Fabrication of Zr-doped TiO₂/chitosan composite catalysts with enhanced visible-light-mediated photoactivity for the degradation of Orange II dye

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ABSTRACT

Zirconium/titanium/chitosan (Zr/Ti/CHT) composite catalysts were synthesized by sol-gel method using different chitosan amounts (5–20 wt.%) and their activity in the photocatalytic degradation of Orange II dye was evaluated for the first time. The results were compared with Zr/Ti, Zr/CHT and Ti/CHT catalysts. The composite catalysts were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy, scanning electron microscopy and X-ray photoelectron spectroscopy analysis. XRD analysis revealed that the Zr/Ti/CHT composite catalyst showed high crystallinity of anatase TiO₂ phase. Photocatalytic experiments showed that adding CHT into the catalyst structure increased the photocatalytic degradation under visible light irradiation. Also, the first-order reaction rate constant, $k_{\text{app}}$, was calculated using the Langmuir–Hinshelwood (L-H) equation. The $k_{\text{app}}$ values were found to be 0.009, 0.0013, 0.012 and 0.014 min⁻¹ for Zr/Ti, Zr/CHT, Ti/CHT and Zr/Ti/CHT, respectively. According to stability tests, after the first cycle Orange II dye degradation was found to be 95%, while it was 37% after the fifth cycle. The results showed that the composite catalyst could be used several times for Orange II dye degradation.

Key words | chitosan, Orange II, photocatalyst, TiO₂, zirconium

INTRODUCTION

Azo dyes are used in various industrial applications such as textile, leather, pharmaceutical and plastics (Zhang et al. 2014). During the dying processes, 15% of the produced dye is released to the environment (Houas et al. 2001). Having carcinogenic and mutagenic effects, dyes pose risks for ecosystems. Orange II, also called Acid Orange 7, is an anionic dye, which has one azo group, one sulfonated group and two aromatic rings in its structure. It is one of the synthetic dyes, which causes serious problems when released into the water. As with the other synthetic dyes, Orange II is poorly biodegradable and has a stable structure in different conditions. Therefore, removal of Orange II from wastewaters is one of the important problems from the environmental point of view.

Elimination of Orange II was studied using adsorption (Jin et al. 2014; Zhang et al. 2014), oxidation (Inchaurrondo et al. 2016), chemical degradation (Luo et al. 2015; Luo et al. 2016) and photocatalysis (Cai et al. 2015). Photocatalysis technology is the most effective method for removal of Orange II from wastewater (Liu et al. 2011). Titanium dioxide (TiO₂) is generally used as the photocatalyst, due to its inexpensive, non-toxic and photostable properties (Ibusuki & Takeuchi 1986; Zou et al. 2006). However, TiO₂ cannot be used properly under visible light due to its large band gap (3.2 eV for anatase TiO₂). Therefore, a second element such as zirconium, tungsten, cerium or silica can be added to increase its photocatalytic activity under visible light irradiation and thermal stability of the phase transition (Tian et al. 2009). Zirconium is a non-toxic, biologically inert material and has high ion-exchange capacity. Zr/Ti composites are extensively used as photocatalyst (Wang et al. 2006; Zhou et al. 2008).

Chitosan is an abundant biopolymer, which includes amino (−NH₂) and hydroxyl (−OH) groups in its structure, making it an excellent adsorbent for the removal of organic and inorganic compounds from wastewaters (Nawi et al. 2010; Sokker et al. 2011). The high amount of amino and hydroxyl groups in the chitosan structure improves the
photocatalytic activity of the heterogeneous photocatalyst as the adsorption is a part of photodegradation. Hamdi et al. (2015) synthesized phthalocyanine/chitosan-TiO2 photocatalyst for the photodegradation of aniline. Nawi et al. (2010) reported the adsorption of reactive red 4 on chitosan/glass adsorbent. They also prepared TiO2/chitosan/glass photocatalyst and investigated its photocatalytic activity on reactive red 4. They found that the adsorption capacity of chitosan/glass composite has an effective role in the photocatalyst–adsorption system (Nawi et al. 2010).

