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Photocatalytic removal of phenol from refinery wastewater: Catalytic activity of Cu-doped titanium dioxide

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ABSTRACT

A series of Cu-doped TiO_2 catalysts were prepared by a sol–gel method and the effect of various synthesis parameters, including solvent type; solvent/catalyst amount; amount of water; catalyst type/amount; and acid type, on removal of phenol from refinery wastewater under UV-irradiation was investigated. Among the three solvents used, ethanol (En); isopropanol (Iso) and 2(2-Ethoxyethoxy) ethanol (Exy); undoped-TiO_2 catalysts prepared with ethanol (En) solvent showed the highest phenol degradation rate even though the surface area of isopropanol is 6 times higher than ethanol. However, for Cu-doped TiO_2 catalysts, isopropanol showed the highest photodegradation rate of phenol. Increasing the amount of water increased the surface area of the catalyst accordingly but no clear trend between phenol degradation rate and the amount of water used was observed. In contrast to NaOH, the addition of HCl improved the photodegradation rate of phenol while H_2SO_4 was twice as effective with respect to the phenol degradation.

1. Introduction

Phenols are organic compound bonded directly to hydroxyl group, and has limited solubility in water [8.3 g/ 100 mL] and slightly acidic. The main sources of phenolic waste water are coal chemical plants, oil refineries, petrochemical industries, fiber glass units, phenol—based polymerization processes, pharmaceuticals, plastic, paints and varnish producing units and many others. In the refining industry, the washing processes of middle-distillates using caustic solutions generate phenol [1]. In addition, caustics are usually added to desalting water to neutralize acids and are added to desalted crude in order to reduce the amount of corrosive chlorides in the tower overheads. In addition, they are used in some refinery treating processes in order to remove contaminants from hydrocarbon streams. The spent caustic liquors generated therefore contain phenols. The phenol found in an oil refinery wastewater is usually a mixture of phenols containing phenol (benzenol), ortho, meta, para-cresols, xylenols and polyphenols [2–5].

In the refinery, waste water treatment units are designed to remove contaminants from water by using physical, biological, and chemical treatment steps [1]. Titanium dioxide (TiO_2) photocatalysis is considered as one of the most promising methods for the effective degradation of a wide range of organic pollutants, especially phenol [2–11], and destruction of microorganisms in wastewater due to its properties, such as phase composition and structure, sur-face hydroxyl groups, particle size. In addition, its surface defects play a very important role in the activity of this oxide in photocatalytic reactions [3]. Furthermore, it is generally accepted that most of the TiO_2 photocatalyst applications are limited to UV-light irradiation because the light absorption edge is at wavelengths shorter than 420 or 380 nm for the rutile and anatase phases, respectively [3,12]. It has been reported that doping with ions of different transition metals such as Cr, Fe, Ni, Zn, Co, and Cu can enhance the photocatalytic activity of TiO_2 as this process extends the light absorption wavelengths of the catalysts to the visible region [13].

Among these metals, Cu has been less explored as a dopant compared to the other transition metals [14]. Sreethawong and Yoshikawa [15] compared the photocatalytic activities of Au-, Pd-, and Cu-loaded mesoporous TiO_2, and found that the Cu-loaded TiO_2 exhibited the highest photocatalytic activity. Labiadh et al. [16] investigated the photocatalytic performance of Cu-doped ZnS quantum dots for the degradation of salicylic acid. The TiO_2/Cu:ZnS nanocomposite material was found to have the highest photocatalytic performance compared to pure TiO_2 nanoparticles and TiO_2/ZnS. Chand et al. [17] successfully modified TiO_2 immobilized

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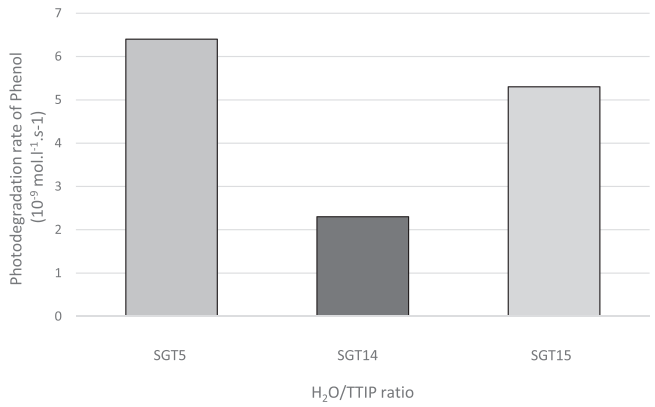

Fig. 1. The removal of phenol on undoped-TiO_2 catalysts prepared using different solvents: ethanol (SGT5), isopropanol (SGT7) and 2(2-Ethoxyethoxy) ethanol (SGT8). Container size = 100 mL, catalysts dose = 1 g/L, initial phenol concentration = 50 mg/L, pH = 6.3, T = 25 °C.

on SiO_2 beads by doping with Cu; this improved the photocatalytic efficiency of the TiO_2/SiO_2 composite significantly. In a previous publication, Cu-doped TiO_2 was reported to exhibit the highest photocatalytic activity for phenol degradation compared with Fe-, Mn-, and humic acid-doped TiO_2 [4].

