



Application of visible light on copper-doped titanium dioxide catalyzing degradation of chlorophenols



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ABSTRACT

Chlorophenols are extensively used in the anthroposphere, and their fates in the atmosphere, hydrosphere, biosphere and lithosphere and their degradations under natural light of great interests. The homogeneous photocatalytic degradation of 2-chlorophenol (2-CP) in titanium dioxide suspensions containing copper ions or/and sulfates has been well examined. In this study, TiO₂ is directly doped with copper sulfate by a sol-gel method to promote its visible light activity (VLA) following a post-calcination step. The effects of three parameters of synthesis (calcination temperature, amounts of dopant and nitric acid) on 2-CP degradations were experimentally investigated using a three-factor, two-level factorial design in the first stage. Catalysts of the most significant synthetic parameters were further synthesized at five calcined temperatures and characterized in the second stage. 2-CP was completely removed using catalysts that were doped 0.21 mol.% CuSO₄ with 0.1 vol.% nitric acid and then calcined at 300 °C for 6 h. Morphological variations with doping amount are observed from scanning electron micrographs. XRD patterns demonstrated a transformation from amorphous to the anatase phase, with replacement of Ti⁴⁺ by Cu²⁺ in the crystal structure of TiO₂. UV–visible light diffuse reflectance spectra of the doped catalysts exhibited red-shifts, revealing their VLA. Surface areas, measured by the BET method, decreased as the calcination temperatures increased, and the pore sizes increased. Moreover, effect of three operational parameters, including: (del) initial concentration of 2-CP, initial pH and the photocatalyst dosage, under visible-light irradiation were investigated to simulate the scenarios of degradation in the natural and artificial conditions. Optimal operational parameters were obtained at a catalyst dosage of 3 gdm⁻³, an initial 2-CP concentration of 20 ppm and a solution pH of 5.5. The pH_{zpc} of the undoped and CuSO₄-doped TiO₂ were determined to be 3.5 and 3.84.

1. Introduction

Chlorophenol compounds and their derivatives (CPs) are widely and frequently used in the anthroposphere, such as intermediates in the manufacturing of pharmaceuticals, synthetic dyes, petrochemicals, biocides, paints, textiles, leather products and wood preservatives. CPs are classified as refractory xenobiotics and known to be precursors of the highly toxic polychlorodibenzo-*p*-dioxins and polychlorodibenzofurans (PCDD/Fs) during the incineration of industrial wastes. The release of CPs either from petroleum refining effluents, residual pesticides and insecticides in the soils, or from degradation of complex chlorinated hydrocarbons among the atmosphere, hydrosphere, and lithosphere causes considerable environmental problems and ecological effects in the biosphere [1,2]. CPs not only cause unpleasant tastes and odors on drinking water but also cause oxidative

stress. It is irritating to the skin, eyes, and damage the DNA of living organisms, as well as induce histopathological alterations, genotoxicity, mutagenicity and carcinogenicity in humans and animals. Consequently, their fates and aqueous environmental photochemistry are processes of great concerns [3,4]. 2-Chlorophenol (2-CP, or *ortho*-chlorophenol) is one of the toxic pollutants identified by the EU and US as priority contaminants [5]. Meanwhile, the monochlorophenol can be precursors of the higher-substituted CPs, and it is soluble in water (with a solubility of 28 gL⁻¹) at room temperature with a melting point of 9.3 °C [6]. Consequently, it easily enters to aquatic ecosystems. Therefore, its transportation properties were addressed high concerns [7] as well as its toxicity and genotoxicity on bacteria, fish and human cells were recently re-evaluated [8].

