Photocatalytic degradation of VOCs from air stream using Mo:TiO$_2$/GAC nanocomposites

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Abstract

Modification of TiO$_2$ is one of the techniques used to enhance its photodegradation efficiency and to make it visible-light-active. In this study, Mo-doped TiO$_2$ nanoparticles were synthesized using a fast sol-gel technique and then coated on granular activated carbon (GAC) as both substrate and adsorbent to obtain Mo:TiO$_2$/GAC composite. The fabricated composite was characterized by many techniques such as powder XRD, SEM, EDX, FTIR, and N$_2$ adsorption-desorption analysis. Then, the composite was applied to photodegrade volatile organic compounds (VOCs) under both UV and visible light irradiations. The characterization results showed high crystallinity and purity. Mo:TiO$_2$/GAC composite gave a higher photodegradation efficiency compared with bare TiO$_2$ and bare GAC. Moreover, studying operational parameters showed that the optimum condition for photodegradation efficiency of VOCs was at a flowrate of 1 L min$^{-1}$, VOCs concentration of 20 ppm, and light intensity of 400 and 600 W m$^{-2}$ for UV and visible light, respectively. The results suggest that Mo:TiO$_2$/GAC is a visible-light-active composite and can be acceptably used to decompose VOCs under visible light with adequate efficiency and without the generation of harmful by-products such as O$_3$ as compared with UV.

1. Introduction

Recently, the wide production and release of volatile organic compounds (VOCs) in indoor and outdoor environments have been occurring and their tremendous detrimental effects on the environment and human health have been reported. It is highly essential to remove these chemicals from the air using efficient and cost-effective technologies with safe and healthy outlets [1]. The healthy outlets are especially of crucial importance in the cases where the effluent is released into the indoor environment as in the case of portable air purifiers [2].

Nanomaterials have recently been proposed to solve these issues [3]. On account of their unique physical and chemical properties, different nanomaterials have been satisfactorily applied in various fields such as medicine and pharmacy [4], water and wastewater treatment [5], as well as air pollution control [6, 7]. Heterogeneous catalysis using titanium dioxide (TiO$_2$) nanomaterials has particularly attracted special interest in the last two decades [8, 9]. Some exceptional properties for TiO$_2$ such as low cost, non-toxic nature, chemical inactivity, compatibility with the environment, long-term stability, as well as having lower bandgap energy (3.02 eV) have made it to get widely used [8–10]. However, there still exist some drawbacks with the pure TiO$_2$ being used alone as photocatalyst and it is needed to be improved.

Pure TiO$_2$ does not show a strong photocatalytic activity because of rapid electron-hole recombination and it also is a polar chemical structure resulting in its low tendency to the most VOC molecules [11]. Morphological
modifications have been considered as a good solution, among which coating TiO2 on a porous substrate has been most commonly employed to increase both the specific surface area and its affinity towards VOC compounds [12, 13]. Adsorbent materials such as silica, zeolites, and activated carbon (AC), have played an important role as substrates, among them, AC is considered to be a phenomenal supports [14–16]. Thus, AC has been used as a desirable substrate because of the favorable properties of AC such as porous molecular structure, high affinity towards VOC molecules, large surface area, availability in various forms and sizes, and low cost [14].

Although the bandgap energy of TiO2 is low compared with many other photocatalysts, it is still high enough that can only be activated under irradiation with light wavelengths of below 387 nm falling into the ultraviolet domain. This is along with the activation of catalyst, which results in the production of a high concentration of ozone gas that is classified as an air pollutant and highly irritant to the respiratory system [17–19]. It may be thought that ozone is used on a large scale to sterilize water as well as air. Since its half-life is low in calm and stable air, especially at high temperatures and humidities. Therefore, the resulting pollution at the reactor outlet will be negligible [20, 21]. In addition, although some reports showed that ozone was a strong oxidative agent and helpful for the mineralization of VOCs over the photocatalyst and it is consumed during the photocatalytic degradation process [22–25]. However, other studies reported that the outlet ozone concentrations were still very hazardous to the indoor environments especially where sensitive people were suffering from respiratory diseases [26–28].

