [21]. In light of this, it would be beneficial to develop a cost-effective, heterogeneous catalyst exhibiting high activity and long-term stability so as to obtain improved catalytic efficiency and a wider range of applications.

In a previous study, our group used sewage sludge as the raw ingredient for the facile synthesis of an effective and stable heterogeneous catalyst to promote the photo-Fenton reaction [20]. However, it was determined that a portion of the organic matter in the sludge (which could, alternatively, have been converted into biogas by advance anaerobic digestion) was either evaporated, combusted or carbonized during the calcination process. Therefore, to make more efficient use of the organic matter in the sewage sludge, we instead employed the less-useful DS to synthesize the catalysts. The refractory organic compounds, biomacromolecules and bacteria in DS can serve as scaffold templates for the preparation of a mesoporous material from sewage sludge. This may represent a more efficient and environmentally friendly way to use sewage sludge compared with energy generation via anaerobic digestion. The aim of the present study was to optimize the catalyst synthesis by varying the type of Fe-based salt, the concentration of iron compounds added and the calcination temperature.

2. Experimental

2.1. Preparation of the catalysts

The dewatered sewage sludge that was used for anaerobic digestion trials in this study was obtained from the Anting Wastewater Treatment Plant in Shanghai, China (with a design capacity of 150000 m^3/d) [22]. The collected sludge was stored at 4 °C in preparation for daily feeding. An reactor with a working liquid volume of 6.0 L and equipped with helical stirring blades was operated at 60 r/min, using repeated cycles composed of 2-min stirring and an 8-min break. The volumes of biogas generated in the reactor were measured with wet gas meters (XMF-1, China) on a daily basis. On the first day of the experimental trials, 6.0 L of seed sludge was added to the reactor, which was operated semi-continuously with a once daily draw-off and feeding at 35 ± 1 °C. During these trials, the reactor sludge retention time was on the order of 20 d. The DS parameters were found to stabilize 60 d after starting the reactor operation, and so DS samples obtained between the 60 and 70 d marks were used to synthesize catalysts. The parameters of the dewatered sludge and the DS used in this study are summarized in Table 1.

Table 1
Parameters of dewatered sludge and digested sludge.

Parameter	Dewatered sludge	Digested sludge
pH	7.31 ± 0.15	8.07 ± 0.13
TS (wt%)	16.50 ± 0.03	14.01 ± 0.04
VS/TS (wt%)	58.83 ± 0.04	46.34 ± 0.04
TA (mg/L)	5850.3 ± 103.4	15848.4 ± 135.8
TAN (mg/L)	759.9 ± 35.2	4120.7 ± 112.1

TS: total solids; VS: volatile solids; TA: total alkalinity; TAN: total ammonia nitrogen.

All the organic and inorganic reagents used in this work were analytical grade unless otherwise stated. All solutions were prepared with water from a water purification system (Hitech Instrument Co., Shanghai, China).

The DS-derived, Fe-loaded mesoporous materials were prepared by adding 10 g DS to 20 ml of various Fe-loading solutions followed by stirring for 3 h at room temperature. The Fe-loaded DS was subsequently separated by centrifugation and dried overnight in air at 105 °C. As a final step, the material was calcined in air for 3 h.

Four Fe-based compounds, $(NH_4)_2Fe(SO_4)_2$ (FAS), $FeSO_4$ (FS), $FeCl_3$ (FC) and $Fe(NO_3)_3$ (FN), were used. A DS sample was heated to 350 °C in a muffle furnace in air for 3 h to obtain the catalyst designated herein as DS-350, while the other samples are named based on the salt, the Fe(III)/Fe(II) concentration and the calcination temperature employed during the synthesis process. As an example, FS-1-350 indicates that the DS-derived, Fe-loaded mesoporous material was prepared by adding 10 g DS to 20 mL of a 1 mol/L $FeSO_4$ solution followed by stirring for 3 h at room temperature, recovery via centrifugation, drying in air at 105 °C overnight, and finally calcination in air at 350 °C for 3 h. Based on these same rules, the other samples are named FAS-1-350, FC-1-350, FN-1-350, and so on.

2.2. Characterization of the sludge and the synthesized catalysts

The TS, volatile solids (VS), total alkalinity (TA), and total ammonia nitrogen (TAN) contents of the dewatered sludge and DS were determined according to standard methods [23]. The