Removal technologies of phenolic contaminants in the fluid streams were classified in two types as separation (such as distillation,

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extraction, adsorption, membranes-related processes) and destructive ones (such as supercritical, wet air, thermal and catalytic oxidations) [9,10]. Advanced oxidation processes (AOPs) [11], such as heterogeneous photocatalysis [12] and Fenton-like oxidation [13], were categorized to the destructive type and reported that can effectively remove CPs [14]. Titanium dioxide (TiO₂) is the most popular photocatalyst due to its highly stable chemical structure, relatively low cost, lack of toxicity, and photo-generation of highly oxidizing holes [15]. It is applied as one of the versatile AOPs. Commercial TiO₂ (Degussa P-25) has been intensively utilized to decompose 2-CP either irradiated by UV alone [16,17] or with concomitant UV (UV-A, -B, and -C) irradiation [18]. P-25 is also combined with adsorption (as with clay mineral) [19], with H₂O₂ [20], or with applied external bias voltage [21]. A TiO₂-UV suspension system with another semiconductor (CdS) efficiently degrades 2-CP [22]. Ga,I-co-doped TiO₂ was synthesized for photocatalytic degradation of 2-CP [23]. Nanoporous S-doped and N-doped TiO₂ were prepared to degrade 2-CP under LED irradiations [24,25]. Except TiO₂, other nanoparticles like Cu-nano zeolite [26], ZnO [27], and ZrO₂-doped ZnCo₂O₄ [28] can remove 2-CP under irradiation by UV or visible light. Recently, cobalt oxide-loaded TiO₂, supported with reduced graphene oxide, was synthesized and applied to degrade 2-CP under visible light irradiation [29]. Table 1 compares the 2-CP photo-degradation efficiencies under various irradiation systems.

The function of copper ions in TiO₂ suspension as a homogeneous photocatalytic system has been well examined. The effects of dissolved transition metal ions (such as Cu²⁺, Fe³⁺ and Ag⁺) in several heterogeneous photocatalytic systems have been reviewed [30]. The effects of Cu²⁺ ions (from CuCl₂) on the formation of H₂O₂ from photocatalytic TiO₂ particles have also been investigated [31]. The effect of the charge trapping species, Cu²⁺ ions from Cu(NO₃)₂, on the photocatalytic oxidation of resorcinol was studied [32]. The surface and interfacial Cu²⁺ sites in CuO–TiO₂ nanocomposites improved their photoactivity [33]. The effect of adding small amounts of Cu²⁺ (from 0.001 to 0.8 mmol·L⁻¹) in aqueous solution on photocatalytic degradation of methamidophos under UV irradiation has also been investigated [34]. Cu²⁺ behaves as an electron scavenger, described by Eq. (1). It prevented the recombination of electron–hole pairs, and increased the probability of the formation of ·OH and ·O₂⁻ on the TiO₂ surface. However, the photodegradation efficiency decreased markedly as Cu²⁺ concentration increased above 0.006 mmol·L⁻¹. This may be caused by the photogenerated holes on the surface of TiO₂ particles or ·OH, as presented in Eqs. (2) and (3):



Rate constants of phenol photodegradation with three types of TiO₂ (Degussa P25, TiO₂ of anatase and rutile phases from Sigma–Aldrich) under UV or visible-light irradiations in the presence of Cu²⁺ ions showed higher than those of the Cu²⁺-absence solutions [35]. The co-addition of Cu²⁺ and F⁻ has been reported synergistically and significantly to improve the degradation rate constant of phenol relative to that obtained by adding one of the two ions [36]. The reversible photoreductive deposition and oxidative dissolution of Cu²⁺ in TiO₂ aqueous suspensions has also been reported [37]. The role of superoxide radicals in the catalyzing effects of adding copper ions on photo-oxidation in TiO₂ suspensions has been investigated [38]. Therefore, Cu²⁺ ions in solution considerably facilitate TiO₂ photocatalysis.