The UV-active TiO2 also limited the application of solar energy, with only around 4% of which falling into the UV region, whereas about 40% of it was made up of visible photons with an energy range of 1.63 to approximately 3 eV [29]. In reply to this issue, chemical modifications have been applied to develop visible light-active TiO2 by doping or even coupling it with metals [30, 31], non-metals [32], and other semiconductors [33–35].

One of the common and effective strategies for chemical modification of TiO2 was its doping with noble and transition metals such as Fe, Pt, Au, Mo [36]. Despite some limitations like photo-corrosion and improved electron-hole recombination, the literature showed that the introduction of metals into the titania crystal lattice led to the formation of new energy levels between conduction and valence band, causing a shift of photocatalytic performances towards the visible light domain [12, 34].

In this work, Mo-doped TiO2 nanoparticles were synthesized using a fast sol-gel technique, and granular activated carbon was used as support for TiO2 to be deposited. The study focused on the synthesis of Mo:TiO2/GAC nanocomposites for photocatalytic removal of VOCs from air streams under UV and visible light radiations.

2. Materials and methods

Tetra n-butyl titanate (Ti(OBu)4) (98%), ammonium molybdate, ethyl alcohol, nitric acid (with purity of 99.8%), chloroform (with purity higher than 99%) were all obtained from Merck, Germany. Granular activated charcoal having pellets with a mean diameter of 3 mm was purchased from NORIT, Netherland.

Mo:TiO2/GAC composite was synthesized using a fast sol-gel technique [37]. A mixture solution (solution A) was first prepared by dissolving 10 ml of 0.01 M ammonium molybdate, in 30 ml of deionized water under continuous stirring. Simultaneously, mixture solution B was prepared by mixing 10 ml of tetra n-butyl titanate, 5 ml nitric acid (5% weight), and 10 ml deionized water in 200 ml of ethanol. Solution B was continuously agitated for 0.5 h. Next, solution A was added dropwise into solution B and then the mixture was continuously stirred for 1 h or until a homogenous transparent gel, which was obtained. At this point, 10 g of AC was added into the previous mixture and subjected to vibrate in an ultrasound bath for 0.5 h. Afterward, the mixture was filtered and then dried at 60 °C for 6 h. The dry composite was finally calcined at 450 °C for 4 h to obtain Mo:TiO2/GAC composite. Figure 1 shows the schematic diagram of catalyst synthesis and preparation steps.

X-ray diffraction (XRD) tests were employed to identify the crystalline structure of the composites (Philips powder diffractometer type PW 1737 goniometer, with Cu Kα, λ = 1.5418 Å) radiation source). The patterns were recorded in the 2θ range between 10–80° at a scanning speed of 2° min-1. Moreover, scanning electron microscopy (SEM), energy dispersive X-ray microanalysis (EDX), Fourier-transform infrared spectroscopy (FTIR), and N2 adsorption-desorption tests were carried out for the surface, elemental, functional groups, surface area, and pore volume characterizations of the composites, respectively.

A honeycomb plate made up of Teflon with dimensions of 150 × 150 × 10 mm was employed as catalyst reactor. The diameter of each honeycomb cell was 5 mm. A plastic mesh was applied at both ends of the honeycomb cells to prevent particles leaving from the reactor. In front of the reactor, a multi-chips circuit visible LED lamp with a wavelength of 415 mm and 150 × 150 mm dimension (Philips TUV 1 W G-8 T-5 Bulb, 32 lamps wired and positioned in 4 separate strings each one controlled by own switch), was placed in parallel with the reactor as the visible light radiator. In addition, 4 UV-C lamps with dimensions of 15 × 120 mm were
located on two parallel strips with 4 outlet switches (Philips 4W). The distance between the lamp sets and the reactor wall was adjusted to be 20 mm. The reactor was placed inline in a set-up system consisting of air supplying, air measuring, pollutant injection, mixing, and analysis units (figure 2). A 1000-liter air compressor was employed to supply normal air and it was allowed to flow through suitable flow meters and needle valves. By placing a Dust-Gas filter in the airflow path, the water vapor and background air contaminants were eliminated. Chloroform was then introduced as an air pollutant (300 ppm) through a septum port using a motor driving syringe pump (SP-510, JMS). Moreover, inlet water vapor was subjected to the air stream and was adjusted so that the relative humidity (RH) level remained constant at 30%. The airflow containing CHCl₃ and H₂O was ultimately reached the reactor after passing through a mixing chamber. The liquid chloroform was vaporized easily at 40 ± 2°C for the constant temperature and evaporator temperature was controlled using a temperature controller. All set-up parts were always inspected to be gastight during the experiments.

