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A A Aziz[1] and S Ibrahim[2]

[1]Faculty of Engineering Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, Gambang, 26300 Kuantan, Pahang, Malaysia
[2]Department of Civil Engineering, Faculty of Engineering, University of Malaya, 50603, Kuala Lumpur, Malaysia

[1]azrinaaziz@ump.edu.my, [2]shaliza@um.edu.my

Abstract. A synergetic improved composite TiO_2 photocatalysts was successfully synthesized by using nitrogen (N) as a dopant and activated carbon (AC) as synergetic compound. Two different types of AC prepared from Garcinia mangostana shell and commercial AC obtained from palm shell were chosen as synergetic compound. Thus synthesized composites was further characterized by Brunauer-Emmett-Teller (BET) surface analyzer and UV-visible light spectroscope. The doping of N resulted in a better solar light utilization potential. Furthermore, synergizing with AC contributed for the improved BET surface area and pore size distribution. The synergetic adsorption-photocatalytic activity was investigated by removing a commercial batik dye namely Remazol Brilliant Blue (RBB) under direct solar irradiation. The synergetic experiments showed that commercial AC synergized with N-TiO_2 resulted with a maximum removal efficiency of ~80% in 6 h.

1. Introduction

Over the decades, textile industry is gaining popularity in Malaysia especially in East Coast of Peninsular Malaysia like Kelantan and Terengganu. Among them locally well know batik industries are traditionally inherited over generations. In present days, these industries are commercialized and contributed significantly for the Malaysian Gross Domestic Product (GDP). However, this industry produces multiple dye waste that is released into the aquatic environment without proper treatment. Among the batik dyes, Remazol Brilliant Blue dye (RBB) has a major commercial contribution. Thus released dyes exert great harmfulness to the well-being, flora and fauna of the aquatic ecosystem [1]. Moreover their chemical structure makes more resistivity towards the natural photodegradation [1, 2]. Therefore, in order to protect the environment and to meet the stringent government law, it has driven many researchers to develop an effective and economical way to treat the dye wastewater [3].The developed methods include chemical coagulation, precipitation, biological techniques, adsorption, advanced oxidation processes (AOPs), membrane process, etc. [1-3]. Among them photocatalytic oxidations process, a classification of AOPs is more significant route over the others. They are highly efficient oxidation process with lower cost, zero toxicity with greater chemical and biological stability. This process employs semiconductors include TiO_2, ZnO, CeO_2, WO_3, SnO_2, ZrO_2, CdS and ZnS. They have been widely examined over the last few decades. Off these, titanium dioxide (TiO_2) has been proved to be an effective in removing organic pollutants from water bodies. Though they are efficient, their activity highly depends on recombination rate of photogenerated electron (e^-) and hole (h^+) pairs as well as the band gap energy [4-6]. The conventional TiO_2 has wider band gap energy (3.2 eV) and faster recombination rate of e^- and h^+ pairs. This wider band gap hinders its activation only to the ultraviolet (UV) region (λ <380 nm) than that of visible.

Many researchers had attempted to overcome these limitations either by doping metal ions or non-metal ions into the TiO_2 lattice. These doping could narrow the band gap energy in order to utilize visible light irradiation [7]. These photocatalysts can be employed as either as slurry, on a support,

immobilization with glass fibers, glass beads or steel. However, they have issue due to adhesion force between the photocatalyst surface and the support. Therefore in present years researchers are moving towards a synergetic approach. Among them AC is one of the cost effective synergist with enriched adsorption capacity [4-6]. Hence in the present study N doped TiO_2 photocatalyst (N-TiO_2) was successfully synthesized and thus was synergized with low cost AC prepared from *Garcinia Mangostana* shell (N-TiO_2/GAC) and commercial activated carbon derived from palm shell (N-TiO_2/CAC). The fabricated photocatalysts was characterized and functionalized for the synergetic adsorption-photocatalytic removal of commercial batik dye viz., RBB under sunlight irradiation.