In this study, a novel photocatalyst, zirconium/TiO2/chitosan (Zr/Ti/CHT) nanocomposite was synthesized for the first time and its photocatalytic activity was investigated using Orange II dye. Zr/Ti, Zr/CHT, Ti/CHT and Zr/Ti/CHT samples were characterized by using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy. The effects of chitosan amount, initial solution pH and catalyst dosage were investigated. Also, recycle tests were studied to reveal the applicability of Zr/Ti/CHT as an effective photocatalyst.

MATERIALS AND METHODS

Chemical and reagents

Chitosan (degree of deacetylation of 90%), zirconium oxychloride octahydrate ZrOCl2.8H2O (analytical grade), Orange II (C16H11N2NaO4S, purity > 99%) and tetrabutyl titanate (97%) were purchased from Sigma-Aldrich. All the reagents used in this study were of analytical grades.

Catalyst preparation

To investigate the photocatalytic activity, Zr/Ti, Zr/CHT, Ti/CHT and Zr/Ti/CHT samples were synthesized. Chitosan (0.5 g) was dissolved in 50 mL 2% acetic acid solution by overnight mixing. Twenty milliliters of tetrabutyl titanate was also dissolved in 40 mL ethanol with 0.5 g zirconium oxychloride octahydrate. After 30 min mixing, 2 mL concentrated HCl and 4 mL H2O were added to the solution and mixed for another 30 min. The gel was aged for 1 day and hydrothermal treatment was applied in a Teflon-lined stainless steel autoclave at 180 °C for 18 h. Then, the products were filtrated, washed with distilled water and calcined at 500 °C for 2 h.

Zr/CHT sample was prepared by dropwise addition of ZrOCl2.8H2O solution (dissolved in ethanol) into 1 wt.% chitosan solution. After 1 h mixing, the solution was dried and calcined at 500 °C for 2 h.

Ti/CHT catalyst was prepared by adding tetrabutyl titanate solution (dissolved in ethanol) into 1 wt.% chitosan solution. After 1 h mixing, the solution was dried and calcined at 500 °C for 2 h.

Characterization of the catalysts

The photocatalysts were characterized by using several methods. XRD was undertaken using a Rigaku D/Max-IIIC diffractometer with 1.54 Å Cu-Kα radiation and a 2θ range of 10–80°. The FTIR spectrum was recorded by a Perkin Elmer Spectrum One using attenuated total reflectance method, in the wavenumber range of 600–4,000 cm⁻¹. The surface composition of the samples was investigated using XPS (Thermo Scientific K-Alpha X-ray photoelectron spectrometer). Scanning electron microscopy (SEM-EDAX) analyses were carried out using a Philips XL30 ESEM-FEG/EDAX to investigate the surface morphology of the composites.

Determination of photocatalytic activity

The photocatalytic activity of the samples was investigated for degradation of Orange II dye solution (10 mg L⁻¹). The UV-A light photocatalytic experiments were carried out under 18 UV lamps placed into a columned-shaped stainless steel cabinet. Visible light irradiation experiments were conducted in a photoreactor with two visible metal halide lights as visible light source. To perform the experiments, 50 mL 10 mg L⁻¹ Orange II solution was added into 0.01 g catalyst. Before the light irradiation, the solution was mixed in the dark for 30 min to achieve adsorption–desorption equilibrium. Samples (4 mL) were regularly collected at different time intervals and analyzed by a UV-visible spectrophotometer at 485 nm.

Solution pH (3, 6.50, 10), CHT amount (5%, 10%, 15%, 20%) and initial solution concentration (5, 10, 20 mg L⁻¹) effects on photocatalytic activity were investigated.
Durability tests of Zr/Ti/CHT/20 were conducted by mixing 100 mL Orange II solution (10 mg L\(^{-1}\)) with 0.08 g catalyst. The cycles were performed five times and each cycle was examined for 180 min.

RESULTS AND DISCUSSION

Characterization of catalysts

XRD patterns of Zr/Ti and Zr/Ti/CHT/20 composites are shown in Figure 1. TiO\(_2\) has three crystalline forms (rutile, anatase, and brookite) and among these crystal forms anatase phase shows the highest photocatalytic activity (Calatayud et al. 2015; Fagan et al. 2016). The samples show the diffraction peaks at (101), (004), (200), (105), (211), (204), (116), (220) and (215) corresponding to tetragonal anatase phase of TiO\(_2\). Zr/Ti catalyst did not show a ZrO\(_2\) peak, which might be due to the result of small particle size of metal oxides, which is not detectable by XRD (Tasdemir et al. 2015). The presence of CHT in the structure does not affect the crystallinity of anatase phase of TiO\(_2\), which indicates the good dispersion of CHT over Zr/Ti/CHT catalyst (Kim et al. 2015).

