Preparation of Composite Banana Peel-TiO$_2$ for Methyl Orange Dyes Removal

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Abstract. Composite banana peel activated carbon-TiO$_2$ has successfully prepared using the sol-gel method. In this research, banana peel was activated using KOH activator. This study aimed to compose biomass wastes (banana peels) with TiO$_2$ catalyst for Methyl Orange (MO) dye removal. The banana peel-activated carbon (BPAC) composition varied from 20, 50 and 70 wt. %. The prepared samples were calcined at 400 $^\circ$C for 4 h. The structure and properties of the prepared samples were characterized by X-ray Diffraction (XRD), Fourier Transmission Infra-Red (FTIR), Scanning Electron Microscope (SEM) and Ultraviolet-Visible Spectrophotometer (UV-Vis). The results obtained from XRD showed the presence of anatase, rutile and potassium formate. The morphological analysis TiO$_2$ showed agglomeration whereas pores were observed in BPAC. FTIR results indicated a C-O stretching and CH functional group formation through a modification that it does not exhibit in pure TiO$_2$. The sample with 50 wt% BPAC-TiO$_2$ has the highest MO removal (72.5%) within 3 h of irradiation time. From the current finding, banana peel-activated carbon-TiO$_2$ can be commercialized for wastewater remediation especially in treating dye pollution.

1 Introduction

Dye production in the world is around 800,000 tonnes per year. About 10-15% of synthetic colours are lost during various textile manufacturing operations. Synthetic dyes are used in multiple industries, including textiles, food, leather, pharmaceuticals, and cosmetics. Nearly 70% of the 10,000 dyes used in textile manufacturing alone are azo dyes that are complex in structure and synthetic in nature [1, 2]. Therefore, methyl orange (MO), an example of azo dyes, was treated in this work.

TiO$_2$ is a well-known photocatalyst can be used for wastewater and air remediation [3-6]. There are three polymorphs related to TiO$_2$ which are anatase, rutile, and brookite. Each polymorph has different structures and their efficacy depends on the various environmental conditions.
applications due to their chemical stability, high reactivity, and non-toxicity. However, anatase TiO$_2$ is only active under UV light irradiation due to the large bandgap energy of 3.20 eV. Therefore, higher implementation costs are needed since UV-light lamps consume higher energy and are not environmentally friendly. There were numerous modifications of TiO$_2$ that can be executed to produce visible light active TiO$_2$, including non-metal doping, metal decomposition, dye sensitization, coupled semiconductors, etc. [7-9].

The sol-gel process was used to synthesize a TiO$_2$-decorated banana peel composite in this study. The waste from banana peels and titanium isopropoxide serves as a source of carbon and titanium, respectively. FESEM, XRD, FTIR and UV-Vis were used to study the properties of the samples as-prepared. The effects of adding banana peel-activated carbon (BPAC) to TiO$_2$ characteristics have been studied and discussed. MO as a dyes compound model was also used to assess photocatalytic performance under visible light irradiation.

2 Experimental procedure

2.1 Synthesis of BPAC

500 g of banana peel was washed and rinsed with distilled water then being dried at 100 °C for overnight to remove moisture. The dried banana peel was cut, ground and sieved through a 100 mesh sieve. The powder was carbonized in a furnace at 500 °C with 5 °C/min heating rate for 4 hours. Char was produced after carbonization process. 30 g of char was soaked with 45 % w/w KOH solution at an impregnation weight ratio of 2:1 (KOH:char) for 3 hours. The mixture was dried first in an oven at 100 °C for overnight before second carbonization. The second carbonization was carried out again in furnace but with a temperature of 750 °C and duration of 2 hours. The banana peel activated carbon was produced and then cooled down in room temperature. The BPAC was then dried again at 100 °C in an oven for 5 hours. It was stored in a sample bottle for further usage after completion.

2.2 Synthesis of TiO$_2$/BPAC

The prepared BPAC earlier was added into the mixture of Titanium isopropoxide, anhydrous isopropanol, acetic acid, and distilled water under vigorous stirring at room temperature. The molar ratio of TTIP/isopropanol/acetic acid/H$_2$O is generally set as 1:100:0.2:50 in the typical procedure. A milky suspension was formed after the mixing happened. It was then continuously agitated for another 1 hour then the solution was left to settlement and the precipitates were filtered out using filter paper. The powder sample was then dried in an oven for overnight at 100 °C. Lastly, the powder formed was calcined at 400 °C for 4 hours at a heating rate of 5 °C/min. The end product obtained will then be denoted as TiO$_2$/xBPAC according to their respective weight ratio of BPAC to TiO$_2$ which is 20, 50 and 70 wt. %.