A gas analysis unit equipped with a sampling port was positioned at the set-up effluent. Another sampling port was also located behind the mixing chamber to determine the concentration of inlet gas. Most of the

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**Figure 1.** Schematic diagram of MoTiO₂/GAC synthesis and preparation steps.

**Figure 2.** Schematic of photocatalysis set-up system (1. Air compressor, 2. Air filter, 3. Control valve, 4. Rotameter, 5. Syringe pump, 6. Temperature controller, 7. Mixing chamber, 8. Reactor, 9. Gas-tight syringe, 10. Gas detector devices, 11. GC/MS, 12. Flue gas).
analyses were carried out using a gas chromatograph (GC/FID, Shimadzu-2010), equipped with a SGE capillary column with an inner diameter of 0.22 mm, film diameter of 0.25 μm, and length of 25 m. Some gas samples were also analyzed using GC/MS (Varian 3800 GC/Saturn 2200 mass spectroscope) equipped with the same column mentioned above. A 100 μl gas-tight sampling syringe was used for gas sampling. CO and CO₂ gases were also analyzed using an online gas detector (AQ9901sd) to determine the carbon balance.

3. Results and discussion

3.1. Characterization of composites

SEM was used to observe the surface morphologies of nanocomposite samples. A non-smooth porous structure was observed for the GAC surface structure before being covered with the nanoparticles displayed in figure 3. It could also be observed that GAC was well covered with a smooth layer of Mo:TiO₂ nanoparticles. Although some clusters were detected in Mo:TiO₂/GAC structure but in general, a good homogenous distribution with a good nanoparticle dispersion could be recognized observed in figure 3. It was considered that due to more extensive surface and thereby higher reactive sites for the reactant molecules, a good dispersion of nanoparticles over the substrate surface, could be in favor of photocatalytic efficiency [38]. Regarding the size of particles, it was measured manually using Digimizer image analysis software. In brief, firstly, the scale of the image was set as

![Figure 3. Scanning electron microscopy (SEM) images of: a. GAC, b, c, and d. Mo:TiO₂/GAC at different magnifications.](image-url)
determined by SEM. Next, some particles were selected on the SEM image (figure 3(c)), and based on it the mean size of the particles could be easily computed.

XRD patterns of substrate and photocatalyst samples are presented in figure 4. As depicted in figure 4, the XRD pattern of GAC indicated two compacted broad peaks at about 24.9 and 43° that could be attributed to the X-ray reflection in the (002) plane and the (100) plane of carbon crystallite aromatic layers, specifying a primarily amorphous structure of GAC substrate [39, 40]. Figure 4 also shows the XRD pattern of Mo:TiO2/GAC. The results displayed six main diffraction peaks at around 24, 38.1, 48.0, 54.0, 55.1, and 65.8°, which were attributed to the (101), (004), (200), (105), (211), and (204) planes of a synthetic anatase phase (SS-NNNN 89–4921), respectively. However, the peaks were broad and slightly shifted. It could be considered due to molybdenum doping [41]. In addition, Mo:TiO2/GAC composites were no peak that could be assigned to brookite or rutile phases. Furthermore, the peak positioned at 2θ of 43° ascribed to the (002) plane of GAC is not specified, which might be shielded by the TiO2 peak positioned at 48.0°.