FTIR spectra of Zr/Ti and Zr/Ti/CHT composites are shown in Figure 2. The band at 3,100 cm\(^{-1}\) defines the adsorbed water (H-O-H) (Wan et al. 2012; Shao et al. 2015). The band appearing at 3,155 cm\(^{-1}\) could be attributed to bending N-H groups of CHT (Safari et al. 2015), stretching vibrations of O-H groups and bending vibrations of Ti-OH (Gao et al. 2004; Afzal et al. 2017). The peak around 2,182 cm\(^{-1}\) was assigned to stretching vibration of –CH group. The absorption band around 700 cm\(^{-1}\) confirms the existence of Ti-O-Ti groups in the Zr/Ti/CHT composite structure (Karthikeyan et al. 2017).

SEM analyses are important to investigate the structural properties of the composites. SEM images of Zr/Ti, Zr/CHT, Ti/CHT and Zr/Ti/CHT/20 composites are presented in Figure 3. SEM images of Zr/Ti, Zr/CHT and Ti/CHT showed round-shaped particles on their surface, which indicates the TiO\(_2\) particles. Zr/Ti/CHT/20 composite surface preserves the same round-shape structure. According to EDX results, Zr content in the catalyst was found to be in good agreement with Zr doping amount.

Elemental analysis of Zr/Ti/CHT/20 was done using XPS technique and shown in Figure 4. The photoelectron peaks for C 1s, O 1s, Ti 2p and Zr 3d were observed at binding energies of 285.9, 531, 457.7 and 181.8 eV, respectively. The binding energies of C 1s spectral region deconvoluted into C-OH/C-N at 285.9 eV, C-C/C\(\equiv\)C at 284.5 eV and C-Ti at 283.4 eV during the formation of Zr/Ti/CHT/20 composite (Cittadini et al. 2014). The binding energy of O 1s peaks for Zr/Ti/CHT/20 composite appeared at 530 and 531 eV. The high intensity peak of 531 eV was assigned to C\(\equiv\)O/O\(\equiv\)O and low intensity peak of 530 eV was attributed to oxygen bonded to Ti atom (Ti-O) (Lopez et al. 2000; Lin et al. 2002; Cittadini et al. 2014). Also, binding energies indicate Ti/Zr-O and Ti/Zr-OH (Sun et al. 2011). In the Ti 2p region, the peak for Zr/Ti/CHT/20 composite appeared at 457.7 eV, which indicates the lower binding energy of Ti 2p. The binding energies of 457.7 and 463.3 eV correspond to the Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\) levels, respectively. The peak at binding energy of 457.7 eV is evidence of Ti\(^{3+}\) state. Ti 2p spectra of Zr/Ti/CHT/20 indicate the formation of Zr-O-Ti and also show that the Zr was well dispersed in the TiO\(_2\) lattice. In the Zr 3d spectra of Zr/Ti/CHT composite, the peak appearing at 181.8 eV represents Zr\(^{4+}\) oxidation state (Wu et al. 2009). The peaks at 181.8 and 183 eV indicate Zr 3d\(_{5/2}\). Electron transfer between Zr\(^{4+}\) and Ti\(^{3+}\) resulted in a shift in binding energy, which indicates Zr-O-Ti formation (Badli et al. 2016). The results show that the Zr was well dispersed on the catalyst surface.
Adsorption and photocatalytic activity