2.3 Characterization

Scanning Electron Microscope with Energy Dispersive Spectrometer (SEM, Hitachi VP-SEM SU1510) was used to characterize the morphology and elemental composition of the prepared sample. Meanwhile, the material's crystalline structure and chemical bond were identified using X-ray powder diffractometer (XRD, Bruker D2 Phaser) and Fourier transmission infra-red (FTIR, Agilent Cary 600 Series). The photocatalytic activity was analyzed using UV-Vis spectrophotometer (Shimadzu, UV-3600).
2.4 Evaluation of Photocatalytic Activity

The photocatalytic activity of the prepared composite was evaluated by monitoring the degradation of methyl orange (MO) aqueous solution under visible light irradiation as following our previous work [10, 11]. 0.20 g of each different photocatalysts was added into 25 ml of 10 ppm MO dye under stirring condition and was left in the dark for 90 minutes to ensure the adsorption equilibrium to be reached before it is irradiated. After all, visible light was emitted by two fluorescence lamps with each of 34 Watts to irradiate the suspension. 2 ml of MO suspension was extracted out at an interval of 30 minutes during the irradiation period of five hours and left for settlement to eliminate the catalyst. The percentage of MO degradation (D %) was then calculated using the concentration shown by UV-Vis as shown in Eq. 1.

\[
D \% = \left( \frac{C_0 - C}{C_0} \right) \times 100
\]

where \(C_0\) and \(C\) respectively represent the concentrations of MO before and after degradation.

3 Results and Discussion

Fig. 1. below shows the comparison of XRD pattern for all the five catalysts. XRD pattern of TiO2 displayed most of the diffraction peaks at 2θ values 25.30°, 37.77°, 48.04°, 55.06°, and 62.67° were assigned to (101), (004), (200), (211), and (204) crystal planes of anatase [19]. This indicates that TiO2 is existed in anatase state. In addition, a small percentage of rutile phase is present in the TiO2 which match the peak at 55.08°, 62.69° and 75.11°. The XRD patterns of the composites of TiO2 with different composition of BPAC show lesser peaks than pure TiO2 and pure BPAC. The composites' XRD result mainly follow the pattern of pure BPAC. The phase that can be found and being analyzed out for composites are potassium formate (CHKO2), brucite (Mg(OH)2), and dipotassium oxide (K2O) generated by BPAC.
Fig. 1. XRD pattern of (a) TiO$_2$ (b) TiO$_2$/20BPAC (c) TiO$_2$/50BPAC (d) TiO$_2$/70BPAC (e) BPAC
(♦ Anatase, ★ Rutile, • Dipotassium oxide, ▲ Potassium Formate and △ Brucite)
The morphological structure and condition of each catalyst is shown in Fig. 2. The morphology of BPAC can be seen from the image captured where pores can be observed. On the other hand, TiO$_2$ particles shown in Fig. 2. (b) are agglomerated in clump. Therefore, the combination of two types of particles are clearly illustrated in Figure 2 (c), (d) and (e). A difference can be spotted from the surface of Figure 2(c) and (d). TiO$_2$/50BPAC has a rougher background surface and exhibits porous structure similar as BPAC. Apart from that, TiO$_2$/70BPAC with higher composition of BPAC reduces the chance of TiO$_2$ particles to be seen and the image demonstrates that few amount of TiO$_2$ particles are attach on BPAC.

Fig. 2. SEM image of (a) BPAC (b) TiO$_2$ (c) TiO$_2$/20BPAC (d) TiO$_2$/50BPAC (e) TiO$_2$/70BPAC
The distribution of elements on the surface of BPAC, TiO$_2$, TiO$_2$/20BPAC, TiO$_2$/50BPAC, and TiO$_2$/70BPAC was studied using EDX element mapping (Table 1). The element mapping pictures for C and O showed profiles from BPAC, TiO$_2$/20BPAC, TiO$_2$/50BPAC, and The presence of TiO$_2$ in all samples except BPAC is supported by the high-intensity peaks associated with Ti and O. The traces of magnesium, phosphorus, potassium and silicon are detected in the samples consist of BPAC. It is normal to have magnesium, phosphorus, and potassium in BPAC because it is naturally one of the common elements in a banana fruit. Besides, KOH is used in the synthesis of BPAC as the chemical activating agent. In addition, carbon elements that present in it which gives properties to BPAC for attracting the dye particles and hence reducing the concentration.

