Cobalt Oxide-Modified Titanium Dioxide Nanoparticle Photocatalyst for Degradation of 2,4-Dichlorophenoxyacetic Acid

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ABSTRACT

2,4-dichlorophenoxyacetic acid (2,4-D) has been recognized as a possibly carcinogenic compound to human, therefore, 2,4-D should be treated before it is discharged to the environment. Photocatalytic degradation of 2,4-D has been proposed as one of the best methods that offer environmentally safe process. In the present research, titanium dioxide (TiO_2) was modified with cobalt oxide (CoO) and tested for photocatalytic degradation of 2,4-D under UV light irradiation. Different amounts of CoO (0.1, 0.5, 1 and 5 mol%) were added onto TiO_2 by an impregnation method. The photocatalytic reaction was monitored and analyzed by measurement of 2,4-D absorbance using UV spectrophotometer. After 1 h photocatalytic reaction, it was confirmed that the sample with low loading of 0.1 mol% gave the highest photocatalytic activity among the bare and modified TiO_2 photocatalysts. The photocatalytic activity was decreased with the increase of CoO loading, suggesting that the optimum amount of CoO was an important factor to improve the performance of TiO_2. Based on fluorescence spectroscopy, such addition of CoO resulted in the reduced emission intensity, which showed the successful decrease in the electron-hole recombination.

Keywords: *2,4-D herbicide; UV light; titanium dioxide; cobalt oxide; photocatalyst*

ABSTRAK

Asam 2,4-diklorofenoksiasetat (2,4-D) telah dikenali sebagai senyawa yang mungkin bersifat karsinogenik pada manusia, oleh karena itu, 2,4-D harus ditangani sebelum dibuang ke lingkungan. Degradasi 2,4-D secara fotokatalitik telah diusulkan sebagai salah satu metode terbaik yang menawarkan proses yang aman terhadap lingkungan. Dalam penelitian ini, titanium dioksida (TiO_2) telah dimodifikasi dengan kobalt oksida (CoO) dan diuji untuk degradasi 2,4-D secara fotokatalitik di bawah iradiasi sinar UV. Kobalt oksida dengan jumlah yang berbeda (0,1, 0,5, 1 dan 5 mol%) telah ditambahkan ke TiO_2 dengan metode impregnasi. Reaksi fotokatalitik dipantau dan dianalisis dengan pengukuran absorbansi 2,4-D menggunakan spektrofotometer UV. Setelah reaksi fotokatalitik selama 1 jam, sampel dengan jumlah rendah yaitu 0,1% mol memberikan aktivitas fotokatalitik tertinggi di antara TiO_2 dan fotokatalis lain yang telah dimodifikasi. Aktivitas fotokatalitik menurun dengan meningkatnya jumlah muatan CoO, menunjukkan bahwa jumlah optimal dari CoO merupakan satu faktor penting untuk meningkatkan kinerja TiO_2. Berdasarkan spektroskopi fluoresensi, penambahan CoO tersebut menghasilkan pengurangan intensitas emisi yang menunjukkan keberhasilan dalam mengurangi rekombinasi elektron-lubang.

Kata Kunci: *herbisida 2,4-D; sinar UV; titanium dioksida; kobalt oksida; fotokatalis*

INTRODUCTION

2,4-dichlorophenoxyacetic acid (2,4-D) is a common herbicide that has been used for control of broadleaf weeds, which compete with crop production such as wheat and corn, and widely applied to improve grass production by reducing weed competition in pastureland, lawn, recreational lakes, turf, and roadsides. Owing to its excessive use, these herbicides that contained 2,4-D can cause contamination over agricultural land and water bodies. While the toxicity of the 2,4-D herbicide to human health is continually reviewed and debated, a recent review showed that there is no convincing or consistent evidence for any

chronic adverse effect of 2,4-D in humans due to different sample size, imprecise results and misclassification [1]. Even though the inconsistent data were reported, several studies showed significant associations of 2,4-D to cancer, reproductive toxicity, genotoxicity, and neurotoxicity, which could not be neglected. Therefore, the efficient treatment to remove 2,4-D in water still needs to be investigated. There are various methods that have been reported to degrade 2,4-D. One of the most promising methods is by photocatalytic reaction [2-14].

