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Research Paper

Degradation of azo dye Orange II under dark ambient conditions by calcium strontium copper perovskite

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ABSTRACT

This work investigates the effect of calcium strontium copper (CSC) based catalysts for the degradation of an azo dye orange II (OII) under dark conditions without the addition of peroxides or ozone. CSC were synthesized via a combined EDTA-citric acid complexation method. The resultant catalyst was composed of perovskite and metal oxide phases, however, the perovskite phase was the most active for degradation of OII. The content of Ca and Sr in the A-site of the perovskite structure was varied whilst the B-site was Cu rich. CSC compounds with higher Ca content in the A-site were slightly more effective at degrading OII. The degradation kinetics under dark conditions was fast with up to 80% of OII being degraded within 10 min. TOC results showed that the degradation was only partial as more than 60% of the organic carbon remained in the solution, supported by the formation of by-products determined by HPLC. The remainder of the carbon were found to be adsorbed on the surface of the spent CSC catalyst, as by-products of the reaction and OII molecules. The CSC catalyst proved to be effective for breaking $-N{=}N-$ bonds from solutions containing low (10 ppm) to high (100 ppm) OII concentrations. This reaction produced electrons which generated radical species, including hydroxyl radicals as confirmed by 2-propanol, which further degraded OII and its by-products.

1. Introduction

The disposal of wastewaters containing organic pollutants from textile industries is of global environmental concern. Worldwide approximately 280,000 tons of textile dyes are discharged in industrial effluents every year [1,2]. Azo dyes, which contain $-N{=}N-$ bonds, are widely used by the textile industries, accounting for over 50% of all commercial dyes [3]. These dyes are non-biodegradable and toxic [4–6], whilst affecting water transparency even at small concentrations ($1\ \text{ppm L}^{-1}$) [7], limiting the penetration of sunlight necessary for aquatic photosynthesis [8]. For this reason, textile wastewater emissions have been scrutinised by non-governmental agencies and the public resulting in environmental protection agencies around the world developing stringent guidelines to control their emissions and have legislated hefty penalties for non-compliance. To address this problem, many processes based on physical, biological and chemical methods, have been developed and trialled. In general, physical methods (e.g. flocculation, adsorption and membrane filtration) suffer from secondary pollution as they merely transfer pollutants downstream without achieving a real degradation of target pollutants [9]. As such, physical processes still require downstream processing of wastewaters. Bio-treatment of azo dyes is usually considered ineffective due to the resistance of the dyes to aerobic degradation [10,11]. Biodegradation requires the use of living organisms under strict process conditions (e.g., pH and temperature) [12] which tend to be greatly affected in textile wastewaters due to the toxicity of most commercial dyes [13]. Additionally, azo dyes undergo reductive cleavage through anaerobic biological treatment and potentially generate toxic aromatic amines [14,15].

Advanced oxidation processes (AOPs), in which highly reactive oxidative species (e.g. $HO\cdot$, $O_2\cdot^-$, O_2, $HOO\cdot$ and $HO_2\cdot$ [16]) are utilized, have been widely studied as an alternative way of treating organic pollutants [17]. AOPs can be categorized into photo- and dark-oxidation procedures. Photocatalysis, especially using TiO_2 catalysts, is widely known as an efficient method to remove and destroy organic pollutants under light irradiation. For instance, Cd-doped TiO_2 degraded 95% of OII after 2 h when illuminated with visible light [18]. Photocatalysis however is generally energy intensive and greatly inhibited in the absence of light illumination. Dark oxidation (e.g., ozonation, ultrasonication and Fenton process) are alternative methods, dispensing the need of light radiation, by requiring reactants such as O_3 and/or H_2O_2. The heterogeneous Fenton-like reaction has proved to be

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attractive, with the production of new catalysts such as iron oxides compounded with graphene oxide [19], Cu sulfate [20], and vanadium titanate [21]. Compounds containing graphene oxide have been found to greatly improve the degradation efficiency of OII, though Cu sulfate iron oxide proved to deliver the best performance reaching ~100% OII degradation in 60 min. These reactions do however need H_2O_2 to generate the powerful HO· radicals for the destruction of organics. A more interesting approach is the degradation of organic pollutants in wastewaters without the aid of external stimulants or light illumination. In this way, there is no need for extra costs associated with the consumption of chemical products or energy.