The elemental characterization of the resulting photocatalyst was performed using EDX. Table 1 shows the weight and atomic percent of the main elements (i.e., C, O, Ti, Mo) of Mo:TiO2/GAC detected by Energy dispersive X-ray microanalysis (EDX).

| Element | Weight% | Atomic% |
|---------|---------|---------|
| Mo:TiO2/GAC | C | 62.27 | 84.88 |
| | O | 4.81 | 4.92 |
| | Ti | 24.31 | 8.31 |
| | Mo | 2.98 | 0.31 |
| | Fe | 2.22 | 0.65 |
| | Ca | 1.33 | 0.54 |
| | W | 2.08 | 0.19 |
| Total | 100.0 | 100.0 |

FTIR spectra made it possible to identify oxygen-containing and other functional groups on the surfaces of samples. FTIR spectra of the GAC and Mo:TiO2/GAC are illustrated in figure 6. It was noticeable that the most absorption bonds could be referred to as distinguishing characteristic hydroxyl groups that were observed at 2852–3642 and 1550–1800 cm\(^{-1}\). These groups were attributed to the \(-\)OH bonding of molecular water and carboxylic acid functional groups [43]. Some adsorption peaks detected at 1470 and 1396 cm\(^{-1}\) were considered as the representative of CH\(_2\) and CH\(_3\) vibration groups [44]. According to the literature, TiO\(_2\) had three adsorption regions. The broadest adsorption peak was commonly positioned at 3500 cm\(^{-1}\) related to the
stretching vibration of hydroxyl groups of TiO₂ nanoparticles that could be seen in figure 6. Other smaller and narrower peaks of TiO₂ were usually positioned at 1630 and 1383 cm⁻¹ ascribed to Ti-OH and Ti-O bonds of TiO₂ molecules, respectively [45]. Moreover, the peak between 450 cm⁻¹ and 800 cm⁻¹ was assigned to Ti-O stretching bonds. This peak could be observed in the structure of most composite materials. It might be attributed to the activated carbon sites coated by TiO₂ in this study. At 1440 cm⁻¹, CO bonds appeared on carbon-modified TiO₂. It was also obvious where activated carbon was covered by Mo:TiO₂, in which the hydroxyl groups absorption peaks were declined significantly [46].

The specific surface area of GAC and Mo:TiO₂/GAC was calculated by Brunauer–Emmett–Teller (BET) equation from measuring N₂ adsorption-desorption isotherm. The results are illustrated in figure 7. All of the samples showed high adsorption at low relative pressures. In addition, all of the curves displayed II-type isotherm accompanied by the presence of hysteresis loops, indicating microporous structure patterns [47]. The specific surface area, pore diameter, and total pore volume of GAC and Mo:TiO₂/GAC are summarized in table 2. As expected, the volume and surface area of Mo:TiO₂/GAC were lower than GAC support. It might be indicating the dispersion of TiO₂ particles onto the surface and volume of the bed resulting in the blockage of some pores in the substrate structure [48].

Figure 5. Energy dispersive X-ray microanalysis (EDX) spectrum of Mo:TiO₂/GAC.

Figure 6. Fourier transform infrared spectroscopy (FTIR) spectrum of a. GAC and b. Mo:TiO₂/GAC.
3.2. Photocatalytic performance

The photocatalytic performance experiments were carried out in a continuous flow of normal air with given concentrations of chloroform under UV and visible light after adsorption equilibrium obtained in darkness. The constant and stable breakthrough, a sign of adsorption equilibrium, was obtained after around 30 min (it was variable due to the different experiment conditions i.e. changing residence time and chloroform concentration) for GAC and Mo:TiO$_2$/GAC tested for the first time. For the next rounds, a constant breakthrough occurred within 10–15 min in most experiments, therefore the gas sampling was conducted every 15 min of the experiment period. After adsorption equilibrium, the lights were turned on and the time required for the photocatalysis process to reach stability was about 15 min. Each experiment was conducted within the first 32 h after photocatalyst synthesis each time to avoid testing under catalyst deactivation conditions. In contrary previous studies, although photocatalyst color alteration was not observed as the sign of photocatalyst deactivation especially when photocatalysts were tested with pollutant models [49, 50]. Figure 7 shows the removal efficiency (RE) of chloroform from the gas stream using bare GAC and Mo:TiO$_2$/GAC catalysts under different light power conditions (UV and visible). RE of around 60% was obtained for bare GAC with and without light irradiation, indicating a wonderful adsorption capacity of GAC towards chloroform due to its excellent porous structure and high surface area. The CHCl$_3$ used as a VOC pollutant model in this study is a colorless dense liquid with a sweet smell. It is usually categorized as a chemical with a moderate probability of being adsorbed by activated charcoal in the presence of high humidity [51, 52]. Although the chloroform molecule diameter (0.6 nm, which is near the mean pore size of GAC (table 2)) and low humidity amount in the air stream (30%) were set up in the experiment, the results showed an increased affinity of CHCl$_3$ towards GAC. It was generally accepted that GAC was a remarkable adsorbent. It has been used for a long time and is still used today as a successful adsorbent to remove pollutant gases and vapors [2, 44, 53]. Thus, RE of as high as 100% can be obtained with the good design of the reactor and appropriate amount of carbon granules [54, 55]. But, the main drawback with the bare GAC is breakthrough and adsorbent saturation over time as observed obviously in this study. So, when the pollutant concentration and the gas flow rate were subjected to change, the breakthrough time and level also varied significantly. A powerful adsorption capacity of substrate would be beneficial to catalytic oxidation of VOCs because it concentrates the pollutant molecules on the surface and near active sites of catalyst and provides the conditions for a well light and active species exposure [9, 15]. The results showed that Mo:TiO$_2$/GAC could be a suitable alternative for the bare GAC because it changed the

