Research article

Treatment of landfill leachate biochemical effluent using the nano-Fe$_3$O$_4$/Na$_2$S$_2$O$_8$ system: Oxidation performance, wastewater spectral analysis, and activator characterization

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ABSTRACT

Nano-Fe$_3$O$_4$ was used as heterogeneous catalyst to activate Na$_2$S$_2$O$_8$ for the generation of the sulfate radicals (SO$_4^-$·) to oxidize the residual pollutants in landfill leachate biochemical effluent. The oxidation performance, wastewater spectral analysis and activator characterization were discussed. Oxidation experimental result shows that nano-Fe$_3$O$_4$ has obvious catalytic effect on Na$_2$S$_2$O$_8$ and can significantly enhance the oxidation efficiencies of Na$_2$S$_2$O$_8$ on landfill leachate biochemical effluent, with COD and color removals above 63% and 95%, respectively. Based on the analyses of three-dimensional excitation emission matrix fluorescence spectrum (3DEEM), ultraviolet−visible spectra (UV−vis), and Fourier Transform infrared spectroscopy (FTIR) of wastewater samples before and after treatment, it can be concluded that the pollution level of dissolved organic matter (DOM) declined and that the humic acid (HA) fractions were efficiently degraded into small molecules of fulvic acid (FA) fractions with less weight and stable structure. Compared to the raw wastewater sample, the aromaticity and substituent groups of the DOM were lessened in the treated wastewater sample. Moreover, the main structure of the organics and functional groups were changed by the Fe$_3$O$_4$/Na$_2$S$_2$O$_8$ system, with substantial decrease of conjugated double bonds. The micro morphology of nano-Fe$_3$O$_4$ was characterized before and after reaction by the methods of scanning electron microscope spectra (SEM), X-ray diffraction pattern (XRD), and X-ray photoelectron spectroscopy (XPS). The XRD pattern analysis showed that nano-Fe$_3$O$_4$ was oxidized into r-Fe$_2$O$_3$ and that the particle size of it also became smaller after reaction. XPS was employed to analyze the content and iron valence on the nano-Fe$_3$O$_4$ surface, and it can be found that the ratio of Fe^{3+}/Fe^{2+} decreased from 1.8 before reaction to 0.8 after reaction. From the SEM analysis after the treatment, it was determined that the spacing between nano-Fe$_3$O$_4$ was increased, but in turn, the particles decreased in diameter.

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1. Introduction

Advanced oxidation processes (AOPs) have received considerable attention from researchers for their potential advantages in the area of wastewater treatment, and the main mechanism proved to be ·OH oxidation (Amiri and Sabour, 2014; Silva et al., 2015; Wang et al., 2014). A new field using SO$_4^-$· generated by activating Na$_2$S$_2$O$_8$ for treatment of organic wastewater is being developed rapidly both at home and abroad. The oxidation-reduction potential of SO$_4^-$· is 2.5−3.1 V and its oxidation performance even exceeds that of ·OH (Shukla et al., 2011). Moreover, the half-life of SO$_4^-$· is long enough (4 s) to ensure adequate time for the degradation of contaminants by oxidation (Chen et al., 2012).

Generally, although SO$_4^-$· can be generated by activating Na$_2$S$_2$O$_8$ with heat, UV, or transition metals, heat and UV activation are not suitable for large-scale applications because of their high cost (Li et al., 2009; Wang and Liang, 2014). Applying transition metal ions to activate Na$_2$S$_2$O$_8$ has attracted wide attention for its major advantage—no energy is required. The most impressive system is Fe^{2+}/Na$_2$S$_2$O$_8$ due to its high activation efficiency (Rao et al., 2014; Zhen et al., 2012). However, there exist some obvious defects with the Fe^{2+}/Na$_2$S$_2$O$_8$ system. On the one hand, the SO$_4^-$· would be ineffectively consumed in the competitive reaction between redundant Fe^{2+} and SO$_4^-$·, resulting ineffective availability of SO$_4^-$·

and low oxidation efficiency. On the other hand, the optimal range of pH is from 1 to 3 in the $Fe^{2+}/Na_2S_2O_8$ system, which limits its range in some applications (Rastogi et al., 2009). Therefore, the current focus of research in this field is preparation of activators with high oxidation performance and a wide range of pH application, to enhance the oxidation efficiency and effective availability of persulfate.

In order to enhance the oxidation efficiency of $Na_2S_2O_8$, some complexing agents such as EDTA can be used to form EDTA-Fe^{2+} complexes and to catalyze $Na_2S_2O_8$. The catalysis process can govern the decomposition rate of $Na_2S_2O_8$ by controlling the dissolution rate of Fe^{2+} (Liang et al., 2009). However, EDTA-Fe^{2+} complexes would cause secondary pollution for the reason that the residual complexing agent is very hard to be removed from the solution after reaction. In addition, competitive reaction between the complexing agent and $SO_4^-\cdot$ would result in a decline in the utilization efficiency of $Na_2S_2O_8$.