Photocatalytic removal of organic pollutants from water has been a topic of great interest over the years, in which titanium dioxide (TiO_2) and its modifications were mostly reported as the photocatalysts [15-18]. As for photocatalytic degradation of 2,4-D, the most widely used photocatalysts were also TiO_2 and its modifications [2-11]. As a photocatalyst, TiO_2 has a range of useful features, including high photocatalytic activity, stability, low toxicity, ready availability and low cost. Hence, there have been a great number of studies on the preparation, characterization and photocatalytic activities of TiO_2 based photocatalysts. Some strategies have been developed in order to improve the photocatalytic activity of the TiO_2 for degradation of 2,4-D. It was reported that the activity of commercial TiO_2 for degradation of 2,4-D was improved by binding together the pre-calcined TiO_2 in an aqueous sol of TiO_2 nanoparticles with the assistance of chitosan [2]. The activity of TiO_2 for 2,4-D degradation was also enhanced with the addition of reduced graphene oxide and $CuInS_2$ [3] or Ag/reduced graphene oxide [4]. One of the reasons for higher activity on the modified TiO_2 was proposed to be caused by the higher charge separation of the TiO_2 after the modifications [3-4].

Another approach to improve the activity of TiO_2 photocatalyst for degradation of 2,4-D is by introducing transition metal and rare earth oxides, such as copper [5-8], lanthanum [9-10], and iron oxides [11]. In particular, it has been shown that cobalt species has the potential of enhancing the photocatalytic activity of TiO_2 for various reactions [19-21]. The deposition of cobalt species on TiO_2 increased the degradation rate of acid red G due to the increase of the separation in the photogenerated electron-hole pairs [19]. Cobalt doped TiO_2 was reported to be a stable and efficient photocatalyst for hydrogen production from glycerol since the addition of cobalt was able to lower the electron-hole recombination with satisfactory light harvesting [20]. High photocatalytic activity of cobalt ion doped TiO_2 was also reported to against fungi, owing to ability to produce active oxidant species [21]. In these samples, cobalt existed as Co^{2+} [19-21] due to the low loading amount of cobalt precursor (2% or less). In contrast to these reports, cobalt doped TiO_2 showed no

photocatalytic activity for degradation of diquat dibromide monohydrate when the loading amount was high (5%) [22]. It was confirmed that cobalt was present as a mixed Co^{3+} and Co^{4+} that created oxygen vacancies that might act as electron traps that decreased the electrons in the conduction band, thus reducing the activity. The detrimental photocatalytic activity for degradation of Basic Blue 41 was also observed on cobalt modified-TiO_2 photocatalyst when mixed oxide of cobalt titanate ($CoTiO_3$) phase was formed [23]. In the present study, a simple impregnation method was used to prepare cobalt oxide-modified commercial Evonik P25 TiO_2 photocatalysts. The effect of cobalt oxide loading on the photocatalytic activity of TiO_2 was investigated for degradation of 2,4-D as the model pollutant.

EXPERIMENTAL SECTION

Materials

P25 TiO_2 (Evonik), cobalt(II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, Aldrich, ≥ 98%), and 2,4-D ($C_8H_6Cl_2O_3$, Sigma, ≥ 98%) were used without further purification.

Instrumentation

The instruments used for characterizations were X-ray diffractometer (XRD), scanning electron microscopy attached with energy dispersive X-ray (SEM-EDX), reflectance UV-visible and fluorescence spectrophotometers. UV spectrophotometer was also used to monitor the photocatalytic reaction.

Procedure

Preparation of photocatalysts

Certain amount of cobalt(II) nitrate hexahydrate was dissolved in 20 mL of double distilled water, followed by addition of P25 TiO_2 (1 g) in the solution. In order to obtain good dispersion, the mixture was ultrasonicated for 10 min at room temperature. The mixture was then stirred and heated at 80 °C until all solvent was removed. The dried powder was ground to a fine powder and calcined in air at 500 °C for 4 h. After calcination, resulted powder was ground and stored under ambient conditions. The prepared samples were labeled as *x* mol% CoO/P25 TiO_2, with *x* showed the ratio of Co to Ti (mol%) that varied in the range of 0.1–5 mol%. For comparison, the P25 TiO_2 was also treated in the same manner to the samples, except for the addition of the cobalt(II) nitrate hexahydrate.