![Figure 7. N$_2$ adsorption–desorption isotherm of GAC and Mo:TiO$_2$/GAC.](image)

| Sample                  | GAC          | Mo:TiO$_2$/GAC |
|-------------------------|--------------|---------------|
| Specific surface area ($m^2g^{-1}$) | 1088.3       | 713.04        |
| Mean pore diameter (nm)  | 2.271        | 2.4977        |
| Total pore volume (c.c. g$^{-1}$) | 0.6179       | 0.4452        |

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breakthrough time and the reactor outlet concentration even in darkness and without light irradiation with a non-significant difference (Figure 8). As surface area results showed (Table 2), the specific surface area and the total pore volume of Mo:TiO\textsubscript{2}/GAC were less than that of GAC, implying that the slightly higher RE with Mo:TiO\textsubscript{2}/GAC in the darkness could be attributed to other processes than adsorption. In the previous studies, low catalytic activity had been reported for the common photocatalysts like TiO\textsubscript{2} in the absence of light and it made sense here for our results obtained in the darkness to be ascribed to this process called round-the-clock photocatalysis and driven by Fenton-like reactions [34, 35, 56]. The complete and efficient dark catalytic activity had also been reported in the literature [48], although no such results were observed in this study.

As previously mentioned, 30% relative humidity was determined as an optimum amount of water during pre-test experiments. It was noticed in pre-test investigations that when the amount of H\textsubscript{2}O was changed from 10 to 30%, the degradation efficiency increased significantly, but as the water concentration increased further (30%–45%), the RE level remained unchanged, and then it decreased from 45% H\textsubscript{2}O value onwards. This phenomenon can be explained by the fact that H\textsubscript{2}O in low amounts as a major source of ‘OH radicals (valuable active species that are generated in advanced oxidation processes and play an active role in the reactions) helps the degradation efficiency to be improved. On the other hand, at higher H\textsubscript{2}O concentrations, the excess water molecules compete with chloroform in adsorption on the surface of GAC [57–59]. The ozone production would also be restricted by the higher concentrations of H\textsubscript{2}O when UV was used [60, 61]. Furthermore, the excess H\textsubscript{2}O could consume the active species formed within the reactor environment [33]. It should be noted here that an increase in the concentration of water as an H-rich source (despite its effect on reducing RE) could be beneficial in directing the reactions towards the generation of higher values of HCl. Especially, it can be explained by a desirable water-soluble and easily removable product in the decomposition of Cl-rich compounds like CHCl\textsubscript{3} [62].

