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Research Article

Effect of Tea Waste Extract Volume on Synthesis of TiO₂ Nanoparticles for Photodegradation of 2,4-dichlorophenol

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ABSTRACT

Tea is one of the most consumed drinks nowadays due to its exceptional benefits but the increase in demand of tea production has caused an impressive amount of tea waste. It has been known that plant extract containing biochemical which can be used as capping agent for synthesis of nanoparticles. In this study, the effect of volume on tea waste extract in synthesis of titanium dioxide (TiO₂) nanoparticles was investigated. 1, 3 and 5 mL of tea waste extract was selected as the extract volume which denoted as TiO₂-1, TiO₂-3 and TiO₂-5, respectively. The catalysts were characterized by XRD, FTIR, BET, UV-Vis DRS and FESEM. The results show that increasing volume of tea extract increased the band gap and crystallite size, while the surface area was decreased. The role of tea waste extract in formation of TiO₂ nanoparticles was tested to degrade 2,4-dichlorophenol (2,4-DCP) under visible light irradiation. The best photocatalytic degradation of 2,4-DCP was achieved using TiO₂-1 (85%) compared with TiO₂-3 (80%), TiO₂-5 (77%) and P25 (71%) concluded that the optimum volume of tea waste extract was 1 mL. Overall, the role of tea waste extract as capping agent in synthesis of TiO₂ nanoparticles shows that it has a good potential for replacement any organic capping agent.

Keywords: *Tea waste extract; TiO₂ nanoparticles; Extract volume; Photocatalytic degradation; 2,4-dichlorophenol*

1. INTRODUCTION

Clean water is one of the crucial things in our lives, making accessibility to cleaner water a challenge as most of the water these days is heavily polluted with organic and inorganic pollutants. Few persistent organic contaminants in pharmaceuticals, pesticides, personal care products, endocrine disruptors have been found in wastewater effluents on a regular basis [1]. Chlorophenol compounds are generally used in various manufacturing industries especially for the mass production of paints, textiles, pharmaceuticals, petrochemicals and synthetic dyes [2]. Among them, 2,4-dichlorophenol (2,4-DCP) usually functioned as an intermediate for herbicides. The negative effects of phenolic chemicals on the human neurological system have been described and connected to a variety of health problems, including renal failure, liver damage, and lung damage [3]. To prevent future environmental concerns, effective treatment technologies are needed.

The photocatalysis process employing semiconductors is now thought to be advantageous in the degradation of organic pollutants because this process does not require additional chemicals [4]. Within the last forty years, heterogeneous photocatalysis has seen numerous advances, particularly regarding energy and the environment. Titanium dioxide (TiO₂) nanoparticles have become a prospective material in photocatalytic processes due to its excellent qualities, such as its high photodegradation activity, great chemical stability, cheap and non-hazardous. Various synthetic methodologies are utilized to obtain TiO₂ nanoparticles such as physical, chemical and green synthesis method. The physical and chemical methods have a few downsides, including the need for expensive equipment, high temperatures and pressures, as well as the need for sufficient space to set up the reaction [1,4]. The use of toxic substances that are thought to be detrimental for the environment is frequently made by a chemical route synthesis and it also involves sophisticated process.

Biochemical in various plants can help in assisting the production of nanoparticles. It can be facilitated by a range of metabolites found in plant leaf extracts, which are convenient, safe to use, and easily accessible. Additionally, it is believed that extracts of plant leaf function as both

reducing and stabilizing agents to aid in the creation of nanoparticles [5]. The composition of the leaf extract affects how nanoparticles are formed. This is because different leaf extracts have variable quantities of biochemical reducing agents [6]. Additionally, some key phytochemicals implicated in the production of nanoparticles include amides, ketones, aldehydes, terpenoids and flavones [7]. The creation of nanoparticles using plant extracts is also quite novel and provides true green chemistry at a very cost-effective way [8]. To minimize the agglomeration effect and reduce the average particle size for an overall improvement in performance, TiO₂ nanoparticles can be synthesized with a variety of capping agents.