Characterizations of photocatalysts

The crystal structure of prepared samples was investigated by an XRD using a Bruker Advance D8 diffractometer with Cu Kα radiation (λ = 1.5406 Å, at 40 kV and 40 mA). SEM images, mapping, and EDX spectra were measured on a Hitachi Tabletop SEM TM 3000 attached with a Bruker EDX at the voltage of 15 kV. The samples were put on a carbon tape and measured without any coatings. The optical properties of the samples were analyzed by an Avantes spectrophotometer AvaSpec-ULS2048 using a reflection probe holder with angle of 45° and PTFE-coated white material as the reference sample. The emission spectra were measured at room temperature on a fluorescence spectroscopy using a JASCO FP-8500. The samples were put in the solid sample holder and the spectra were monitored at excitation wavelength of 218 nm.

Photocatalytic degradation of 2,4-D

The prepared samples were evaluated for degradation of 2,4-D at room temperature under UV light irradiation. Prior to irradiation, the sample (50 mg) was dispersed in 2,4-D solution (50 mL, 0.5 mM) and stirred in the dark condition for 1 h to achieve the adsorption-desorption equilibrium. The reaction was carried out for 1 h under irradiation by a 200 W Xe-Hg lamp, which light intensity was 15 mW cm^{-2} and it was equipped with an IR cut off filter. The remaining amount of 2,4-D after each reaction was determined by UV spectrophotometer using a Thermo Scientific Genesys 10S. The monitored wavelength was 283 nm. The percentage of 2,4-D degradation was then calculated from the ratio of concentrations between the reacted and the initial concentrations of 2,4-D.

RESULT AND DISCUSSION

Properties of Photocatalysts

Fig. 1 shows XRD patterns of bare P25 TiO$_2$ and cobalt oxide-modified P25 TiO$_2$ samples. It was obvious that P25 TiO$_2$ has both anatase and rutile phases (Fig. 1 (a)). The diffraction peaks of P25 TiO$_2$ were not much influenced by the addition of cobalt oxide (Fig. 1(b)-(e)). Moreover, no other new diffraction peak was observed after the modification, which was in good agreement with reported literature on cobalt-doped TiO$_2$ samples with low loading of cobalt precursor [20]. These results suggested that the amount of added cobalt oxide might be too low to be detected by the present XRD or the cobalt oxide might be dispersed well on the surface of TiO$_2$. Even though the diffraction peaks of cobalt oxide could not be detected by XRD, it has been reported that cobalt oxide would exist as cobalt monoxide (CoO) on supported samples when the loading amount of added
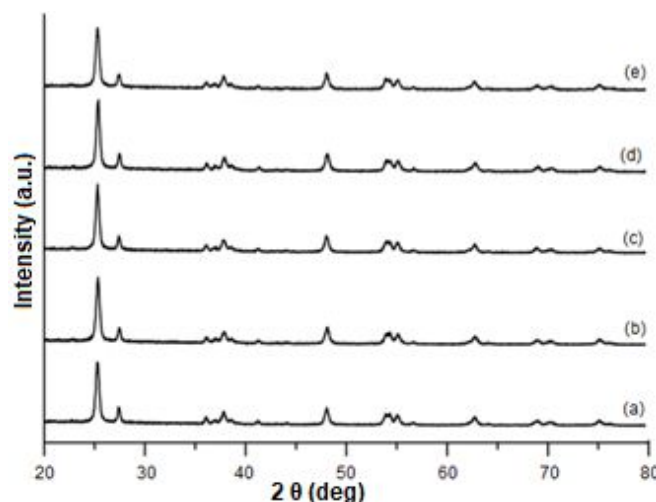
Fig 1. XRD patterns of (a) P25 TiO$_2$, (b) 0.1 mol% CoO/P25 TiO$_2$, (c) 0.5 mol% CoO/P25 TiO$_2$, (d) 1 mol% CoO/P25 TiO$_2$, and (e) 5 mol% CoO/P25 TiO$_2$ samples

