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Research article

Degradation of sodium isopropyl xanthate from aqueous solution using sonocatalytic process in the presence of chalcocite nanoparticles: Insights into the degradation mechanism and phyto-toxicity impacts

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ABSTRACT

In the present work, the sonocatalytic degradation of sodium isopropyl xanthate (SIPX) was investigated in the presence of Cu_2S nanoparticles. Cu_2S nanoparticles were produced by means of a high-energy planetary mechanical ball milling method within the processing times of 0.5, 1.5, 3 and 4.5 h. The physical and chemical characteristics of Cu_2S particles were studied before and after ball milling process using various analytical techniques, including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM) coupled Energy-dispersive X-ray spectroscopy (EDX), atomic absorption spectroscopy (AAS) and nanoparticles size distribution (NSD). The XRD pattern of the samples confirmed the presence of tetragonal and cubic crystalline phases of Cu_2S. In addition, the results of SEM and NSD analysis showed that the increase in the ball milling time from 0.5 to 4.5 h notably decreased the size of nanoparticles to the range of 20–40 nm. Furthermore, AAS result showed that the concentration of Cu^+ ions was much lower than that of the accepted value in the aqueous media (0.009 mg/L) after 60 min of the sonocatalysis. The study on the effects of the main key parameters showed that 93.99% of SIPX (10 mg/L) was removed during 60 min of the sonocatalytic process under the optimum conditions: pH of 7.3, Cu_2S concentration of 1.5 g/L, and ultrasonic power of 150 W. The sonocatalytic degradation mechanism was thoroughly examined in the presence of different organic and inorganic scavenger compounds, including ethanol, EDTA, NaCl and Na_2SO_4. The obtained results confirmed $^{\bullet}OH$ and holes (h^+) as the dominant oxidizing species in Cu_2S catalyzed sonolysis. In order to get the benefits of the integrated sonocatalytic process, different rate enhancing compounds were introduced into the system. For the first time, the $S_2O_8^{2-}$ and Cu_2S catalyzed sonolysis (US/Cu_2S/$S_2O_8^{2-}$) system was introduced as an efficient and novel sonocatalytic system for fast degradation of SIPX. Moreover, the phyto-toxicological assessments proved the reduction in the toxicity of the sonocatalytic-treated SIPX solution by increase in the reaction time, from 20 to 60 min.

1. Introduction

Mining industries play an important role in the massive production of raw materials. Though, the various stages of metal extraction and separation introduce hazardous organic and inorganic contaminants into the environment. Chemical collectors such as sodium xanthate salts are among the most widely used compounds in mining industries at selective separating of sulfide minerals by froth flotation. Sodium xanthate salts are also utilized in some other processes, such as cellulose synthesis, pesticide manufacturing, and as a corrosion inhibitors in engine oil additives (Lotter and Bradshaw, 2010; Molina et al., 2013).

The wide application of sodium xanthate salts, especially in mining industry, has caused its continuous occurrence in mining wastewater. These compounds are harmful to biota and have an extended inhibitory effect on nitrifying bacteria. Hence, it is necessary to remove sodium xanthate salts from mining wastewater before its discharge to the environment (Lotter and

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Bradshaw, 2010; Molina et al., 2013).

The ability for degrading a wide range of organic compounds is the most prominent feature of the advanced oxidation processes (AOPs) (Bustillo-Lecompte and Mehrvar, 2016; Kumar and Rao, 2017; Orge et al., 2012). Heterogeneous sonocatalytic process (HSP) using solid nanocatalysts is one of the recently-introduced AOPs which is recently used for treatment of polluted effluents such as halogenated hydrocarbons, pesticides, and dyes from aqueous solutions (Khataee et al., 2015). Most of the shortcomings accompanied sonolysis alone can be overcome by addition of suitable nanocatalyst to the process (Banerjee et al., 2012; Wang et al., 2011; Zhang et al., 2018). Moreover, nanocatalysts provide more active sites, which lead to the generation of higher quantities of reactive radicals, thus increasing the degradation rate of the pollutant. The remarkable degradation efficiency, complete mineralization of the target compounds, low power consumption, easy separating and reusability of the catalyst and simple operation of the system are a number of the merits of HSP application (Khataee et al., 2015; Wang et al., 2014). A large number of nanomaterials of different morphologies have been used in HSP for degradation of various organic pollutants from water bodies. Nevertheless, the utilization of semiconductor materials in this process was hardly reported (Shimizu et al., 2007; Wang et al., 2008).