Effective photocatalytic degradation reactions of the catalyst can be achieved by the preliminary adsorption of the pollutant (Li et al. 2016). Therefore, to investigate the adsorption equilibrium of the catalysts, dark adsorption experiments were conducted by mixing 10 mg catalyst with 50 mL 10 mg L$^{-1}$ Orange II solution in the dark. Absorption using Zr/Ti, Zr/CHT and Ti/CHT reached the equilibrium within 60 min, 120 min and 120 min, respectively (Figure 5 inset). Removal efficiency of Zr/Ti catalyst was found to be 25% within 60 min. The incorporation of CHT increased the removal efficiency of the catalysts; Zr/CHT and Ti/CHT had removal efficiency around 47% and 45%, respectively. Zirconium ($Zr^{4+}$) is a positively charged cation and has an effect on Orange II dye adsorption by electrostatic interactions. Chitosan also includes the protonated amino group, which contributes to Orange II adsorption. The adsorption mechanism helps to increase the photocatalytic activity of the catalyst by adsorbing the dye molecule to the surface, which makes the dye molecule closer to the active surface and increases the interaction between the dye molecule and the catalyst, which resulted in an increase of the dye degradation. Increasing CHT amount in Zr/Ti/CHT catalyst resulted in an increase in Orange II removal. It was found that the removal efficiencies of Zr/Ti/CHT/5,
Zr/Ti/CHT/10, Zr/Ti/CHT/15 and Zr/Ti/CHT/20 were 28, 38, 46 and 50%, respectively. The results indicate that Zr/Ti/CHT/20 catalyst has the highest removal efficiency for Orange II dye adsorption.

To examine the photocatalytic activity of the catalyst, the photocatalytic degradation of Orange II under UV-A and visible light was carried out. Figures 5 and 6 show the time vs. \( \frac{C}{C_0} \) plots under UV-A light irradiation and visible light irradiation where \( C_0 \) is the dye concentration at the beginning of the photocatalytic degradation and \( C \) is the dye concentration at time \( t \). The degradation efficiencies of Orange II for Zr/Ti, Zr/CHT, Ti/CHT and Zr/Ti/CHT/20 catalysts under UV-A light irradiation after 180 min were found to be 98, 48, 96 and 99%, respectively. Under visible light irradiation, Zr/Ti/CHT/20 (84%) catalyst exhibited highest photocatalytic efficiency among the prepared catalysts (Zr/Ti (67%), Zr/CHT (60%) and Ti/CHT (71%)). Adding Zr into the catalyst structure increased the photocatalytic efficiency by increasing the hydroxyl groups on the surface, which are responsible for the photocatalytic degradation process (Kim et al. 2012). Karthikeyan and colleagues studied the photocatalytic activity of chitosan-TiO\(_2\) for the degradation of cationic rhodamine B and negatively charged Congo red. The photocatalytic mechanism was explained by the electron–hole pair, which is formed by absorption energy. Also, generation of the electron–hole pair involves the oxidation–reduction process (Karthikeyan et al. 2017). Under visible light, as a result of absorbing light on the catalyst surface,
The kinetic results of the photocatalytic degradation process were best described by Langmuir–Hinshelwood (L–H) model as given in Equation (1). (Kumar et al. 2008).

\[
\ln \frac{C_t}{C_0} = k_{app}t
\]  

(1)

where \( k_{app} \) is the apparent pseudo-first-order reaction rate constant (min\(^{-1}\)), \( C_0 \) and \( C_t \) are the dye concentrations at initial and time \( t \) (mg L\(^{-1}\)), \( t \) is the reaction time (min). Determined \( k_{app} \) values from the slope of \( \ln(C_t/C_0) \) versus time plot of the photocatalysts are given in Table 1.

From the data reported in Table 1, using Zr/Ti/CHT/20 composite as a photocatalyst resulted in an enhancement in the photocatalytic activity. Also, degradation under UV-A light irradiation presents better photocatalytic degradation results than visible light irradiation. A higher \( k_{app} \) value was observed for Zr/Ti/CHT/20 followed by Ti/CHT. Hamdi et al. (2015) studied photocatalytic activity of chitosan/phthalocyanine-TiO\(_2\) on aniline. According to kinetic results, increasing phthalocyanine amount increased the \( k_{app} \) value from \( 64 \times 10^{-3} \) h\(^{-1}\) to \( 101 \times 10^{-3} \) h\(^{-1}\). Also, the \( k_{app} \) value of TiO\(_2\) was \( 37 \times 10^{-3} \) h\(^{-1}\), which indicated that adding phthalocyanine enhanced the photocatalytic activity of the catalyst (Hamdi et al. 2015). Zainal et al. (2009) investigated the photocatalytic activity of TiO\(_2\)-chitosan/glass photocatalyst for the degradation of methyl orange dye. Increasing the TiO\(_2\)-chitosan layer on the glass resulted in an increase in photocatalytic activity of the catalyst. Therefore, the \( k_{app} \) values were increased from \( 149.1 \times 10^{-3} \) min\(^{-1}\) (1 layer) to \( 269.1 \times 10^{-3} \) min\(^{-1}\) (four layers) (Zainal et al. 2009).

