



Enhanced degradation of an azo dye by catalytic ozonation over Ni-containing layered double hydroxide nanocatalyst

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ABSTRACT

The catalytic activity of Ni-based layered double hydroxides (Ni-LDHs) nanomaterials was studied for the first time in ozonation of simulated dyeing wastewater for dye degradation (methyl orange (MO)). For the purpose of comparison, degradation of MO by non-catalyzed ozonation was also considered. The degradation experiments were performed in a laboratory scale cylindrical batch reactor. The effect of catalyst was studied using UV–Vis, chemical oxygen demand (COD) and ion chromatography (IC) analyses. The influence of various operating factors such as reaction temperature, dye concentration, catalyst dosage and hydroxyl radical scavengers (bicarbonate-carbonate) on the MO dye degradation rate were investigated. The catalytic ozonation exhibits total discoloration with faster reaction rate and clearly enhances the COD removal. In optimized conditions, after 60 min reaction, COD removal has reached 72% in the catalytic ozonation process, while it reached only 30% in non-catalytic ozonation. Additionally, the characterization results of Ni-LDH catalyst before and after ozonation experiments were discussed. A possible mechanism of degradation was suggested.

1. Introduction

Ozone (O₃) is known as a powerful oxidant in the aqueous medium which exhibits a fast reactivity towards almost all of the organic compounds [1]. Accordingly, ozonation became over the years a well-established technology applied to decolorize wastewaters and to degrade various organic compounds, especially dyes [2–6]. Ozone may react either by a direct electrophilic attack as molecular ozone or via an indirect reaction through a radical pathway which leads to the generation of additional powerful oxidants like hydroxyl radical (·OH) [7]. Indeed, using simply ozonation is effective for discoloration of wastewater, but it does not provide in many cases a complete mineralization (monitored by chemical oxygen demand (COD)) which results in the formation of biodegradable organic matter (e.g. carboxylic acids, carbonyl compounds) [8] or inorganic compounds and water.

Ozonation processes using solid catalysts have gained more interest, which gave an insight into the catalytic ozonation process (COP). The COP as an advanced oxidation process has been investigated in order to provide better degradation efficiency. In the COP, the decomposition of ozone is enhanced due to the presence of a solid substance as a catalyst, which generates radicals that are more reactive. Compared to non-

catalyzed ozonation, these radicals are more powerful than molecular ozone that increase the mineralization rate, reduce the reaction time and so lower costs. Further, solid catalysts are used to promote surface phenomena, where the adsorption process plays a crucial role [9,10]. A wide variety of solid catalysts have been investigated so far, including metal oxides [11–13], zeolites [14], clay minerals [15] and activated carbon [16]. Based on the nature of the used catalyst, the COPs could be classified as heterogeneous and homogeneous processes.

Among these catalysts, layered double hydroxides (LDHs) are synthetic anionic clays having the general formula $[M_1^{2+}_x M_2^{3+}_y (OH)_z] A_{x/m}^{m-} \cdot nH_2O$, where M²⁺ represents a divalent metal, M³⁺ a trivalent metal, and A^{m-} an anion. The wide choice of metal cations, especially from the transition metals, and the abundance of hydroxyl groups in the layer structure give the LDH materials excellent catalytic properties [17]. Consequently, these nanomaterials have been widely used in heterogeneous catalysis whether as precursors, actual catalysts or catalyst supports for various reactions like electrocatalytic reactions [18–20], photodegradation [21–23], and decomposition reactions [24–26].

Despite the growing interest in this field, less attention has been devoted to the investigations on the catalytic activity of LDHs in

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ozonation process, especially for dyes degradation. Nonetheless, Sui et al. [27] studied the catalytic activity of Co- and Mn-containing LDHs in nitrobenzene degradation by ozonation where the mineralization of nitrobenzene increased in the presence of the catalyst compared to non-catalytic degradation. Recently, Ranjbar and Hessam [28] used Cu- and Mg-LDH-chitosan, where chitosan is a supporting agent for the catalyst, to degrade landfill leachate in wastewater. Indeed, the use of catalyst has considerably increased the COD rate due to the formation of $\cdot\text{OH}$, providing more degradation of the landfill leachate effluent rather than in non-catalytic ozonation. This was due to the presence of different transition metals in Cu- and Mg-LDH-chitosan that enhanced ozone decomposition to form $\cdot\text{OH}$ radicals or other reactive species.

Hence, this paper aims to focus on the utilization of LDHs compounds as heterogeneous nanocatalysts for the degradation of azo dye by ozonation. Methyl orange (MO), an azo dye commonly identified as a hazardous contaminant was adopted as the model pollutant herein. To the best of our knowledge, the degradation of MO was solely investigated by ozone [29] and there is no other information reported in the literature concerning its degradation by catalytic ozonation using LDHs as heterogeneous nanocatalysts.

In our previous work [30], we synthesized a 3D flower-like Ni-containing LDH as a highly efficient adsorbent for MO removal from aqueous solution. Thus, in this study, the catalytic activity of the same material in MO degradation by ozonation will be investigated. The discoloration rate and mineralization of MO were studied, and the suggested mechanism of MO degradation was explored. A comparison was conducted between the degradation of MO under catalytic and non-catalytic ozonation.

