Journal of Environmental Management 228 (2018) 441–450

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Visible light assisted Fenton oxidation of tartrazine using metal doped bismuth oxyhalides as novel photocatalysts

Gülen Tekin*, Gülin Ersöz, Süheyda Atalay

Ege University, Faculty of Engineering, Chemical Engineering Department, 35100, Bornova, İzmir, Turkey

ARTICLE INFO

Keywords:
Advanced oxidation
Bismuth oxyhalide
Food dye
Green catalyst
Photocatalysis
Visible light

ABSTRACT

This research focused on the abatement of the model food dye, tartrazine, using visible light photo-Fenton oxidation with novel bismuth oxyhalide catalysts. Bismuth-oxyhalide and metal doped bismuth oxyhalide catalysts (BiOCl, Cu-BiOCl, and Fe-BiOCl) were synthesized via the facile co-precipitation method. The catalysts were characterized by SEM-EDX, XRD, BET, and DRS analyses and the results showed that Cu-BiOCl possess a unique flower-like nanostructure with narrow band gap (2.53 eV) which enhanced its visible light photocatalytic activity remarkably which was proven by catalyst screening experiments. A detailed experimental study was carried out to investigate the effects of operating parameters on the degradation and decolorization of the dye and from this the optimum values were determined as 0.25 g/L for photocatalyst loading, 100 W for visible light power, 6 for initial pH, 6 mM for initial H_2O_2 concentration, and temperature of 70 °C. Approximately 91% degradation, 95% decolorization, and 59% TOC reduction were obtained at optimum conditions. The results for the kinetic study showed that the degradation and decolorization reactions are in the pseudo-first order and obey the simplified Langmuir-Hinselwood kinetic model. The activation energies were calculated as 86.54 and 69.39 kJ/mol for degradation and decolorization, respectively.

1. Introduction

Photocatalysis has become a novel technology in recent years for environmental remediation as well as energy generation e.g. water purification and water splitting (Lee et al., 2017). The basic principle of the photocatalysis is the generation of photo-induced carriers i.e. electrons and electron holes which can react with H_2O and form radicals. In the photocatalytic water purification processes, the radicals (mostly hydroxyl radical) attack the organic molecules. These reactions can enable the destruction of the hazardous organic contaminants and completely mineralize them into harmless end products of CO_2 and H_2O (Park, 2017; Wu et al., 2017).

TiO_2 has been used widely as a photocatalyst because of its properties such as non-toxicity, low-cost and high photocatalytic activity. However, the main focus of the studies on photocatalysis shifted from UV light to visible light since visible light can be provided directly by solar irradiation. Unfortunately, recent studies showed that TiO_2 fails under light irradiation with a wavelength greater than ≈350 nm due the wide band gap between the conduction and valence bands (3–3.2 eV). Since only 3–5% of sun light consists of UV light, an artificial source for UV light has to be used that requires great amounts of energy. These drawbacks led an enormous attraction to development of efficient and eco-friendly visible light photocatalysts instead of TiO_2 (Byrne et al., 2017; Lan et al., 2017; Wu et el., 2017).

Bismuth is an environmentally benign metal that facilitates the usage of it in pharmaceutical and cosmetic industries. Recent studies focused on bismuth compounds such as bismuth oxyhalides (BiOX, X:Cl, Br, I), bismuth oxide (Bi_2O_3), and bismuth vanadate $BiVO_4$) as photocatalyst in water treatment and hydrogen production by water splitting (Di et al., 2017; Han et al., 2017). BiOX particularly provides superior photocatalytic properties among bismuth compounds like narrow band gap, high visible light absorption capacity, and chemical stability (Lee et al., 2017). Moreover, their photocatalytic activity prolongs due to their unique layered structure that these layers and the internal electric fields between the layers enhance the separation and transfer of photo-induced carriers (Han et al., 2016). Bhachu et al. reported that the photocatalytic activity of Bi_3O_4Cl was higher than that of the anatase-type TiO_2 under UV light illumination (Bhachu et al., 2016). Therefore, bismuth oxyhalides have become a viable alternative as an effective photocatalyst in a broader spectrum for environmental applications.

