



Catalytic activity of copper modified bentonite supported ferrioxalate on the aqueous degradation and kinetics of mineralization of Direct Blue 71, Acid Green 25 and Reactive Blue 4 in photo-Fenton process

Olumide Bolarinwa Ayodele^{a,*}, Olayinka S. Togunwa^b

^a Department of Chemical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

^b Department of Geology, University of Malaya, 50603 Kuala Lumpur, Malaysia

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ABSTRACT

In order to enhance depuration of pollutants in photo-Fenton process, copper modified bentonite supported ferrioxalate catalyst (CuMBFOx) was synthesized. The catalyst was characterized with TGA, XRF, XRD, FTIR, BET and SEM techniques. Its catalytic activity was evaluated on the degradation of Direct Blue 71 (DB71), Acid Green 25 (AG25) and Reactive Blue 4 (RB4) dye pollutants in batch photo-Fenton process without pH adjustment. The results showed complete depuration below the detection point of UV–vis spectrophotometer as monitored on their respective UV–vis degradation spectra. The extent of mineralization ability of the CuMBFOx was monitored with chemical oxygen demand (COD) analysis and was used to study the kinetics of mineralization of the dyes using a developed phenomenological mathematical model. The result showed that the efficiency reduced in the order DB71 > AG25 > RB4 owing to their chemical components and structural complexities. CuMBFOx demonstrated excellent qualities toward depuration of DB71, AG25 and RB4.

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1. Introduction

An alarming death rate of 14,000 daily through direct and indirect water pollution caused by industrialization in the developed countries have been reported and this number may increase considering the ever increasing worsening rate of water pollution [1,2]. Water pollutants can enter the aquatic medium in several ways, either dumped directly from wastewater treatment plants (WWTP) that shied away from their obligations or, as industrial effluents from different process plants like pharmaceuticals, textiles and tanning [3] as well as the use biocides and fertilizers in agriculture [4]. Amongst all these water pollutants, dyes such as Direct Blue 71 (DB71), Acid Green 25 (AG25) and Reactive Blue 4 (RB4) seems to be more prevalent in the environmental matrix due to their wide usage in textile, paper mill, photography, etc. They are lethal, hazardous and carcinogenic contaminants and as such they have been classified as one of the foremost pollutants in United State Environmental Protection Agency (USEPA) list with limit of discharge less than 0.5 ppm [1,5].

In order to abide by the USEPA standards to ensure a sustainable environment, there is urgent need to urgently depurate these water pollutants. Typical processes that had been used to

decontaminate wastewaters are biological [5], physical [6,7] and chemical [8]. Unfortunately, these conventional wastewater treatment processes are inefficient to handle these emerging and priority pollutants, for example, physical treatment method like adsorption can only transfer the pollutants from the aqueous organics phase onto a solid leaving the contaminants undestroyed, as such there is need to mineralize the pollutants. Advanced oxidation processes (AOPs) had been identified to provide better alternatives for protection of public health and the environment as per total degradation and mineralization of water pollutants [9–14]. Fenton process seem to be the most studied AOP, it employed hydrogen peroxide (HP) at room temperature and pressure to generate the required HO• from catalyst active sites, and ferrous ion is the traditional Fenton catalyst practiced in the homogeneous phase. However, the inherent setbacks in the homogeneous Fenton process such as difficulty in catalyst recovery, over sensitivity to operational narrow pH range and formation of ferric sludge has necessitated the development of heterogeneous catalysts [2,13,15]. In the development of heterogeneous photo-Fenton catalysts, different materials ranging from rice husk [5,16], pillared montmorillonite [9], acid modified kaolinite [17], zeolite [18], smectite clay [19], etc. has been studied and reported as support for ferrous or ferric ions. Similarly Yip et al., [19] reported that copper deposition on acid-activated bentonite clay as heterogeneous catalyst for the photo-Fenton-like oxidation of textile organic pollutants dyes showed excellent catalytic activity including the ability

* Corresponding author. Tel.: +60 164955453.

E-mail address: ayodele.olumide@yahoo.com (O.B. Ayodele).

to deplete the dyes over wider pH range contrary to the typical Fenton process that has optimum pH around 3. In addition, the presence of oxalate in photo-Fenton catalysts has been reported to enhance its catalytic ability, reduce metal leaching, generate minimal and less toxic intermediate compounds [14,20], and ability to absorb photo irradiation over a wider spectrum range [21,22]. In addition, oxalate based catalysts have the ability to degrade pollutants without the initial pH adjustments of the pollutants [13,23].

The effects of factors affecting the degradation rate of pollutants in traditional Fenton and photo-Fenton process have been well discussed in the literature [9–23]. In one of our recent studies, the hierarchy of importance of these factors, their optimization using response surface methodology (RSM) as well as the development of phenomenological mathematical model for the kinetics of the degradation process based on photo-Fenton chemistry was critically studied and reported [15]. It was observed that increment in both catalyst (Fe^{2+}) and HP dosage increase the degradation efficiency up to the optimum point beyond which further increment leads to reduction in the degradation efficiency principally due to scavenging effects of both Fe^{2+} and HP on the reactive HO^\bullet [9–15]. Similarly, effects and optimization of other parameters such as temperature, initial concentrations of pollutant and time have also been widely studied [13] and reviewed [2]. In almost all the contemporary reports on photo-Fenton process, emphasis is centered on improving the catalyst synthesis and characterization [16–19]. In view of this, copper modified bentonite supported ferrioxalate catalyst (CuMBFOx) was synthesized in this study and characterized with TGA, XRF, XRD, FTIR, BET and SEM techniques. Its catalytic activity was evaluated on the degradation of DB71, AG25 and RB4 in batch photo-Fenton process and the results showed complete depuration below the detection point of UV-vis spectrophotometer as monitored on their respective UV-vis spectra changes. The extent of mineralization ability of the CuMBFOx was monitored with chemical oxygen demand (COD) analysis and employed to study the kinetics of mineralization of each dye.