Recently, perovskites have attracted the attention of the research community due to their ability to oxidize and remove organic compounds from wastewater in dark ambient conditions. Perovskites are crystalline ceramics with a cubic structure described by the general formula ABO_3, where the partial substitution of the cation sites (A or B) with other cations (A' or B') results in $A_xA'_{1-x}B_yB'_{1-y}O_{3-\delta}$ compounds. Rummino et al. [22] showed that $Sr_{0.85}Ce_{0.15}FeO_{3-\delta}$ perovskite-type mixed oxide degraded orange II and rhodamine B as model pollutants without light irradiation. Initial reports using $BaFeO_{3-\delta}$ showed it took 5 days to remove 50% of methyl orange [23]. By replacing Ba in the A-site with Sr and forming a perovskite $SrFeO_{3-\delta}$, acid orange 8 (150 μM) was degraded in 60 min [24]. These results give a clear indication that the cation used in the perovskite compound plays a major role in the catalytic degradation of organics in wastewaters. There are a number of cations that can be used as doping rare earth or earth alkaline elements at the A site and transitional metals at the B site. A transitional metal of interest is Cu, with recent reports for oxygen systems showing outstanding performance in $Ba_{0.5}Sr_{0.5}Co_{0.8}Cu_{0.2}O_{3-\delta}$ (BSCC) [25], or in binary $Co_{0.8}Cu_{0.2}O_x$ [26] compounds. Indeed, Cu has been used as a cation in perovskite compounds and tested for the degradation of organic compounds in solutions. However, these Cu containing perovskites were tested using hydrogen peroxide in a heterogeneous Fenton-like reaction. Examples include Cu doped $LaTiO_3$ perovskite for the degradation of rhodamine B [27] and $LaCuO_3$ perovskite for the degradation of phenol [28].

Therefore, this work investigates the performance of novel perovskites in the degradation of dyes under dark conditions and without any external stimulants (i.e. no ozone or no hydrogen peroxide). We fully substituted Fe in the B-site with Cu, and in the A-site Sr was partially or fully substitute with Ca, in a series of $Ca_xSr_{1-x}CuO_{3-\delta}$ (CSC) with x varying from 0, 0.25, 0.5, 0.75 to 1. OII dye was the model organic pollutant tested as it is widely used in the textile industry. The CSC perovskites were fully characterized to understand their materials properties; and tested from low (10 ppm) to high (100 ppm) OII aqueous concentrations. The relationship between the materials properties and catalytic performance is discussed and an OII degradation mechanism using CSC perovskite under dark condition is proposed.

2. Materials and methods

2.1. Synthesis and characterisation

All chemicals were used as received including strontium nitrate (98% Alfa Aesar), copper (II) nitrate hemi (pentahydrate) (98% Alfa Aesar), calcium nitrate tetrahydrate (> 99.0% Chem-Supply Pty Ltd), aqueous ammonia solution (30% Chem-Supply Pty Ltd), citric acid monohydrate (99.5% Chem-Supply Pty Ltd) and ethylenediamine tetraacetic acid (EDTA, 99% Sigma-Aldrich). The target organic pollutant was OII also known as Acid Orange 7 (Molecular formula: $C_{16}H_{11}N_2NaO_4S$, M_w:350.32 g mol^{-1}, $\lambda_{max} = 485$ nm, > 85% Sigma-Aldrich).