Azo dyes are complex aromatic compounds characterized by nitrogen double bond called as azo groups (R_1–N=N–R_2) and they have been commonly used because of their bright colors and cost-effectiveness (Rawat et al., 2016). Tartrazine is an azo dye widely utilized as

* Corresponding author.
E-mail addresses: gulen.tekin@ege.edu.tr (G. Tekin), gulin.ersoz@ege.edu.tr (G. Ersöz), suheyda.atalay@ege.edu.tr (S. Atalay).

https://doi.org/10.1016/j.jenvman.2018.08.099
Received 9 January 2018; Received in revised form 13 August 2018; Accepted 26 August 2018

colorant in food, cosmetic, and textile industries. However, recent studies on possible adverse effects on human health have implicated serious medical problems. Tartrazine itself causes allergic reactions and hyperactivity syndrome in kids and consumption of its toxic by-products, amines, cause kidney and liver failures as well as brain damage, too. Thus, it has been targeted by the scientific community and its daily uptake has been authorized to a permission level of 7.5 mg/kg body weight and its environmental fate has been carefully monitored (Efsa, 2009; Basu and Suresh Kumar, 2016).

Current treatment technologies for industrial dye-containing effluents mostly include combination of physicochemical and biological processes such as filtration, coagulation, sedimentation, and activated sludge, which are mostly limited by the non-biodegradable and toxic nature of the effluent that decreases the process efficiency and huge amounts of solid waste generated which requires undesired addition of more steps to the treatment processes (Dewil et al., 2017, Habibi-Yangjeh and Shekofteh-Gohari, 2017). Thus, the new technologies have become increasingly significant during the last decade and advanced oxidation processes (AOPs) are considered as an effective technology since many studies show that the azo-dyes tended to be easily destructed by AOPs. It is also reported that combination of AOPs in simultaneous hybrid processes, such as UV light assisted ozonation, accelerated decomposition of the dye remarkably which ensures that photo-assisted processes are more promising for efficient treatment for resistant pollutants (Vacha et al., 2013).

The aim of AOPs is oxidation of organic contaminants which are recalcitrant to chemical oxidation with conventional oxidizing agents like O_2. In this context, highly reactive species, mainly ·OH radicals, are generated which have much higher oxidizing potential than the conventional agents and these radicals are powerful enough to attack the strong chemical bonds in the organic structure (Bello and Abdul Raman, 2017).

UV light assisted processes are proven to be technically effective and it is a natural component of solar radiation. Solar radiation is a sustainable resource that can be employed in photochemical processes. Using solar system-based treatment technologies becomes extremely interesting especially for the countries in the tropical and sub-tropical regions on Earth in which availability of solar radiation is quite high (Vacha et al., 2013). However, as aforementioned, UV light has a low share in solar radiation, so employing these systems are still heavily dependent on the photocatalysts that keep their photocatalytic activity under light irradiation with a wavelength of $\lambda \geq$ 300–350 nm.

The main objective of the study is to investigate the treatment of a model food dye, tartrazine, by light assisted Fenton-like oxidation, namely photo-Fenton-like oxidation, in the presence of a novel environmentally benign photocatalyst, bismuth oxyhalides, under visible light irradiation and to conduct a preliminary study to assess the use of natural sunlight for treatment of organic pollutants. The study has an innovative aspect because it suggests an efficient alternative method for treatment of a food dye which suspiciously causes some serious diseases without generating another severe environmental damage by implementing eco-friendly applications for catalyst preparation and treatment steps. Moreover, the photocatalyst used has recently received a great attention since bismuth has a narrower band gap than the conventional titanium oxide photocatalysts which enhances the photocatalytic applications from artificial UV light to natural visible light and brings it to a more environmentally-friendly level especially in terms of energy and reduces the operational cost greatly. Another aspect of the study is to establish a kinetic study to identify the changes in the reaction medium with respect to time which is a crucial step for assessment of the rate of the process.