2. Materials and methods

2.1. Materials

Direct Blue 71 (DB71), Acid Green 25 (AG25), Reactive Blue 4 (RB4), hydrogen peroxide (HP) solution (30%, w/w) and bentonite were purchased from Fluka, while the iron trihydroxide, copper nitrate and oxalic acid were purchased from Merck (Germany). The basic properties and structure of the three selected model pollutants are shown in Table 1.

2.2. Catalyst synthesis

The catalyst was prepared following a slight modification of an existing method [24] by first hydrolyzing 9.6 g CuCl_2 using 200 mL of 0.45 M NaOH, the resulting bluish solution with pH of about 4 was added drop wisely to a vigorously stirring 20 g/L bentonite dispersion and continue stirring for 12 h followed by filtration and washing. The Cu modified bentonite (CuMB) sample was dried in the oven at 110 °C, calcined at 400 °C for 2 h and grinded to powder. Ferrioxalate complex that was prepared by reacting 1.44 g of oxalic acid and 1.16 g of iron hydroxide to produce 2 g of FeOx complex in a corked conical flask wrapped with aluminum foil because of the FeOx sensitivity to light [21,22] was added to the CuMB dispersion and stirred for 6 h at 50 °C, the product was filtered and dried in the oven at 110 °C for 12 h then grinded to powder. The synthesized copper modified bentonite supported ferrioxalate catalyst (CuMBFOx) was then mixed with polyvinyl alcohol binder (ratio 12:1, w/w) and the mixture was extruded and sieved to obtain particle

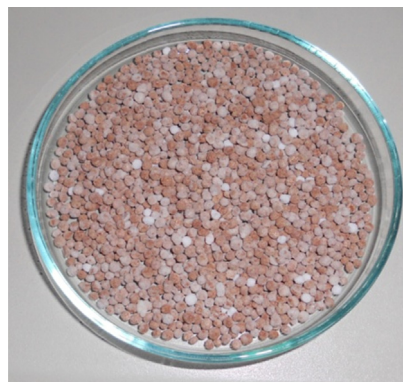


Plate 1. Sample of calcined CuMBFOx.

size of 2.5 mm. The extruded CuMBFOx grains were freeze dried to maintain their capillary structure and calcined at 450 °C. The sample of the calcined catalyst is shown in Plate 1.

2.3. Catalyst characterization techniques

The TGA analyses were carried out with a SHIMADZU DTG-60/60H instrument to determine the weight loss on the samples with temperature increment. 2 g of each sample was heated in a silica crucible at a constant heating rate of 10 °C/min in a stream of N_2 atmosphere with a flow rate of 40 mL/min from 25 to 700 °C. The weight losses per temperature increment and per time were recorded. The elemental compositions of all the samples were determined using EDX microanalysis system (Oxford INCA 400, Germany). The XRF analyses of the samples were done to determine the chemical composition of the sample using a Philips Model-PW2400 and X-ray tube of rhodium anode and scintillation detector operating on a 40 mA current and 40 mV voltage. The samples were bombarded with high-energy X-rays and the X-ray reflections from the excited samples were detected by the scintillation detector, the detected spectra were amplified and recorded using the computer program installed on the XRF analyzer.

The XRD patterns of the samples were measured with Philip PW 1820 diffractometer to determine the crystal phase and structure of the metal oxides earlier detected by XRF analysis. Diffraction patterns of the samples were recorded with $\text{Cu K}\alpha$ radiation and recorded in the range of 5–90° (2θ) with a scanning rate of 2°/min and a step size of 0.01°. The X-ray tube was operated at 40 kV and 120 mA. The FTIR analyses were performed on the samples to determine the functional groups present in order to understand the chemistry of the samples. Perkin-Elmer Spectrum GX Infrared Spectrometer with resolution of 4 cm^{-1} operating in the range of 4000–400 cm^{-1} was used. The samples and analytical grade KBr were dried at 100 °C over-night prior to the FTIR analysis. A mixture of 0.25 mg of each sample and 100 mg of KBr were grinded to fine particles and was placed in a manually operated hydraulic press operated at 8 Mbar to obtain a translucent disk of 12.7 mm diameter and about 1 mm thickness. The obtained spectra during the analysis were automatically plotted by the software (Spectrum version 5.0.2) installed on the computer attached to the FTIR instrument. The surface area, pore size and pore volume values were calculated by Micropore version 2.46 software using Brunauer–Emmet–Teller (BET) equation with an autosorb BET apparatus, Micromeritics ASAP 2020 at liquid nitrogen temperature (–196 °C). Prior to each measurement, the samples were first degassed at 300 °C for 2 h and thereafter kept at liquid nitrogen temperature to adsorb nitrogen that was thereafter desorbed in an automated procedure and operates with the static volumetric technique. SEM was used to study the surface morphology of all the samples. The analysis was

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