Some researchers found that higher oxidation efficiency was achieved when employing nano-Fe_3O_4, instead of Fe^{2+}, to activate H_2O_2 to generate $\cdot OH$ for the degradation of organic contaminants in a Fenton-like system (Wang et al., 2010; Wei and Wang, 2008). Similar to H_2O_2, there is also a $-O-O-$ bond in the structure of persulfate. Compared with Fe^{2+}, nano-Fe_3O_4 has obvious advantages when used to activate $Na_2S_2O_8$ for the oxidation of organic matter via generated $SO_4^-\cdot$ (Fang et al., 2013; Yan et al., 2011). Fe^{2+} on the surface of nano-Fe_3O_4 can quickly activate persulfate to produce $SO_4^-\cdot$. The activation of persulfate and the degradation of pollutants occur on the surface of nano-Fe_3O_4, which can effectively reduce the contact opportunities between the generated $SO_4^-\cdot$ and the Fe^{2+} on the surface of nano-Fe_3O_4, and cut down the risk of side effects, further ensuring highly effective utilization of persulfate (Tan et al., 2014). In addition, nano-Fe_3O_4 can easily be recycled by magnetic collection from the wastewater, which reduces the cost of waste effluent treatment and will not result in secondary pollution.

Previous researches have shown that residual toxic pollutants remain in the effluent from biological units of landfill leachate (Liang et al., 2016). Apparently, such substances are among the main contributors of toxic pollution in urban water environments. These substances, which are subject to bioaccumulation and are hard to degrade, can propagate over long distance, and are known to promote cancer or mutations, and to induce endocrine interference (Zeng et al., 2017). Thus, the problems of water pollution ascribed to these toxic and hazardous substances have drawn more and more attention in recent years (Campagna et al., 2013). Nevertheless, the study of landfill leachate treatment using $SO_4^-\cdot$ oxidation is still in the initial stage. A method using thermal activation to generate $SO_4^-\cdot$ to treat the landfill leachate was conducted by Deng et al. (Deng and Ezyske, 2011), and compared to Fenton oxidation, which showed that $SO_4^-\cdot$ is more effective than $\cdot OH$ for the removal of pollutants in landfill leachate. Abu Amr et al. (2013) evaluated a combination of $O_3/Na_2S_2O_8$ technology for the treatment of stabilized landfill leachate. The encouraging results indicated that it is an efficient method and achieved higher pollutant removal compared with the other applications studied. In addition, the combined process proved to be more efficient than the combined use of O_3/Fenton when treating the same studied leachate. Kattel and Dulova (2017) used ferrous ion to activate persulfate for the treatment of landfill leachate and the modest results of COD and DOC removals indicated that it could be a promising technology for ex-situ as well as in-situ landfill leachate treatment applications.

In this study, nano-Fe_3O_4 was evaluated as a heterogeneous catalyst to activate $Na_2S_2O_8$ for removal of residual pollutants in leachate biochemical effluent. Optimization of related reaction parameters was conducted. Moreover, the wastewater sample, before and after treatment with the $Fe_3O_4/Na_2S_2O_8$ system, was analyzed using 3DEEM, UV–Vis, and FTIR. The nano-Fe_3O_4 was characterized using XRD, XPS, and SEM, before and after use.

2. Materials and methods

2.1. Leachate sampling

The experimental wastewater was a biologically pre-treated leachate sample taken from a municipal solid waste landfill disposal plant in Nanchang City (Jiangxi Province, PR China). Typical characteristics of the wastewater include: COD 780–1160 mg/L, color 380–460 times, pH 6.5–7.1, and ammonia nitrogen 120–160 mg/L.

2.2. Nano-Fe_3O_4 preparation

A certain amount of $FeCl_3 \cdot 6H_2O$ was added to an acetone solution with ultrasonic stirring for 12 min for dissolution, then an organic dispersant was added. A precipitant (37% $NH_3 \cdot H_2O$) was added slowly to the solution until the acetone solution well-dispersed. The resulting precipitant products were filtered and washed and then dried in a vacuum oven at 80 °C followed by grinding on an agate mortar. Finally, the powder was calcined on a pipe heater with N_2 several times. The calcined black-powder product was magnetite particles of nano-Fe_3O_4. The chemical reagents used here were all analytical grades and were purchased from Shanghai Chemical Technology Company (China).

2.3. Sulfate radical oxidation experiments

With and without prior pH adjustment, $SO_4^-\cdot$ oxidation was conducted using $Na_2S_2O_8$ as oxidant. First, 100 mL of leachate secondary effluent was added to a 250 mL Erlenmeyer flask. Next, certain amounts of $Na_2S_2O_8$ and nano-Fe_3O_4 were added to the solution. Then the mixed solution was shaken at 150 r/min using a shaking water bath at a controlled temperature. Oxidation was initiated by addition of a certain amount of $Na_2S_2O_8$. At designated time intervals, the samples were withdrawn from the surface of the wastewater. The collected samples were neutralized by NaOH to precipitate the leached iron ions and then centrifuged for 10 min at 2000 rpm using a centrifuge for further analysis. Each oxidation test was conducted in duplicate, and the results reported in this paper were the arithmetic average of the two tests. The COD, ammonia nitrogen, and color were measured according to The Manual of Standard Methods for the Examination of Water and Wastewater produced by the China Environmental Protection Agency. The pH was measured using a pH Meter (model PHS-3C). The residual $Na_2S_2O_8$ concentration was analyzed using an iodometric titration method. Since the residual $Na_2S_2O_8$ would interfere with COD measurements, the correction for the residual $Na_2S_2O_8$ interference on the COD test was performed by the correlation equation as described previously in Zhang et al. (2014).

2.4. Spectrum analysis of wastewater sample

2.4.1. 3DEEM fluorescence spectra

The excitation emission matrix (EEM) fluorescence was determined using a fluorescence spectrophotometer (Hitachi F-2000). After referring to literature and optimizing the experiment many times, the scanning parameters were set as follows: excitation wavelength: 220–500 nm, scan wavelength intervals: 20 nm, slits: 10 nm; emission wavelength: 250–600 nm, scan wavelength speed: 1200 nm/min, slits: 10 nm; photomultiplier voltage: 700 V,