Table 1. Crystallite size and anatase-rutile ratio of P25 TiO$_2$ and cobalt oxide-modified P25 TiO$_2$ samples

Samples	Crystallite size (nm)	Anatase-rutile ratio (%)
Bare P25 TiO$_2$	17.0	72:28
0.1 mol% CoO/P25 TiO$_2$	17.1	75:25
0.5 mol% CoO/P25 TiO$_2$	17.5	75:25
1 mol% CoO/P25 TiO$_2$	16.6	75:25
5 mol% CoO/P25 TiO$_2$	15.3	74:26

cobalt precursor was low [20,24]. Therefore, the most possible cobalt species formed on the present samples would be CoO.

Table 1 lists the crystallite size and the ratio of anatase to rutile for the P25 TiO$_2$ and cobalt oxide-modified P25 TiO$_2$ samples. The crystallite size was determined by Scherrer equation using the most intense peak around 2θ of 25.3°, while the anatase to rutile ratio was calculated based on the intensity of the most intense peaks at around 2θ of 25.3 and 27.4° for anatase and rutile, respectively. It was obtained that all samples have similar crystallite size to each other, which was in the range of 15–17 nm, and also similar anatase to rutile ratio, which anatase composition was in the range of 72–75%. These results confirmed that the addition of CoO did not affect the structural properties of P25 TiO$_2$.

In order to confirm the presence of CoO on the modified P25 TiO$_2$ samples, the samples were analyzed by the SEM-EDX. As representatives, mapping images of the modified P25 TiO$_2$ with the lowest and largest loading amounts of CoO, which are 0.1 and 5 mol%, respectively, are shown in Fig. 2(a) and (b). It was obvious that carbon, oxygen, titanium, and cobalt were detected on these samples. Carbon
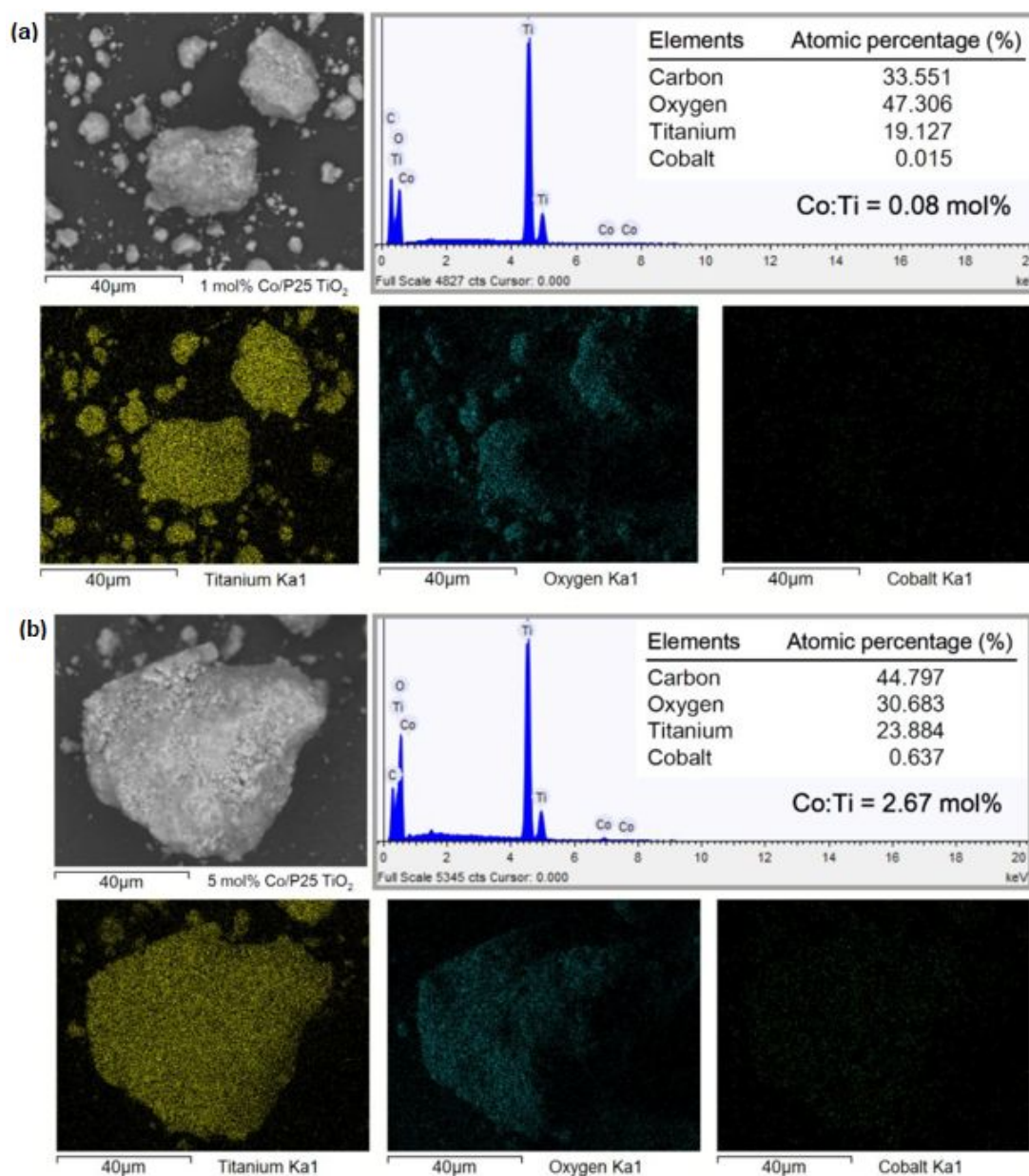
Fig 2. SEM images with element mappings and EDX spectra of (a) 0.1 mol% CoO/P25 TiO$_2$ and (b) *5* mol% CoO/P25 TiO$_2$ samples