CSC ($Ca_xSr_{1-x}CuO_{3-\delta}$, x = 0, 0.25, 0.5, 0.75 and 1) was prepared via a combined EDTA-citric acid complexation method. The molar ratios of total metal ions, EDTA, citric acid, and ammonium hydroxide were kept at 1:1.1:2:10. Initially, ammonia aqueous solution was added to a beaker containing EDTA under stirring until EDTA was completely dissolved and a clear solution was formed. In a separate beaker, stoichiometric quantities of nitrate salts and citric acid were dissolved in deionized water to obtain a mixture solution. Subsequently, the EDTA solution was added into the mixture solution under stirring to get the desired solution, which was heated while magnetically stirred to evaporate most water until a viscous fluid was attained. This final mixture was initially sintered in atmospheric air in a furnace up to 450 °C with a dwell time of 8 h utilizing heating and cooling rates of 5 °C min^{-1}. A second sintering step was applied up to 1000 °C using the same dwell time and ramping rates.

The crystalline phase of the ground samples was characterized by X-ray powder diffraction (XRD, D8 Advance, Bruker, USA) with Cu-Kα radiation ($\lambda = 1.5406$ Å) at 40 kV and 40 mA by step scanning in the range of $10° \leq 2\theta \leq 100°$. X-ray photoelectron spectroscopy (XPS) was performed on X-ray photoelectron spectrometer (Kratos Axis ULTRA) equipped with monochromatic Al Kα (hv = 1486.6 eV) radiation and calibrated internally by carbon deposit C 1s binding energy (BE) at 284.8 eV to quantitatively analyse the chemical composition of samples and chemical state of elements. The powder morphology was analysed using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS). Nitrogen adsorption at 77.4 K on degassed samples at 150 °C was carried out using a Micromeritics TriStar 3000 to determine BET surface area. The remaining TOC in the sample solutions was monitored using a Shimadzu TOC-Vcsh Total Organic Carbon Analyzer. Mass loss analysis was performed using a TGA-DSC 1 Thermogravimetric Analyser (Mettler Toledo) by heating the samples from 28 to 800 °C at a heating rate of 5 °C min^{-1} under air atmosphere at a flow rate of 80 mL min^{-1}. The infrared absorption spectra were recorded using a Fourier transform infrared (FTIR) spectrophotometer (IRAffinity-1, Shimadzu).

2.2. Catalyst evaluation

The catalytic degradation of OII over dispersed CSC was conducted in a 250 mL beaker, in which 200 mg of the catalyst was suspended in 200 mL of OII aqueous solution in dark at room temperature without any external stimulant. The dispersion of CSC in water was achieved by magnetic stirring during the degradation process. At designated intervals, ~5 mL of reaction suspension was sampled and filtered using 0.45 μm Milipore syringe filters. The samples were analysed using a UV–vis spectrophotometer (Evolution 220, Thermo Fisher Scientific) to determine the degradation yield (d) of OII at its characteristic wavelength $d = (A_0–A_t)/A_0$, where A_t is the absorbance of treated OII solution at time t and A_0 is the absorbance of the initial OII solution. Recyclability of CSC was evaluated using OII (20 ppm). At the time interval of 15 min, 5 mL reaction mixture was sampled and analysed by UV–vis spectrometer. After each cycle (1 h reaction), 20 mL 2000 ppm OII stock solution was added to the remaining reaction mixture (180 mL) to compensate the consumed OII and to maintain the 200 mL reaction mixture volume. 2-propanol (Alfa Aesar, 0.10 M) mixed in an OII solution was used as hydroxyl radical (HO·) scavenger.

A fully computer controlled HPLC system (UltiMate 3000, UHPLC$^+$ focused, Thermmo Scientific) comprising a quaternary solvent delivery pump, diode array and fluorescence detectors and an auto sampler was used to follow OII concentration-time profiles. Potential products were separated on an Eclipse XDB-C8 5 μm, 150 mm × 4.6 mm column using 70:30 aqueous solution of ammonium acetate (20 mM): acetonitrile as an isocratic mobile phase at 1 mL min^{-1} and ambient temperature. The injection volume was 20 μL and detection was achieved with the diode array detector set at 253 nm. Degradation products were determined using liquid chromatography-mass spectrometry (LC–MS) system. A LC system (UltiMate 3000, UHPLC$^+$ focused, Thermmo Scientific) was equipped with a C18 column (4.6 mm × 150 mm × 5 μm) and coupled online to an electrospray ionisation mass spectrometer (ESI–MS, Thermo Fisher Scientific Orbitrap Elite).