2. Materials and methods

2.1. Preparation of dyeing wastewater

The commercially available MO dye was utilized without further purification. Fig. 1 illustrates the molecular structure and UV–visible absorption spectra of MO. The simulated MO containing wastewater stock was prepared by dissolving 0.5 g of MO dye in a 1 L volumetric flask (500 mg/L) then the solutions with the desired concentration were obtained by diluting the stock solution using distilled water.

2.2. Preparation of the nanocatalyst

Ni-LDH was synthesized in our previous work by a modified co-precipitation method [30]. A solution of mixed metal nitrates (Ni

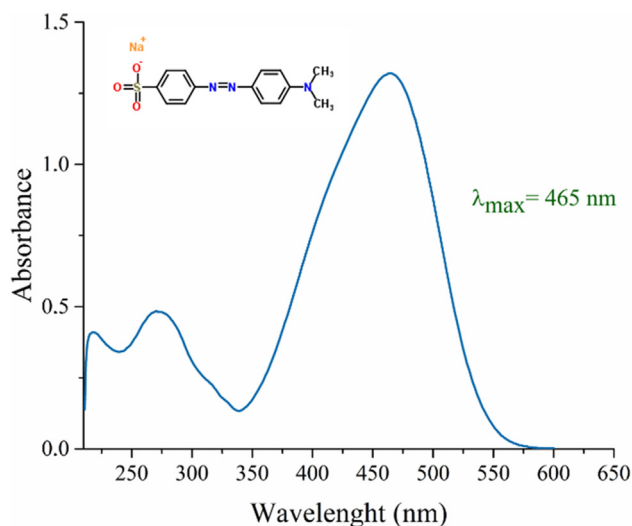


Fig. 1. UV–Visible spectra and molecular structure of MO dye.

$(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was added dropwise under vigorous stirring into a reactor initially containing aqueous NaOH solution (10^{-4} M, 200 mL). During the co-precipitation process, the pH was kept at around 10 by adding alkaline solution (0.5 M Na_2CO_3 , 2 M NaOH). After aging at room temperature $25 \pm 2^\circ\text{C}$ for 18 h under vigorous stirring, the obtained suspension was filtered and repetitively washed with deionized water. The green gel was dried for 18 h at 80°C .

2.3. Characterization and analytical methods

Ni-LDH catalyst was characterized previously by Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), and the Brunauer, Emmett and Teller (BET) analyses [30]. Surface functional groups of the catalyst after ozonation experiments were determined using Fourier Transform Infrared spectrometer (FT-IR, Varian 800 Scimitar Series, Australia) via Attenuated Total Reflectance (ATR, GladiATR™ mode). Spectra were recorded in the range of $400\text{--}4000\text{ cm}^{-1}$ with spectral resolution 4 cm^{-1} and 50 scans. Morphological changes of the catalyst were also investigated using Scanning Electron Microscope (SEM, Phenom XL) with an accelerating voltage of 10 kV. The samples were spread on carbon tape, coated with a thin gold layer and loaded onto a SEM stage.

The degradation efficiency of MO dye during catalytic ozonation was determined by the color removal and the COD reduction. Color measurements were done on Evolution™ 300 UV–Vis Spectrophotometer (Thermo Scientific, USA).

COD measurements were performed using accelerated and modified COD method. The main difference from the ISO 6060:1989 method was manifested in working in excess concentrated sulfuric acid medium in order to reach a temperature of $\sim 105^\circ\text{C}$. The value of COD was determined by a titration according to ISO 6060:1989 method.

2.4. Experimental set-up

A 500 mL capacity glass column reactor was used for the ozonation experiments and the schematic set up is shown in Fig. 2. Another study investigated a similar experimental system [31]. Ozone was produced by “Cold Corona” process using PORTAZONE™ ozone generator. As shown in Fig. 2, the reactor has an inlet for the ozone gas coming from the ozone generator, an outlet for the residual gas, and another one for sampling. Ozone was continuously purged into 400 mL of dye solution through a porous ceramic stone diffuser that can produce fine bubbles while the solution was kept under magnetic stirring. Ozone flow rate represents the ozone inlet mass flow rate in the reactor that equals 109 mg/h. The residual ozone was captured in a gas washing bottle containing distilled water and NaNO_2 . At each regular time, a sample was pipetted via the sampling port of the reactor, diluted if necessary then separated from the suspended catalyst particles. The supernatant was used for absorption and COD measurements.

3. Results and discussion

3.1. Effect of the nanocatalyst

In order to explore the catalytic activity of Ni-LDH on MO degradation, four processes were performed: (1) single ozonation, (2) catalytic ozonation, (3) adsorption test where air but not ozone was purged into the reactor and (4) a test under air alone where air was fed into the reactor without the presence of catalyst. The evolution of discoloration rate and COD removal under the same experimental conditions in all the processes are given in Fig. 3. As shown in Fig. 3a, the effect of air was completely negligible towards MO dye degradation rate. The adsorption test without ozone showed a little effect at reaction conditions, where the discoloration rate achieved 16% at 10 min then remained constant, while an insignificant COD removal rate was observed.

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