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Solar photocatalytic degradation of *o*-phenylenediamine by heterogeneous CuO/X zeolite catalyst

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ABSTRACT

The present study involves the photocatalytic degradation of *o*-phenylenediamine (OPD) employing heterogeneous photocatalytic process. The CuO/X zeolite catalyst was prepared by supporting CuO on the zeolite X matrix and photocatalytic activity of the catalyst under solar irradiation was investigated. The parent zeolite, ion exchanged media and photocatalyst were characterized by atomic absorption spectroscopy, X-ray diffraction, infrared spectroscopy, BET and thermal analysis methods. The degradation process was monitored during the experimental runs through UV/Vis absorption as well as COD and TOC concentration determination and HPLC methods. Effect of key operating factors affecting photocatalytic degradation efficiency of OPD was investigated and the optimum values were obtained as: 0.3 g L^{-1} of photocatalyst, 25 ppm for *o*-phenylenediamine, pH of 7.1, 20 mM of H_2O_2 and 10 mM of $KBrO_3$. The obtained results showed that photocatalysis under sunlight is effective process for the degradation of OPD and the degradation kinetic of OPD obeys Langmuir–Hinshelwood equation.

1. Introduction

o-Phenylenediamine is an aromatic amine used as a component of polymers, drugs, and dyeing substrate in dyeing compositions [1–3]. OPD has been found to be hazardous in case of ingestion, inhalation, eye contact and mutagenic [4]. Existing methods for the removal of aromatic amines from water include adsorption, microbial, chemical oxidation, electrochemical techniques and irradiation [5]. However, all of these methods suffer from serious shortcomings such as high cost, incompleteness of degradation, formation of hazardous by products, and low efficiency [5]. In order to remove *o*-phenylenediamine from wastewater, a few studies such as hydrogen peroxide-oxidation of *o*-phenylenediamine catalyzed by horseradish peroxidase and cobaltoxime(II) derivatives have been done [6,7].

Recently, there has been considerable interest in the utilization of the advanced oxidation processes (AOPs) for the destruction of organic compounds in contaminated water. Two of them seem very promising: the UV/oxidation process, which involves ultraviolet irradiation in conjunction with hydrogen peroxide and the heterogeneous photocatalysis. The key advantage of the former is its inherent destructive nature. It does not involve mass transfer; it can be carried out under ambient conditions and may lead to complete mineralization of organic carbon into CO_2. Moreover, photocatalytic process is receiving increasing attention because of its low cost when using sunlight as the source of irradiation [8]. Despite that AOPs have shown to be adequate for the degradation of persistent organic compounds, they may involve considerable energy consumption, related to the UV lamps that provide photons to the system. Some disadvantages of this method are: the price of consuming scarce resources and generating pollutant emissions and waste, associated to the electricity needed. On the other hand, it is well known that several AOPs can be performed under solar irradiation, as the sun provides photons with the wavelength required for these processes. This is a key point, since solar irradiation is a renewable and clean energy source [9].

Sunlight is the source of illumination to perform different photocatalytic reactions. Visible light is a major component of sunlight as compared to UV–vis light, which is only about 4% of total solar radiation. Due to this point, development of a stable photocatalytic system, which should be effective in the presence of visible light, is indispensable from the view point of efficient utilization of sunlight [10].

Heterogeneous photocatalysis is an emerging valuable technique for air and water purification. When a photon of energy higher or equal to the band gap energy of a semiconductor is absorbed, an electron from the valence band is promoted to the conduction band with simultaneous generation of a hole. In aqueous solutions, the photoholes (h^+) can oxidize H_2O or OH^- and the photoelectrons that are trapped at the surface sites can be adsorbed by O_2. Thereby, the •OH radicals, the superoxide radical anion ($O_2{\bullet}^-$) and its conjugated acid ($HO_2{\bullet}$) will be produced. [11]. Oxidizing power of the OH radicals is strong enough to break bonds of the compound molecule adsorbed on the surface of the photocatalyst leading to the formation of CO_2 and inorganic ions [12].