parts of the samples. It is worth noted that the presence was observed as the carbon tape was used for the measurements. On the other hand, as expected the titanium and oxygen were distributed uniformly in all of cobalt was clarified even at the 0.1 mol% Co/P25 TiO$_2$ (Fig. 2(a)). The cobalt was found to be dispersed on the P25 TiO$_2$ for both samples. Other samples, which are the 0.5 mol% Co/P25 TiO$_2$ and the 1 mol% Co/P25 TiO$_2$ also showed similar mapping images to these samples (not shown).

Fig. 2 also shows the composition of the elements based on the quantification of the EDX spectra. The ratio of cobalt to titanium was determined to be 0.08 mol% for the 0.1 mol% CoO/P25 TiO$_2$ and 2.67 mol% for the 5 mol% CoO /P25 TiO$_2$. Therefore, it can be proposed that the detected amount of cobalt was very close to the theoretical added amount for samples with the low loading of CoO. As for high loading sample, the detected cobalt amount was relatively less than the added one. This might be due to the loss of the cobalt precursor during the preparation process since not all of CoO can be impregnated successfully on the P25 TiO$_2$ when the amount was too high. As for other samples, the ratio of cobalt to titanium was determined
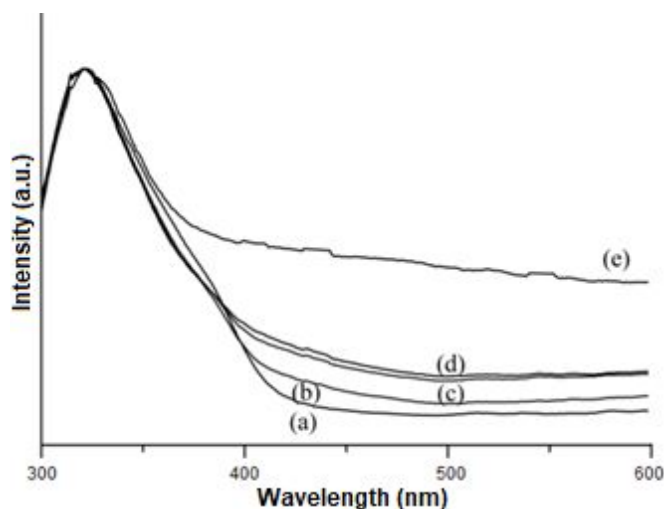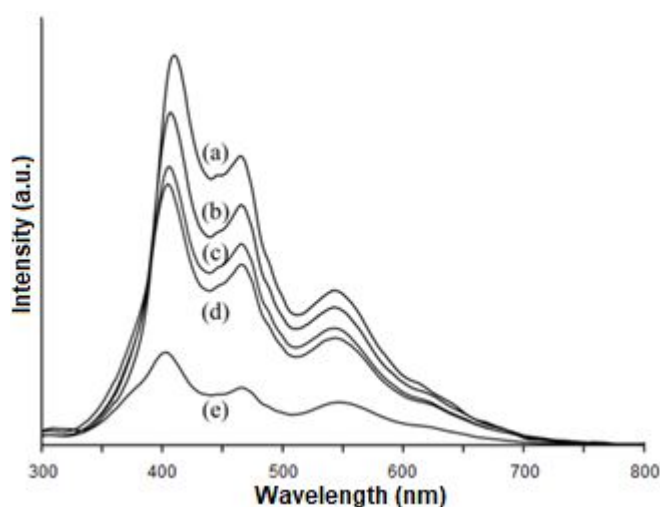
Fig 3. Normalized UV-visible spectra of (a) P25 TiO$_2$, (b) 0.1 mol% CoO/P25 TiO$_2$, (c) 0.5 mol% CoO/P25 TiO$_2$, (d) 1 mol% CoO/P25 TiO$_2$, and (e) *5* mol% CoO/P25 TiO$_2$ samples