2. Materials and methods

2.1. Materials

The commercial AC (CAC) of < 1 mm, manufactured using commercial palm oil mill waste as precursor was obtained from Bravo Green Sdn Bhd, while the *Garcinia Mangostana* shell derived AC was synthesized in our laboratory. The chemicals including orthophosphoric acid, H_3PO_4 (≥ 99% trace metals basis), sodium hydrogen carbonate, $NaHCO_3$ (99.5-100.5%), sodium sulphate (Na_2SO_4, ≥ 99% trace metals basis), barium chloride ($BaCl_2$, ≥ 99% trace metals basis) and titanium (III) sulphate solution ($Ti_2(SO_4)_3$, ≥ 99% trace metals basis) were purchased from Sigma Aldrich and used without further purification. Milli-Q water (≥ 18.2 M Ω cm) was used for all experiments.

2.2. Synthesis of photocatalyst

The synthesis of the AC from *Garcinia Mangostana* shell and N doping procedure is detailed in our earlier reports [8, 9]. The synergization with AC was prepared by using 1 g of N-TiO_2 and 1 g of AC mixed into 1 L of Milli-Q water. The mixture was stirred for 24 h at room temperature (27°C±2°C) to obtain a homogeneous solution. Then the product was centrifuged and dried over night at 100°C ±2°C. The dried product was then carbonized in the furnace at 400 °C for an hour.

2.3. Characterization

Brunauer-Emmett-Teller (BET) surface area, pore volume, and Barret-Joyner-Halenda (BJH) pore size distribution (PSD) based on N adsorption-desorption isotherms were analyzed by Quantachrome Autosorb Automated Gas Sorption System. The optical absorption study was evaluated using UV-Vis (Shimadzu UV-2600) equipped with $BaSO_4$ diffuse reflectance integrating sphere (DRS) at ambient temperature in the wavelength range between 200 and 800 nm.

2.4. Adsorption-photocatalytic oxidation study

Synergetic adsorption-photocatalytic oxidation study was carried out in a batch reactor of 1 L capacity with a working volume of 250 mL. The reactor adopted is a simple glass beaker, under stirred condition using a magnetic stirrer in presence of sunlight as a light source. All the experiments were carried in a good sunny day under identical conditions. The intensity of sunlight varied between 2100 and 101200 lx. Solar luminance was measured using LT Lutron LX-101 Light Meter and the average luminance for the experimental run was calculated.

The photocatalytic experiments were performed with a catalyst loading of 1 g and 50 mg/L of initial dye concentration. The dye was vigorously stirred by a magnetic stirrer for uniform dye concentration and better mass transfer. This photocatalytic experiments were followed by a one hour dark reaction, which was sufficient to attain adsorption equilibrium. The samples were collected at regular time interval, filtered and the supernatant was subsequently analyzed for the residual dye concentration. The concentrations of RBB solution were determined by measuring the absorbance at 596 nm with the UV-Vis spectrophotometer (Shimadzu UV-2600). Figure 1 shows the experimental set-up for the photocatalytic study [8, 9].