Semiconductors play the most promising role in several areas of research. Different semiconductor metal oxides or metal sulfides such as TiO_2, CdS, ZnO, Fe_2O_3, ZnS, etc. are known as photocatalysts and have

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their own merits and demerits in visible light [13]. The CuO is a p-type semiconductor whose band gap is 1.7 eV and has a higher rate of degradation as compared to ZnO and NiO. The observed effect may be attributed to the adsorption characteristics of the given pollutant on the solid catalyst [14,15]. Many adsorbents based on transition metal complexes supported on porous materials, zeolites, supported transition metals, mixed metal oxides, etc. have been developed and used for selective adsorption at ambient temperature [16]. Several supports for the CuO were investigated. Xiaoyuan et al. found that the activity of CuO/Al_2O_3 in CO oxidation was increased with increasing CuO loading. It may be concluded that highly dispersed CuO was the main active center and crystalline CuO enhanced the catalytic activity [17]. A photocatalyst based on CuO/SiO_2 was prepared and evaluated for the degradation of the methylene blue in aqueous medium. Photodegradation assays showed that CuO/SiO_2 was efficient for degradation in the presence of UV irradiation [18]. The CuO/zeolite sandwich type adsorbent-catalysts were prepared by wet impregnation of parent synthetic zeolites (NaA, CaA, NaX and CaX). These catalysts were active for the oxidation of alcohols into CO_2 and H_2O in the temperature range of 100–350 °C [19].

Zeolites (three-dimensional aluminosilicates) have been investigated as potential supports for photocatalytic systems. They offer several distinct advantages over the other used supports. Zeolites have cages and channels which can confine substrate molecules so as to enhance the photocatalytic reactivity. Dispersion of molecules in the zeolitic intracrystalline space is an added advantage. Thus, transition metals can behave as chromophores and thus help in visible light absorption. Zeolites behave as electron donors and as acceptors of moderate strength to the guest species depending on the adsorption sites [10]. Zeolite X can be described as an ensemble of sodalite cages or β-cages joined by hexagonal prisms. In general, this structure can be envisaged as a stacking layers of sodalite cages joined by double six rings in tetrahedral arrangement with a center of inversion at the center of the double six rings. The β-cage surrounds an even larger cage, the supercage (cavity with diameter about 13), which forms a three-dimensional network with each cage connected tetrahedrally to four other supercages through the 12-membered ring opening with a crystallographic aperture of 7–8 [20]. Zeolite X which was synthesized in this paper has a Si/Al ratio about 1.21 which is close to 1.22 presented in the literature [21]. In this paper, the objective is to prepare heterogeneous copper oxide catalyst supported on zeolite NaX and evaluate its photocatalytic activity in the degradation of OPD at the presence of sunlight. In our previous work [22], we studied the degradation of OPD by the same catalyst under UV irradiation and our results showed a maximum degradation of 70–75% after 500 min of UV irradiation, while in the present work, the degradation efficiency reaches above 90% after 240 min of sunlight irradiation. In addition, use of sunlight decreases of the cost of the method and the obtained results were very different and more promising from the results presenting in the literature.

2. Experimental

2.1. Materials and preparations

Sodium hydroxide pellets (99%), alumina trihydrate (65% Al_2O_3), sodium silicate solution (27.35% SiO_2, 8.30% Na_2O, $d = 1.37\ g\ L^{-1}$), were used as source of synthesis of NaX zeolite. Copper(II) nitrate trihydrate, was used as source of Cu^{2+}, *o*-phenylenediamine, H_2O_2 (30%), $KBrO_3$ (99%), HCl and all used reagents were obtained from Merck. Double-distilled water, prepared in the laboratory, was used throughout the experiments.