The effect of light intensity on catalyst performance was also investigated in this study. According to Figure 8, as expected, in the presence of Mo:TiO\textsubscript{2}/GAC, RE increased once light power was raised under both UV and visible light irradiation. These results were in agreement with the data reported previously by the other researchers [10, 13, 14]. Using a Lux meter and a UV radiometer the light intensity was measured and the light power was set so that the intensity of radiant light was the same under both UV and visible light irradiation modes. Mo:TiO\textsubscript{2}/GAC showed a better chloroform removal behavior under UV than when exposed to visible light as displayed in Figure 8. It seems that in addition to the direct photodegradation and hydroxyl radical–based reactions, another process called catalytic ozonation was also effective in chloroform decomposition under UV radiation [18, 24]. Figure 9 shows ozone concentration generated under both UV and visible light radiation. It could be found that ozone level was greatly increased under UV compared with under visible light, although the same energy level was delivered to the reactor environment in both UV and visible irradiations. These findings were a good agreement with the results of previous studies [41, 60]. It was well known that a gas stream containing a high level of oxygen (air) was exposed to the ultraviolet rays having sufficient energy (\(\lambda \leq 240\) nm), in which ozone was produced through the following reactions (equations (1)–(3)) [41, 61]:

![Figure 8. Effect of light source and intensity on the photocatalytic performance of GAC and Mo:TiO\textsubscript{2}/GAC.](image-url)
O\(_3\) is a powerful oxidizing agent having a high oxidation potential (2.07 V) that can react directly with the VOC molecules and break them down into smaller products (equation (4)) [24]:

\[
O_3 + M \rightarrow M_{ox}
\]

It can also play a precursor role in the generation of other strong oxidizing agents such as hydroxyl radicals (redox potential = 2.86 V) and indirectly trigger the VOC decomposition reactions (equations (5)–(8)) [18, 23]:

\[
O_3 \rightarrow O^•_3 \rightarrow \text{HO}_x; \rightarrow \text{'OH}
\]

\[
O_3 + H_2O \rightarrow H_2O_2 + O_2
\]

\[
\text{H}_2\text{O}_2 \xrightleftharpoons{\text{UV}} \text{2'OH}
\]

\[
\text{'OH} + M \rightarrow M_{ox}
\]

According to the literature, the OH radical yield would increase significantly when O\(_3\) was present in the reactor. Because, in the presence of ozone, the OH radicals would be dominantly produced through the one-electron reduction pathway shown in equation (5). It was much shorter and more efficient than the two-electron reduction pathway (O\(_3\) → O\(_2\) → HO\(_2\) → H\(_2\)O\(_2\) → 'OH) that was the main route to the generation of OH radicals in the presence of O\(_2\) [63].

The effect of VOCs concentration and contact time on RE was also assessed during the present study. The results are illustrated in figure 10. According to the illustration, RE was decreased with the increase of contaminant concentration and the decrease of contact time. It was difficult to compare these results with the reports of the previous works because of the variation of experimental conditions, reactor size and design, VOCs concentration range, light intensity, surface area, bandgap, and other effective factors. Specifically, the effect of VOCs concentration on RE was controversial [1, 27, 64]. Some of the researchers believe that higher numbers of pollutant molecules benefit the RE due to the precursor supply for the production of more active species, but others believe the opposite [17, 59, 64, 65]. Although indicators like OH radical yield per molecule and specific input energy have recently been introduced to address the issue, the challenges are continuing [66–68]. It might be concluded from the literature that an increase of VOCs concentration in an appropriate range might be beneficial in cases where there was sufficient residence time (> 10 min) like water and wastewater purification. Nevertheless, the cases of airlow treatment were very low residence times (< 1 min), which might have the opposite effect [8, 25].

Figure 9. Effect of light intensity on the O\(_3\) generation in the reactor outlet after photodegradation.
4. Conclusion

In this study, the Mo:TiO$_2$/GAC nanocomposite photocatalyst was successfully prepared using the fast sol-gel technique with satisfactory performance. The photocatalytic performance of the Mo:TiO$_2$/GAC catalyst for decomposition of chloroform as a VOC model was investigated under UV and visible light irradiation. GAC played an important role as both substrate and adsorbent. Both the removal efficiency and ozone concentration were higher under UV than the visible light. The optimum conditions were detected to be 30% relative humidity, 1 l/min flowrate, 20 ppm of VOC concentrations, and 300 and 500 W/m$^2$ light intensity for UV and visible radiations, respectively. The study suggests that the visible light irradiation can be satisfactorily used to activate Mo:TiO$_2$/GAC composite for dissociation of gas phase VOCs with acceptable efficiency and much safer outlet products compared with under UV irradiation.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflict of interest

The authors declare that they have no conflict of interest.

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