Bio-capping agents offer a one-step, cost-effective, synthesis of nanoparticles that is friendly which is sustainable and easy to scale up to industrial manufacturing. A range of synthetic processes, including eco-friendly, chemical, and physical can be used to create TiO₂ nanoparticles. Metal oxide nanoparticles' synthesis has lately switched to green biological routes that use plant-based capping agents in comparison with physical and chemical approaches which are costly and environmentally dangerous due to the use of hazardous chemicals, as well as require complex processes [9]. Previously, tea waste extracts containing phenolic and flavonoid as capping agent was used as alternative solvent for synthesis of ZnO using electrolysis method [10]. Thus, in this study the use tea wastes as plant extract in synthesis of TiO₂ nanoparticles as the alternative method which highlighted the green method. The effect of tea wastes extract volume was studied on formation of TiO₂ nanoparticles and their photoactivity was studied using 2,4-DCP under visible light irradiation.

2. MATERIAL AND METHOD

2.1 Materials

Tea wastes were obtained from cafeteria in Universiti Sains Malaysia in Penang, Malaysia. Titanium (IV) butoxide (TBOT) (97% purity), titanium P25 and 2,4-dichlorophenol (2,4-DCP) was purchased from Sigma-Aldrich (Greece). Ethanol (99.7% purity), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were acquired from R&M Chemicals (Malaysia). All the materials were of an analytically pure quality and were used directly without any purification needed.

2.2 Preparation of Tea Leaves Extract

Tea waste extract was prepared using 100 g of tea leaves wastes in 200 ml of distilled water. The mixture was heated at 60°C and stirred for 10-15 minutes to ensure homogeneity. After that, the solution was left to cool before filtering the extract.

2.3 Preparation of Catalyst

The TiO₂ nanoparticles were prepared by adding 50 ml distilled water and 1 ml of tea waste extract. Then, NaOH was added dropwise into the solution until pH 12 was achieved before stirring for 30 minutes. After that, 0.3 ml of TBOT was added into solution and the mixture was left to stir at room temperature for another 3 hours follow by centrifuging the resulting suspension for 10 minutes at 3500 rpm. The precipitate was filtered and washed with distilled water repeatedly followed by ethanol. The product was dried overnight at 90°C in an oven continued by calcination at 550°C for 3 hours and the catalyst was denoted as TiO₂-1. The same procedure was repeated by changing the volume of tea waste extract to 3 and 5 ml and denoted as TiO₂-3 and TiO₂-5, respectively. In this study, commercial TiO₂ known as P25 was used as the control for synthesized catalysts.

2.3 Material Characterization

The crystalline structures of each catalyst were determined using a Bruker Advance D8 X-ray powder diffractometer (XRD) with Cu Kα radiation (λ = 1.5418 Å). The bandgap of the catalysts was determined in the air at room temperature using a UV-Vis DRS (Perkin Elmer Lambda 900) spectrophotometer. The morphology of catalysts was observed using FEI Quanta FEG 650 Field-Emission Scanning Electron Microscope (FESEM) (Holland). Fourier transfer infrared spectroscopy (FTIR) (Perkin Elmer Spectrum 2000 FT-IR) was used to observe and identify the chemical functional groups present in the catalysts. The surface area was determined using the Brunnauer-Emmett-Teller method (BET).