2. Materials and methods

All of the chemicals including tartrazine (Sigma-Aldrich, Dye content ≥ 85%), $Bi(NO_3)_3.5H_2O$ (Merck, ≥ 98.0%), KCl (Merck, ≥ 99%), $Cu(NO_3)_2{\cdot}3H_2O$ (Merck, ≥ 99.5%), and $Fe(NO_3)_3.9H_2O$ (Merck, ≥ 99.0%) were used as received without further purification. Deionized water was used in all experiments and supplied from water purification system (Merck Millipore-Direct Q3).

2.1. Catalyst preparation

Metal doped bismuth oxyhalide catalysts were prepared in two steps. In the first step, bismuth oxychloride (BiOCl) was synthesized by a facile precipitation method with minor modifications using $Bi(NO_3)_3.5H_2O$ as a bismuth precursor and KCl as chlorine precursor (Janani et al., 2016). Briefly, $Bi(NO_3)_3.5H_2O$ was dissolved in acetic acid at a ratio of 1.5 ml acetic acid/mmol $Bi(NO_3)_3.5H_2O$ and 1 mmol KCl/mmol $Bi(NO_3)_3.5H_2O$ was added to 15 ml deionized water/mmol KCl. Then the Bi and Cl precursor solutions were mixed and the mixture was stirred magnetically for 30 min followed by the centrifugation of the BiOCl precipitate. The precipitated BiOCl particles were dried in an oven for 12 h at 110 °C and referred to as BiOCl catalyst. The metal doping of BiOCl catalyst was performed with Fe^{3+}/Cu^{2+} ions via the wet impregnation method using metal nitrate salts as metal precursors at a weight ratio of 10% metal to catalyst. The impregnation was carried out with simultaneous heating to evaporate the water content. The wet solid impregnated catalyst was dried in the oven at 110 °C to remove residual moisture. The obtained Cu and Fe doped particles were referred to as Cu-BiOCl and Fe-BiOCl catalysts. An additional calcination step was applied at 300 °C in a chamber furnace with air atmosphere for 3 h to increase the catalyst stability for the most successful catalyst from screening experiments. The calcination temperature was limited based on the previous studies to avoid destruction of the oxyhalide structure (Yu et al., 2011).

2.2. Catalyst characterization

Several characterization techniques were performed to determine the textural, physical and chemical properties of the undoped, metal doped, and calcinated metal doped catalysts. Scanning electron microscopy (SEM) analysis was performed to determine the surface morphology. The scanning electron microscope at a scanning voltage of 5 kV was equipped with a back scattered emission detector to determine the atomic distribution on the catalyst surface by contrast imaging (Thermo Scientific, Quanta 250FEG). Additionally, SEM analysis using an energy dispersive X-ray spectroscopy (EDX) detector was employed for elemental analysis. The phase structure of the catalysts was investigated by X-Ray diffraction (XRD) analysis between 5 and 80° (2θ) with an X-ray diffractometer operating at 40 kV of voltage and 40 mA of tube current with Cu-Kα radiation (Phillips, X'Pert Pro). The surface area and pore size distribution analyses were carried out by multi-point BET analysis using an N_2 adsorption apparatus operating at 77 K (Quantachrome, Autosorb-6). The diffuse reflectance spectra (DRS) analysis of the catalysts were used to determine the band gap energies. The DRS analysis was performed using a UV–Vis spectrophotometer in reflectance mode equipped with an integrating sphere attachment using as $BaSO_4$ as standard (Shimadzu, UV 2600-ISR). The band gap energies were estimated by converting the diffuse reflectance spectrum between 200 and 800 nm to the Kubelka–Munk function $F(R_\infty)$ where R_∞ is the absolute reflectance of an infinitely thick layer of the material and equal to the ratio of reflectance of the sample and reflectance of the reference standard material ($R_\infty = R_{sample}/R_{standard}$). The band gap was determined by extrapolating the intercept of the Kubelka-Munk plot linearly for each catalyst (Yener and Helvaci, 2015).

2.3. Experimental set-up and experimental procedure

Degradation-decolorization experiments for the photo-Fenton-like oxidation of tartrazine were carried out using an experimental set-up which mainly consists of a beaker, a temperature controlled magnetic