2.1.1. Synthesis of NaX zeolite

The procedure for the preparation of NaX zeolite describes as follows [21]: 100.00 g water and 100.00 g sodium hydroxide were stirred until dissolved. 97.50 g alumina trihydrate was added to the obtained solution and stirred at 100 °C until dissolved and cooled to 25 °C and then was mixed with 202.50 g water. 100.00 g of the obtained solution, 612.00 g water and 59.12 g sodium hydroxide were mixed until dissolved. 219.70 g sodium silicate solution, 612.00 g water and 59.12 g sodium hydroxide were mixed until dissolved and finally two later solutions were combined quickly and stirred for 30 min. The resulting suspension was transferred to a polyethylene bottle and aged at 90 °C for 8 h in an oven. The solid product was filtered and washed with double-distilled water until the pH of the filtrate dropped to 8. The product was dried at 100 °C and then it equilibrated over saturated aqueous of NaCl.

2.1.2. Preparation of CuO/X zeolite

The general procedure for doping of Cu^{2+} in NaX zeolite describes as follows: 0.2 g of NaX zeolite was added to the 20 mL copper(II) nitrate 0.1 M and shaken for 8 h in the polyethylene bottle at room temperature. The solid product was filtered and washed with double distilled water until the Cu^{2+} ions was not seen in the solution. Then it was dried at room temperature. The obtained sample was referred to as CuX zeolite. Finally, the CuX zeolite was calcined at 450 °C in muffle furnace for 4 h.

2.2. Characterization techniques

The X-ray diffraction patterns of samples were measured by using a diffractometer Bruker, D8ADVANCE, X-ray tube anode: Cu, wavelength: 1.5406 Å (Cu Kα radiation), filter: Ni. The samples were measured in the 2θ range of 5–70°. Fourier transformation infrared (FT-IR) spectra of samples, on KBr pellets, were recorded with a Nicolet single beam FT-IR (Impact 400D) spectrometer in the range of 400–4000 cm^{-1}. Differential scanning calorimetry (DSC), TG and DTG thermograms were performed for samples (6 mg) using Model Setaram (STA) units in the range of 50–800 °C with a temperature rise of 10 °C min^{-1}. Amount of copper was measured by atomic absorption spectrometer, Perkin Elmer AAnalyst 300 (Air-C_2H_2, $\lambda = 324.8$ nm) and was 10.4% w/w of Cu^{2+} cation. The surface texture properties of samples were determined in equipment Quantachrome Corporation (model Nova 1200). Before the study, all samples were dehydrated at 250 °C for 3 h. The absorption spectra were registered on a double beam spectrophotometer (Carry 100 Scan) in suprasil quartz cells of 1 cm optical path length and the absorbance of samples was measured in the wavelength range of 190–900 nm. In order to remove photocatalyst particles before analysis, the suspensions were centrifuged with "type-H-11n" and 3500 rpm for 5 min. The influence of pH on the absorption was studied by adding HCl or NaOH solutions to the suspensions.

Total organic carbon (TOC) measurements were carried out by TOC analyzer of Shimadzu TOC-VCSN (Japan). The degradation of pollutant was monitored by high performance liquid chromatography (HPLC, Merck Hitachi Lachrom).

2.3. Experimental setup

The experimental procedure is described briefly here. To study the OPD removal from water, the important parameters which significantly affect the product yield are: amount of catalyst, initial concentration, pH etc. The stirring rate was kept constant for all studies while the other parameters were carefully optimized. The photo-catalytic removal of OPD from water was studied by suspending an optimized amount ($0.3\ g\ L^{-1}$) of CuO/X zeolite powder at 25 ppm of OPD solution under sunlight irradiation. The blank solution had the same conditions of analyte with any photocatalyst. Then the suspension was centrifuged for 10 min and the absorbance was measured in 417 nm by using a calibrated UV spectrophotometer. The degradation efficiency of OPD was estimated by applying the following equation:

$$Degradation\ \% = 100 \times (A_o - A) / A_o \quad (1)$$