2.3 Photocatalytic Degradation of 2,4-dichlorophenol

A 100 mL of 10 ppm 2,4-DCP solution was transferred into 250 mL beaker containing 0.019 g catalyst. The solution was stirred continuously in the dark for 1 hour to reach the adsorption-desorption equilibrium before being exposed under visible light irradiation for another 7 hours. The experiment was performed in a photoreactor accommodating 4 low-wattage fluorescent lamps (9 Watt, 385 nm) as the sources of the visible light irradiation. The visible lamps light source was placed 10 cm around the solution. A 3 mL of sample solution was taken within 30 minutes interval. Then, the samples were centrifuged at 9000 rpm for 15 minutes before being analyzed using UV-Vis spectrophotometer at 284 nm. Every experiment was carried out in triplicate to improve accuracy. The degradation percentage was calculated using the following equation:

Degradation efficiency (%) =

$$\frac{Initial\ concentration - Final\ concentration}{Initial\ concentration} \times 100\% \tag{1}$$

3.   RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of P25 and TiO$_2$ nanoparticles synthesized using different volumes of tea waste extract. Peaks at 25.40°, 36.88°, 37.99°, 47.73°, 54.03°, 55.30°, 62.70°, 67.23°, 70.29° and 75.04° which corresponded to (101), (004), (112), (200), (105), (211), (204), (116), (220) and (215) planes, respectively were observed for all catalysts indicated the peaks of TiO$_2$ anatase. All catalysts showed sharp peaks indicating that there is high crystallinity in their structures. Rutile peaks can only be observed for P25 (Figure 1a) at 29.11° and 55.30° corresponding to (110) and (220) planes, respectively. All synthesized catalysts only consist of anatase phase due to the calcination temperature in this study which was 550°C. Calcination temperature played an important role in determination of the catalysts' phase. It was reported that anatase transformation to rutile phase started at 600°C [11]. Calcination not only helps to further accelerate the degree of crystallization, but it can also help to promote the order of structure in the catalysts [12].
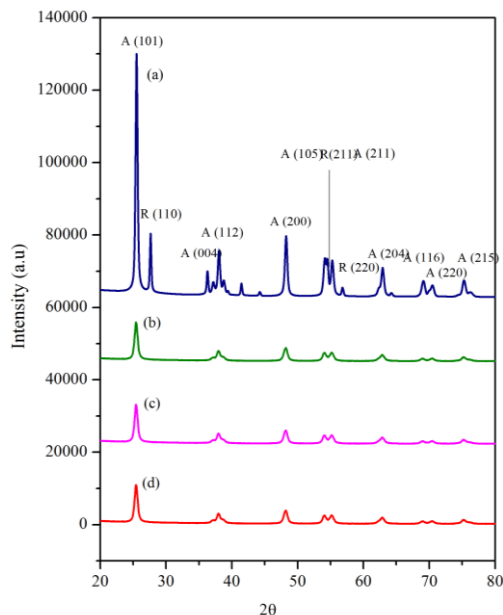
Table 1 listed the textural properties of the catalysts. Among them, TiO$_2$-1 illustrated the smallest crystallite size and band gap while the highest surface area compared to others. These results due to higher volume of tea waste extract caused agglomeration which increases the particle size consequently decreasing the surface area [13].

Figure 2 shows the chemical properties of all catalysts in the range of 3500-550 cm^{-1}. Bands at 3420 cm^{-1}, 1269 cm^{-1} and 1029 cm^{-1} were attributed to the O-H stretching of surface-adsorbed water, hydroxyl (OH) functional groups in alcohols and phenolic compounds and C–O stretching in amino acid, respectively. The strong band at 600 cm^{-1} and 900 cm^{-1} showed the formation of Ti–O and Ti–O-Ti bending vibrations, respectively. The metal oxide bonds like Ti–O–Ti and Ti–O confirmed the existence of TiO$_2$ in the prepared TiO$_2$ nanoparticles [14]. The presence of the Ti–O–Ti bond is due to the strong interaction (capped) of biomolecules with TiO$_2$ nanoparticles which resulted in the presence of polyphenols including flavonoids, and catechins. These plant compounds were responsible in reduction process of TiO$_2$ nanoparticles in green synthesis [15].
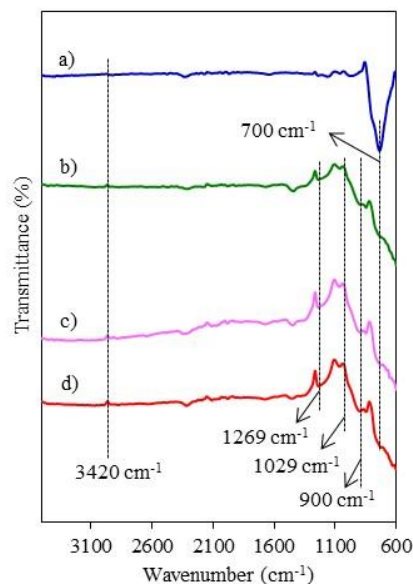