In contrast to homogeneous photocatalysis, copper ions can be directly incorporated into TiO₂ by various synthetic methods and formed a heterogeneous photocatalytic system. As the band-gap of pristine TiO₂ is rather large (3.0–3.2 eV), only a small fraction (about 5%) of the solar spectrum can be utilized. Researchers are making consistent efforts to improve the visible light activity (VLA) of TiO₂ [39]. Surface modification [40] and doping with either anions (such as nitrogen,

sulfur, and halogen) or cations (such as rare earth, noble and transition metals) are popular approaches [41]. Cu-doped TiO₂ has been compared with N- and S-doped TiO₂, which are obtained by adding nitric or adding sulfuric acid, during sol-gel synthesis. The preparation in the presence of H₂SO₄ has been concluded by improving the photocatalytic activity [42]. To enhance photocatalytic activity of phenol degradation, CuP, CuO and CaO have been utilized as modifiers of TiO₂ [43], a cooperative effect between the cation (Cu²⁺, acting as an electron scavenger) and the phosphate anion (acting as an organic adsorbent) in the dopant CuP has been reported. Cu-doped TiO₂ that is synthesized in a low temperature hydrolysis reaction reportedly has a very low band gap (1.6 eV) [44]. The linear and nonlinear optical properties of bare and Cu-doped TiO₂ prepared by the sol-gel method have been examined [45]. Liu et al. [46] synthesized Cu-doped TiO₂ via a conventional sol-gel method. UV–vis diffuse reflectance spectra (UV–vis DRS) of their Cu-doped TiO₂ that was prepared with various amounts of dopant exhibited considerable shifts of the peaks toward the visible range of approximately 400–800 nm. The demonstrated red-shift phenomena show the absorption bands extending to the visible or even the near-infrared range, favoring VLA. Cu-doped TiO₂ that is formed by wet-impregnation or the sol-gel method is popularly used in disinfection under either UVA [47] or visible light [48,49]. Cu-doped TiO₂ that is prepared by an incipient wetness impregnation method has been used continuously to photocatalytically degrade a gaseous contaminant [50]. 2-Propanol has been decomposed to CO₂ by acetone under visible light (> 400 nm) using Cu-grafted TiO₂ [51]. Recently, Cu-doped TiO₂ that had been prepared by a solvo-thermal method was utilized in the simultaneous photocatalytic reduction of CO₂ and the production of H₂, which may has the potential double benefits of reducing the carbon footprint of the generation of alternative energy source [52].

As co-doping TiO₂ with two or multiple elements cause promising results in the utilization of visible light, the use of these photocatalysts is attractive in terms of less energy required, safety hazardous and environmental impacts in comparing with utilising traditional UV irradiation source (e.g. mercury lamps). For example, triple-elemental doping (K, Al, S) with TiO₂ has been synthesized to oxidize efficiently 2-CP under illumination by visible light. It was found to exhibit higher photocatalytic performance than pristine or commercial TiO₂ [53]. Currently, CuSO₄-doped TiO₂ that had been prepared by a wet impregnation method was used in the selective catalytic reduction of NO by NH₃ [54]. CuSO₄-doped TiO₂ has been prepared by a single-step sol-gel method for the degradation of methyl orange in visible light [55]. Hence, in this work CuSO₄ is used as a multifunctional dopant in a sol-gel process to improve the VLA of TiO₂. The effects of three synthetic parameters of CuSO₄-doped TiO₂ on the degradation of 2-CP were investigated using a preliminary 2³ factorial experimental design, and the degradation efficiencies were experimentally evaluated in fine-tuning parameters. The as-prepared catalysts were characterized by scanning electron microscopy (SEM), X-ray diffractometry (XRD), the Brunauer-Emmett-Teller (BET) method, UV–vis DRS and dynamic light scattering (DLS) to reveal their morphology, crystalline structure, surface and particle properties. The pH values at zero point charge of the pristine and CuSO₄-doped TiO₂ were determined. Three operational parameters of the photocatalytic degradation of 2-CP under simulated visible light irradiation (blue LEDs) were evaluated.

2. Experimental

2.1. Synthesis of catalysts

CuSO₄-doped TiO₂ catalysts were prepared using a popular sol-gel method, as shown into our previous study with some modifications [53]. A 0.05 mole amount of titanium butoxide (Ti(OBu)₄, 98%, Alfa Aesar) was firstly mixed with 70 mL analytical grade ethanol (EtOH, 99.5%, Merck) in a 250 mL flask with vigorous stirring at ambient temperature to yield a clear solution (Solution I). The flask was then

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