Recently, copper sulfide (Cu_xS) compounds have received particular attention (Grozdanov and Najdoski, 1995) for optical and electrical applications. Among the Cu_xS compounds, such as chalcocite (Cu_2S), djurleite ($Cu_{1.9375}S$), anilite ($Cu_{1.75}S$), and covellite (CuS), Cu_2S is of great interest owing to its special properties and potential applications. Cu_2S is a p-type semiconductor, with a direct band gap of 1.2 eV (Gorai et al., 2004). The availability of Cu_2S nanostructures with well-defined morphologies and dimensions enables new type of applications and/or enhancing the performance of the currently existing photoelectric devices due to the quantum size effects (Du et al., 2006). So far, Cu_2S nanoparticles were prepared in diverse morphologies, but by utilizing different costly materials and through complex methods. Moreover, there is no report on the production of Cu_2S nanomaterials with a high-energy planetary ball milling method. This method is simple, cost-effective and can efficiently generate fine and uniform nanostructures during a short processing time. These advantages cannot be achieved using conventional chemical synthesis methods for production of large amount of nanomaterials (De Carvalho et al., 2013; Xu et al., 2013). For example, Farhadi and Siadatnasab (2016) synthesized Cu_2S nanoparticles via thermal decomposition of Cu(II) diethyldithiocarbamate complex using an electric furnace at 220 °C for 0.5 h. The size of the produced nanoparticles was in the range of 40–60 nm. In another work (Mousavi-Kamazani et al., 2013), Cu_2S nanoparticles were synthesized via an ultrasonic-assisted method by employing Na_2SO_3 as a reducing agent at 80 °C for 5 h. The average crystallite diameter of the produced nanoparticles was about 25 nm. Obviously, in the above synthesis methods of the nanomaterials, the processes require higher operating temperatures with relatively costly substrates.

In the present work, for the first time, the degradation of sodium isopropyl xanthate (SIPX) was investigated via heterogeneous sonocatalytic process in the presence of Cu_2S nanoparticles. These nanoparticles were produced in large scale by mechanical high-energy planetary ball milling method using natural Cu_2S sample, at different time sets of ball milling namely, 0.5, 1.5, 3 and 4.5 h. In order to examine the physical and chemical characteristics of the unmodified sample and the produced nanoparticles, the X-Ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscope (SEM), Energy-dispersive X-ray spectroscopy EDX, nanoparticles size distribution (NSD) and atomic absorption spectroscopy (AAS) were fulfilled. Subsequently, the effects of the main operational parameters including milling time, pH, catalyst concentration, reusability and stability, ultrasonic power and SIPX initial concentration were investigated on its removal efficiency. Afterwards, the presence of different compounds such as enhancers and scavengers were studied on the removal efficiency. The efficiency of the degradation system in the presence of ethanol was assessed under different ultrasonic power. Moreover, the degradation mechanism was proposed using the data obtained from the degradation steps. Finally, the phyto-toxicological effects of the treated and untreated SIPX samples during the degradation process were examined on an aquatic species.

2. Experimental

2.1. Chemicals

Sodium isopropyl xanthate (SIPX) was obtained from Yantai Lunshun Huitong Biotechnology Co (China). The properties of SIPX are presented in Table S1. As it is given in Table S1, its molecular weight (g/mol) and λ_{max} (nm) is 158.22 and 300, respectively. NaOH, H_2O_2, $K_2S_2O_8$, EDTA, KIO_4, NaCl, Na_2SO_4 and ethanol were obtained from Merck Co (Germany).

2.2. Preparation of Cu_2S nanoparticles

Chalcocite ore was extracted from Sungun copper mine and then crushed by jaw and cone crushers. The obtained sample was crushed further by rod and ball milling to reduce the size of Cu_2S sample. Finally Cu_2S microparticles were subjected to a high-energy planetary ball mill (RETSCH - PM400, Germany) at a rotation speed of 320 rpm for 0.5, 1.5, 3 and 4.5 h to prepare nanostructured Cu_2S. The ball milling process was performed under ambient conditions (25 °C and 1 atm). Different balls with sizes of 1 and 2 mm (10 balls with the size of 1 mm and 5 balls with the size 2 mm) were used in the milling procedure. Both the balls and bowl of the ball milling process were made from stainless steel. The ratio of ball-mass to powder-mass was chosen 10:1.

2.3. Sonocatalytic procedure

The sonocatalytic degradation of SIPX was done in ultrasonic machine Ultra-8060D-H, operating at an ultrasonic frequency of 36 KHz and output power of 150 W. Ice cubes were used to adjust the bath water temperature at 25 °C. For each test, particular dosage of sonocatalyst particles was added to the Erlenmeyer flask containing 100 ml of SIPX solution at specified concentration. The original pH of SIPX solution was 7.3, and the experiments were conducted at this pH value without any pH adjustment. All experiments were conducted in dark to prevent photo excitation of chalcocite nanoparticles. At a defined time interval, a small portion (2 ml) of the reaction solution was taken out and then 2 ml ethanol was added in it to prevent $^{\bullet}OH$ radicals oxidation. After sedimentation of sonocatalyst particles, the top clear solution was used to examine SIPX concentration. Solution absorbance was measured at $\lambda = 301$ nm by using UV–visible spectrophotometer (Analytic Jena, Specord 250, Germany). The removal efficiency was calculated by this equation: $(A_0\text{-}A_t)/A_0 \times 100\%$, where A_0 and A_t are the SIPX absorbance before and after sonocatalytic process. To investigate the influence of some inorganic and organic ions, they were added separately to the SIPX solution.

2.4. Characterization of the catalyst

In the present work, the following analyses were performed to