Figure 1. XRD diffractograms of (a) P25, (b) TiO$_2$-1, (c) TiO$_2$-3 and (d) TiO$_2$-5

Figure 2. FTIR spectra of (a) P25, (b) TiO$_2$-1, (c) TiO$_2$-3 and (d) TiO$_2$-5

Table 1. Textural analysis of the catalysts.

Catalyst	Polymorphic Phase	[a]Crystallite Size (nm)	Surface area (mg^2 g^{-1})	[b]Band gap (eV)
P25	101	22.4	4.21	3.4
TiO$_2$-1	101	21.3	8.09	3.2
TiO$_2$-3	101	23.6	7.04	3.3
TiO$_2$-5	101	24.9	6.59	3.4

[a]Crystallite size calculated using Debye–Scherrer equation at $2\theta = 25.4°$

[b]Band gap calculated using Tauc plot eV $= \dfrac{hc}{\lambda}$

FESEM was used to study the surface morphology of the as shown in Figure 3. All catalysts seemed to be spherical and were non-uniform in shape and size like previous studies [16]. The FESEM images illustrated that increasing volume of tea waste extract caused the particles possibly to tend to agglomerate, and the solution started to form aggregates [17]. This agglomeration could happen because smaller particles diffuse through the solution. The diffusion that occurred added to the surface of other nuclei or nanoparticles which is regarded as growth by ripening [18]. Phytochemicals act as reducing and capping agent that helps to reduce agglomeration by controlling the morphology as well as protecting and stabilizing the catalyst. Oxygen atom

of phenolic hydroxyl group moiety bind with metal by chelating effect to form metal-phenolate hydroxyl complex [19]. Black tea's polyphenols, catechins, and caffeine are examples of water-soluble phytochemicals that are effective at reducing metal ions and forming stable, capped metallic nanoparticles [20]. From the figure, TiO_2-1 shows the smallest particle size compared to TiO_2-3 and TiO_2-5 due to less amount of OH^-. These findings were in correlation with results in Table 1.
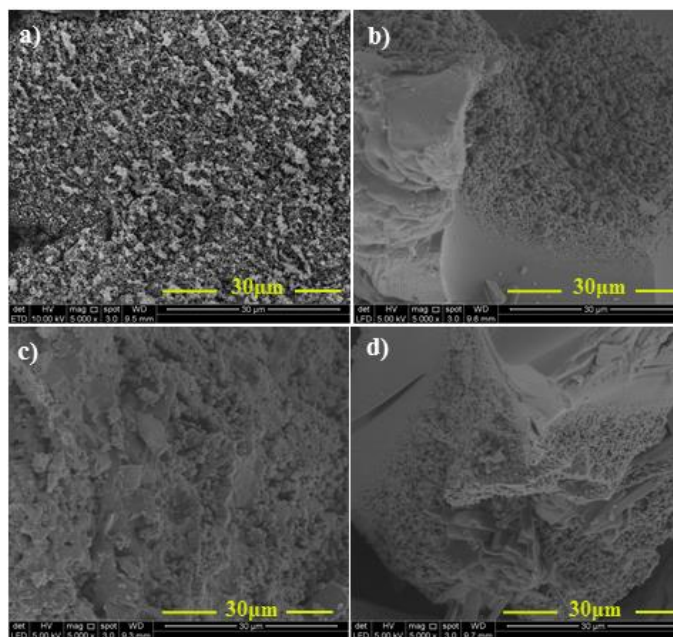

Figure 3. FESEM images of (a) P25, (b) TiO_2-1, (c) TiO_2-3 and (d) TiO_2-5.