Fig 4. Emission spectra of (a) P25 TiO$_2$, (b) 0.1 mol% CoO/P25 TiO$_2$, (c) 0.5 mol% CoO/P25 TiO$_2$, (d) 1 mol% CoO/P25 TiO$_2$ and (e) *5* mol% CoO/P25 TiO$_2$ samples

to be 0.30 and 1.14 mol% for the 0.5 mol% CoO/P25 TiO$_2$ and the 1 mol% CoO/P25 TiO$_2$, respectively.

The absorption spectra of P25 TiO$_2$ and the prepared cobalt oxide-modified P25 TiO$_2$ samples are shown in Fig. 3. Since the P25 TiO$_2$ has white color, the P25 TiO$_2$ did not show any absorption in the visible region (Fig. 3(a)). On the other hand, cobalt oxide-modified P25 TiO$_2$ samples have olive-green color that indicated the presence of CoO, in which the color became darker with the increase amount of CoO loading. In good agreement with the color appearance, these modified samples gave the additional absorption band above 400 nm (Fig. 3(b)-(e)). The background level absorption above 400 nm could be more observed with more addition of CoO, clearly suggesting that the CoO was the source of such visible light absorption. Even though the addition of CoO was found to shift the absorption of TiO$_2$ to longer wavelength, the absorption edge of P25 TiO$_2$ was not much influenced. This result suggested that CoO did not much alter the band gap of P25 TiO$_2$. This was reasonable since the cobalt precursor was impregnated on the surface of P25 TiO$_2$ as CoO. Therefore, it was different from the case when the cobalt ion was doped into the TiO$_2$ after reduction process, where the cobalt caused prominent shift of band edge from UV to visible region (from 3.2 to 2.7 eV) [20].

Fig. 4 shows the emission spectra of P25 TiO$_2$ and the prepared cobalt oxide-modified P25 TiO$_2$ samples when they were monitored at the excitation wavelength of 218 nm. As shown in Fig. 4(a), it was confirmed that the P25 TiO$_2$ showed strong emission spectrum with emission peaks at 410, 465, and 544 nm. It has been reported that the peak around 410 nm would correspond

to the radiative recombination of self-trapped exciton and the other two emission peaks at 465 and 544 nm would be due to the charge transfer of an oxygen vacancy trapped electron [11]. Addition of CoO did not give the formation of any new emission peaks, but decreased the emission intensity of the bare P25 TiO$_2$ (Fig. 4(b)-(e)). The emission intensity was decreased with the increase of the CoO loading. It has been generally understood that the emission spectrum is attributed to the radiative recombination of the excited electron and holes [25-26]. Therefore, the decrease in the emission intensity could indicate the role of cobalt species to lower the electron-holes recombination as has been proposed previously [19-20]. Even though the suppression of electron-hole recombination can be helpful to improve the efficiency of P25 TiO$_2$, there would be a balance between the suppression of the recombination and availability of electrons in the conduction band for the reaction.