**Effect of pH**

Solution pH plays an important role in degradation of the dye molecule, due to the effect on surface properties of the catalyst and ionization of the dye molecule. The plots of Orange II degradation at different pH values are presented in Figure 7. At pH 3, Orange II degradation was found to be 89%. In basic medium (pH 10), degradation percentage decreased to 38%. In acidic medium, positively charged Zr and protonated –NH\(_2\) groups on chitosan serve as available adsorption sites for anionic Orange II dye molecule. Electrostatic attractions occur between positively charged surface groups and negatively charged sulfonate groups of the dye molecules. In contrast with acidic medium, electrostatic repulsion forces would be dominant between the surface and anionic Orange II dye molecules. Anionic dye molecules compete with OH\(^{-}\) molecules in the solution at higher pH values and also the surface has lower protonated –NH\(_2\) groups. Therefore, a decrease in adsorption and
degradation of Orange II occurred. Zhang et al. (2014) investigated the adsorption efficiency of chitosan/doceyltrimethyl ammonium chloride using orange G and acid orange 7. For both of the dye molecules the highest adsorption capacity was found at pH 3. They explained that the maximum adsorption capacity at lower pH values was due to electrostatic interactions between protonated amino molecules on chitosan and anionic sulfonic groups of the two dye molecules (Zhang et al. 2014).

Effect of CHT amount

To investigate the effect of CHT amount on Orange II degradation, photocatalytic degradation of Orange II was examined at different percentage weight ratios (5–20%) of CHT catalysts under visible light irradiation. According to Figure 8, the highest Orange II degradation was observed using Zr/Ti/CHT/20 (99%), followed by Zr/Ti/CHT/10 (98%), Zr/Ti/CHT/15 (96%) and Zr/Ti/CHT/5 (89%). This was due to increasing available adsorption sites on catalyst surface by increasing CHT amount.

Effect of initial dye concentration

Initial dye concentration has a powerful effect on dye degradation. Initial Orange II concentrations were changed between 5 and 20 mg L\(^{-1}\) (Figure S1, Supplementary information, available with the online version of this paper). Under visible light irradiation, Orange II dye degradation of 5 mg L\(^{-1}\) solution was found to be 91%, while it was 84% and 33% for 10 mg L\(^{-1}\) and 20 mg L\(^{-1}\), respectively. The difference between the degradation percentages depends on the occupation of active sites by the Orange II dye molecules. The active sites on the catalyst become occupied by Orange II dye molecules up to a certain concentration, leaving no further active sites for occupation at higher dye concentrations (Debnath et al. 2018), which causes a decrease in Orange II dye degradation.

Stability of photocatalyst

Stability of photocatalyst is one of the most important parameters from an economical point of view (Abdelwahab & Helaly 2017). After each degradation test, the catalyst was separated, washed with distilled water several times, dried and reused for a new degradation experiment by adding fresh Orange II dye solution. Degradation of Orange II dye for the first cycle was 95% while it decreased to 79% after the fifth cycle. The result showed that the Zr/Ti/CHT/20 photocatalyst could be used four times for dye degradation effectively.

CONCLUSION

Photocatalytic activity of Zr/Ti/CHT was investigated under visible light irradiation through degradation of Orange II dye molecules. It was found that increasing the amount of CHT enhanced the photocatalytic activity of Zr/Ti/CHT owing to the synergistic effect of the photocatalysis/adsorption process. Increasing CHT amount resulted in an increase...
in active adsorption sites on Zr/TiO2/CHT catalyst surface, which enhanced the photocatalytic activity of the catalyst. Also, Zr has an important effect on photocatalytic activity due to lowering of the band gap of Zr/TiO2/CHT catalyst by electron transfer from Zr4+ to Ti4+. The catalyst was found more effective in acidic medium due to protonated –NH2 groups on the chitosan surface. Zr/TiO2/CHT photocatalyst could be used four times for dye degradation effectively. A highly effective TiO2 photocatalyst was synthesized using Zr and CHT, which can be extensively used in photocatalytic degradation of dye molecules.

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