Many chemical and physical methods have been employed to prepare TiO_2. Among these, the sol–gel process is one of the most suitable methods owing to several advantages [18,19]. The photocatalytic activity of TiO_2 catalysts prepared using the sol–gel method is affected by several synthesis parameters. Accordingly, in this paper, several parameters, which may affect the final properties of Cu-doped TiO_2 prepared by a sol–gel method, were investigated in this study. This paper presents a systematic study of the effect of solvent type/amount, amount of water, catalyst type/amount, and acid type on the photocatalytic properties of Cu-doped TiO_2 for obtaining optimized materials for application in phenol removal from wastewater.

2. Material and methods

2.1. Preparation of TiO_2-based photocatalysts using a sol–gel method

Materials used in this method are shown in Table 1. All the chemicals were laboratory grade. Titanium(IV) isopropoxide was selected as metal oxide precursor due to its relative stability, which is an important factor in controlling the reaction rate. Isoproponal, 2 (2-ethoxyethoxy) ethanol and ethanol were used as stabilizing agents and solvents for the otherwise immiscible TTIP and H_2O. HCl and H_2SO_4 were used as hydrolysis catalysts, while $CuCl_2$, $CuSO_4$ and $Cu(NO_3)_2$ were employed as dopants. Undoped and Cu/TiO_2 catalysts were prepared via a sol–gel method, Titanium(IV) isopropoxide and alcohol (ethanol, 2(2-ethoxyethoxy) ethanol or isoproponal) were vigorously stirred in a beaker. A mixture of fixed amount of deionsed water (DI water), acid (HCl or H_2SO_4) and alcohol was added drop-wise into the previous TTIP/alcohol solution and magnetically stirred. After gelation, it was dried at 60 °C in an oven overnight. The powder was then annealed at a specific temperature for 2 h in furnace. Finally, the catalysts was pulverized through 75 μm sieves and kept in a sealed jar for use. For Cu doped TiO_2, a given amount of copper precursor (1–10 mol% to TiO_2) was mixed with DI water, acid and alcohol solution before the mixture was added into a TTIP/alcohol solution. The rest of the preparation procedure was the same as with undoped TiO_2 [4]. Catalyst samples were given short names, SGT, where SG is for sol–gel method and T stand for TiO_2.

2.2. Measurement of photocatalytic activity

2.2.1. Solar box system

A solar box system (similar to that developed and reported by the authors in [4]) consists of a lamp chamber installed on top of a reactor chamber. Two UVA lamps were used: a commercial rutile fluorescent tube lamp and a fluorescent blacklight blue-tube lamp (18 W, Silva), which transmits ultraviolet radiation having a peak at 365 nm. In the reactor chamber, Pyrex glass flasks were employed as batch reactors.

2.2.2. Phenol degradation in water

The photocatalytic activity of each prepared catalyst was evaluated in terms of phenol degradation using the solar box system. Phenol concentration was measured by a double-beam UV–vis spectrophotometer (M350 double beam, Camspec Scientific Intruments Ltd., UK), using a centrifuged (4500 rpm for 5 min) aliquot (ca. 2 mL) of the suspension. All experiments were carried out in triplicates under identical conditions. The reproducibility of concentration measurements was within 5%.

2.3. Characterization

The specific surface area and porosity measurements were carried out by using the Brunauer–Emmett–Teller (BET) N_2 adsorption method at −196.15 °C using a Quantachrome NOVA 2200e instrument (Boynton Beach, FL). Each sample was out-gassed for 8 h at 105 °C. X-ray diffraction (XRD) patterns were measured using an M18XHF X-ray diffractometer (Mac Science Co., UK) with Cu Kα radiation (λ = 0.15418 nm, 30 kV, and 15 mA). The samples were scanned from 20 to 80° (2θ) at a rate of 0.02°/min. The average crystalline size of each phase (anatase and rutile) was determined by using the Scherrer equation. The phase contents of the synthesized TiO_2 samples were calculated from the integrated intensities of the anatase peak (1 0 1) at 25.5° and the rutile peak (1 1 0) at 27.6°.

Table 1
Materials used in sol–gel method.

Name	Chemical formula	Manufacturer	Description
Titanium(IV) isopropoxide(TTIP)	$Ti(OC_4H_9)_4$	Acros Organic, UK	Metal alkoxides precursor
Anhydrous isoproponal	$(CH_3)_2CHOH$	Acros Organic, UK	Alcohol solvent
Anhydrous 2(2-ethoxyethoxy) ethanol	$CH_3CH_2OCH_2CH_2O\text{-}CH_2CH_2OH$	Acros Organic, UK	Alcohol solvent
Anhydrous ethanol	CH_3CH_2OH	BDH chemicals, UK	Alcohol solvent
37% Hydrochloric Acid	HCl	Fisher Chemicals, UK	Hydrolysis catalyst
Sulphuric acid	H_2SO_4	BDH chemicals, UK	Hydrolysis catalyst
Anhydrous copper(II) chloride	$CuCl_2$	Acros Organic, UK	Dopant
Anhydrous cupric sulphate	$CuSO_4$	BDH chemicals, UK	Dopant
Anhydrous copper(II) nitrate	$Cu(NO_3)_2$	Fisher Chemicals, UK	Dopant