Photocatalytic Activity and Proposed Mechanism

After 1 h under dark condition, all samples gave similar adsorption of 2,4-D in the range of 10.6-13.2%, suggesting that the present addition of cobalt oxide did not much vary the amount of surface sites interacting with 2,4-D molecules. In order to investigate the effect of the CoO loading on the photocatalytic activity of P25 TiO$_2$, the samples were evaluated for degradation of 2,4-D under UV light irradiation for 1 h. Fig. 5 shows the dependence of photocatalytic activity on the amount of CoO loading after excluding the adsorption part. It can be clearly shown that the photocatalytic activity of P25 TiO$_2$ increased from 49.6 to 54.6% with
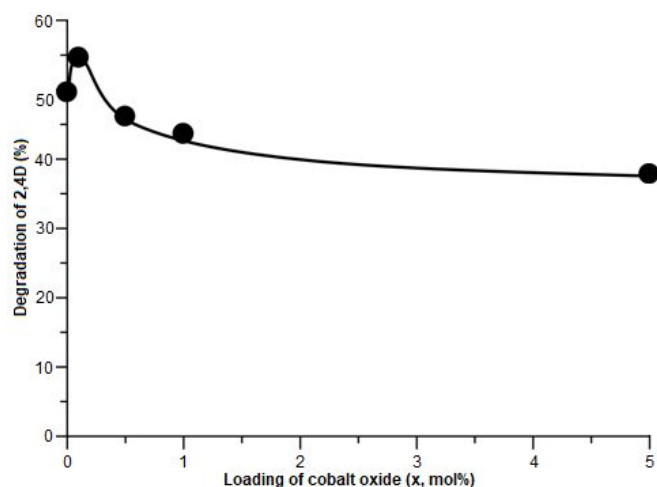
Fig 5. Photocatalytic degradation of 2,4-D on the P25 TiO$_2$ and cobalt oxide-modified P25 TiO$_2$ photocatalysts

addition of 0.1 mol% CoO. Unfortunately, higher loading of CoO caused lower photocatalytic activity. When the loading amount was 5 mol%, the activity dropped to only 37.8%. This result clearly suggested that the small amount of CoO, which was 0.1 mol%, was the optimum amount to give the optimum activity for this cobalt oxide-modified P25 TiO$_2$ series. The higher photocatalytic activity would be originated from the lower electron-hole recombination, which enhanced the possibility for the degradation of 2,4-D pollutant. On the other hand, the addition of higher loading might result in the less available electrons in the conduction band of P25 TiO$_2$, and thus reducing the efficiency of the P25 TiO$_2$.

Based on the characterization and photocatalytic activity results, the pathways of charge transfers can be proposed below. When the CoO/P25 TiO$_2$ was irradiated under UV light irradiation, electrons in the valence band of P25 TiO$_2$ would be excited to the conduction band resulting in the formation of holes in the valence band. The excited electrons would react with adsorbed oxygen to produce superoxide radicals, while holes would oxidize 2,4-D. Holes could also oxidize water to produce hydroxyl radicals. However, the contribution of hydroxyl radicals to degrade 2,4-D would not be as high as those of superoxide radicals and holes due to the low formation of hydroxyl radicals [11]. In addition to this pathway, electrons could be also trapped by cobalt species, which in turn caused a better separation of electrons and holes, and thus, higher photocatalytic activity.

CONCLUSION

The cobalt oxide-modified P25 TiO$_2$ photocatalysts were successfully prepared by the impregnation method, followed by the calcination process. The addition of CoO

did not affect much on the structural properties of P25 TiO$_2$. Its presence was confirmed by SEM-EDX in which the added CoO was dispersed well on the P25 TiO$_2$. The CoO gave additional absorption at visible light region but did not alter the band gap of the P25 TiO$_2$. Small amount of CoO was found to decrease the fluorescence emission intensity that represented the reduced electron-hole recombination process. It was obtained that the CoO with 0.1 mol% gave the optimum photocatalytic activity.

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