Table 1. Elemental composition of BPAC, TiO$_2$, TiO$_2$/20BPAC, TiO$_2$/50BPAC and TiO$_2$/70BPAC

| Elements   | Weight % |
|------------|----------|
| Titanium, Ti | 53.70    |
| Oxygen, O   | 46.30    |
| Carbon, C   | 3.71     |
| Potassium, K| 10.32    |
| Aluminium, Al| 1.43    |
| Silicon, Si | 1.16     |
| Chlorine, Cl| -        |
| Magnesium, Mg| -       |
| Phosphorus, P| -       |

Fig. 3. below shows the overall result of the FTIR spectrum for five samples. The reaction between TiO$_2$ and BPAC are clearly shown in the FTIR spectrum especially some of the peaks are altered when the increasing amount of BPAC were added. There are significant peaks at 1379 cm$^{-1}$, 1371 cm$^{-1}$, and 1360 cm$^{-1}$ from catalysts TiO$_2$/50BPAC, TiO$_2$/70BPAC and BPAC, respectively, indicating the presence of a C-H stretching band in-plane bend from alkene group. C-H stretching band is the additional form of bonding that cannot be found in pure TiO$_2$. This phenomenon describes the role of BPAC as a modification towards the structure of TiO$_2$. Additionally, this also determines that some organic compounds from BPAC remain in the catalysts' structure [12]. However, there is no relevant peak at the range in TiO$_2$/20BPAC may due to the structure of TiO$_2$ has been disturbed but not that significant yet. Moreover, the broadband from 2400 cm$^{-1}$ to 3400 cm$^{-1}$ was assigned to -OH stretching of carboxylic functional groups and bending vibrations of adsorbed water molecules [13]. The broader width of the peak explains that the doping of BPAC with TiO$_2$ has diminished the C-O stretching bond. The new peaks in the range of 400 cm$^{-1}$ to 900 cm$^{-1}$ correspond to Ti-O and Ti-O-Ti stretching vibrations, indicating the presence of TiO$_2$ in composite catalysts [14].
Fig. 3. FTIR spectrum of (a) TiO$_2$ (b) TiO$_2$/20BPAC (c) TiO$_2$/50BPAC (d) TiO$_2$/70BPAC and (e) BPAC

Fig. 4. illustrates the comparison of concentration change from an initial concentration of 10 mg/L. The lowest concentration that MO was degraded to is 2.75 mg/L whereas the highest concentration remained in MO is 4.34 mg/L which done by catalyst TiO$_2$/20BPAC. Apart from that, the percentage of degradation is shown in Figure 10 where MO had been 72.50% degraded by TiO$_2$/50BPAC. The poorest performance is TiO$_2$/20BPAC which only able to carry 56.61% of MO to be degraded. Other than that, the percentage of degradation decreased from 65.11%, 63.60%, and 62.42%, which was performed by BPAC, TiO$_2$/70BPAC and TiO$_2$ respectively. The results described that the addition of BPAC into the precursor solution enhanced the performance of the pure photocatalyst under visible light. It is believed that the addition of BPAC could adapted the higher porosity and better adsorption properties of TiO$_2$. Therefore, a better photoactivity performance than TiO$_2$ alone was exhibited. This statement is consistent with the degradation results obtained by the optimum photocatalyst of TiO$_2$/50BPAC. The main factor that influencing the photocatalytic activity of TiO$_2$/xBPAC is the interfacial contact between the carbon and TiO$_2$ [13].

Fig. 4. Percentage of photocatalytic degradation of MO for 300 min by using photocatalysts
4 Conclusion

The effect of composition of BPAC added into the precursors of TiO$_2$ on photocatalytic activity and their characterization was studied. It is noticed that TiO$_2$/50BPAC performs the highest percentage of degradation compared to other compositions of BPAC and pure TiO$_2$. From the evaluation of photocatalytic activity, it can be concluded that adding too much or lesser amounts of BPAC into the precursor would cause lower percentages of degradation. Therefore, 50% of BPAC is much more suitable in this application.

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