The photocatalytic activity of the catalysts was tested using photodegradation of 2,4-DCP as shown in Figure 4. As control, photolysis was tested and the result showed that only 13% degradation of 2,4-DCP indicating the role of catalyst to this reaction. TiO_2-1 shows the highest degradation with 85% compared with TiO_2-3 (80%), TiO_2-5 (77%) and P25 (71%). The highest degradation was achieved with TiO_2 nanoparticles prepared using 1 mL tea waste extract illustrated that 1 mL is a sufficient volume for reduction and capping. In addition, adsorption study using TiO_2-1 was done for 8 hours with the absence of light resulting in only 15% degradation of 2,4-DCP indicating the importance of light source to this reaction. This result shows that variation in the biological materials is the main factor that greatly influenced the green synthesis of catalysts. The manipulation of quantity or volume of the plant extract used could alter the size and morphology of the nanostructure. Optimum quantity is needed as too low results in incomplete capping ability and too high can cause agglomeration. This statement is supported by FESEM analysis which increasing the amount of plant extract caused the nanoparticles to be agglomerated, which results in blocking of pore that lowered the surface area and limits the active sites for photodegradation. In addition, these results show that band

gap, surface area and crystallite size have synergetic effects in photoactivity of the TiO_2 nanoparticles.
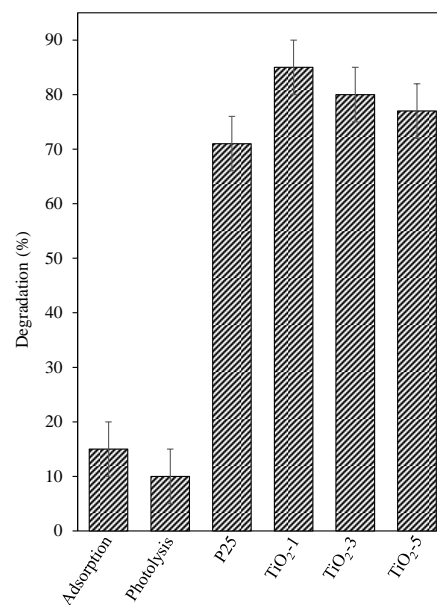

Figure 4. Adsorption and photocatalytic performances of the catalysts ($C_{2,4\text{-DCP}}$ = 10 ppm, pH = 3, W = 0.019 g, t = 8 h).

4. CONCLUSION

The TiO_2 nanoparticles with different volumes of tea waste extract was successfully synthesized and used as a photocatalyst to degrade 2,4- DCP. The catalysts were characterized by XRD, FTIR, BET, UV-Vis DRS and FESEM. XRD analysis showed that all synthesized catalysts were in the anatase phase and crystallite size increased when the volume of tea waste extract increased. The bandgap energy of TiO_2 increases when tea waste volume increases from 1 mL to 5 mL. In contrast, surface area decreases with increasing volume of tea waste. The agglomeration also occurred when the volume of tea waste extract increased. This phenomenon shows that the optimum volume of tea waste extract acts as reducing and capping agent is required to reduce agglomeration. The best photocatalytic degradation of 2,4-DCP was achieved using TiO_2-1 (85%) compared with TiO_2-3 (80%), TiO_2-5 (77%) and P25 (71%). The results reflect the decrease value of the bandgap and crystallite size with increasing surface area plays an important role in TiO_2 nanoparticles as photocatalyst.

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