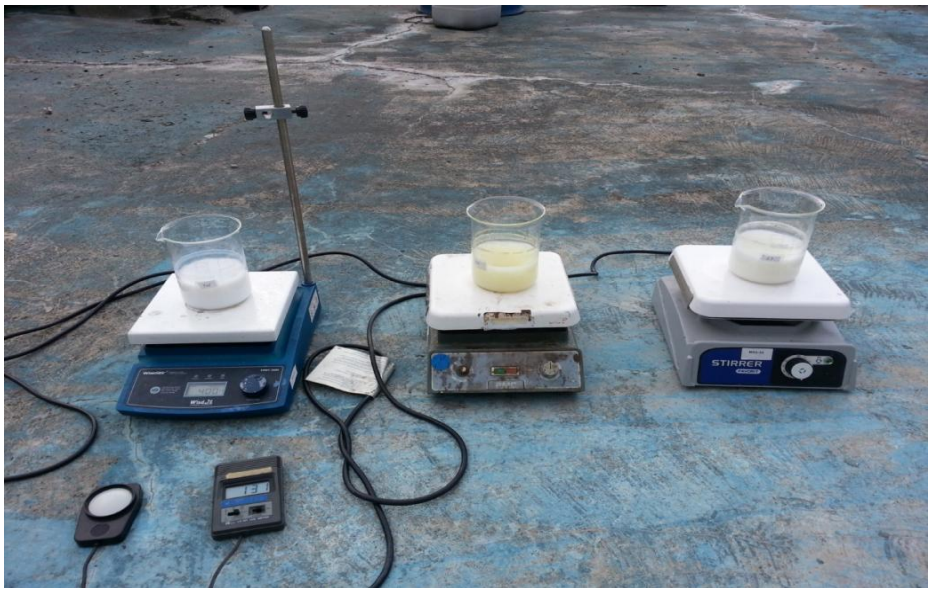

Figure 1. Photograph of experimental set-up for the photocatalytic study.

3. Results and discussion

3.1. BET analysis

Table 1 lists the BET surface area, pore volume and average pore diameter of the both prepared photocatalyst and synergized photocatalysts.From the table, it is observed that the surface area and pore volume of GAC is higher than that of CAC. N-TiO_2 showed Type II BET isotherm which attributes to the cylindrical pores of the prepared TiO_2. On the other hand GAC synergized photocatalyst showed a Type IV isotherm, common isotherm type for AC, indicates that N-TiO_2 is condensed inside the tiny pores of the AC. Furthermore, after doping with N, the surface area and pore volume for N-TiO_2/GAC is lower compared to N-TiO_2/CAC. This proved a proper method of N doping for N-TiO_2/GAC where majority N-TiO_2 covered the pores of GAC which leads to a better photocatalytic process.

Table 1. BET surface area, pore volume and average pore diameter of the AC and prepared photocatalysts.

Samples	**BET surface area [m^2 g^{-1}]**	**Pore volume [cm^3 g^{-1}]**	**Average pore diameter [nm]**
N-TiO_2	106.3	0.3592	13.51
GAC	1218.0	0.7510	2.47
CAC	974.8	0.4480	1.84
N- TiO_2/GAC	343.6	0.3968	4.62
N- TiO_2/CAC	689.0	0.4357	2.53

3.2. UV-vis absorption spectra

The UV-visible absorption spectra obtained for the samples were presented in Figure 2. The figure illustrates the response of both N-TiO_2 and AC synergized N-TiO_2 between 200 – 800 nm of the spectrum. All the prepared photocatalysts exhibited an enhanced absorption in the visible light region along with a markable shift towards visible spectrum. Among them N-TiO_2/GAC emerged with slightly higher absorption and better shift towards the visible spectrum. This was further attributed to the contribution of the N and carbon support as a result of absorption under the visible light region.

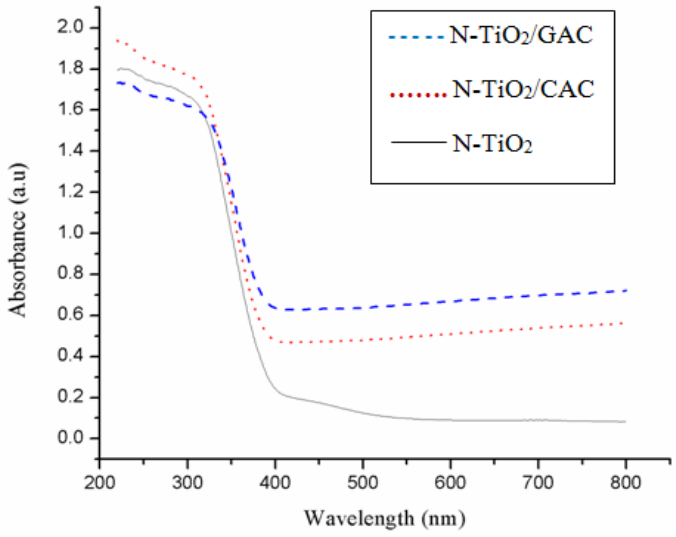

Figure 2. UV-visible absorption spectra of prepared photocatalysts.

3.3. Synergetic adsorption-photocatalytic oxidation study

The synergetic adsorption-photocatalytic degradation of RBB dye with the prepared photocatalysts were shown in Figure 3.

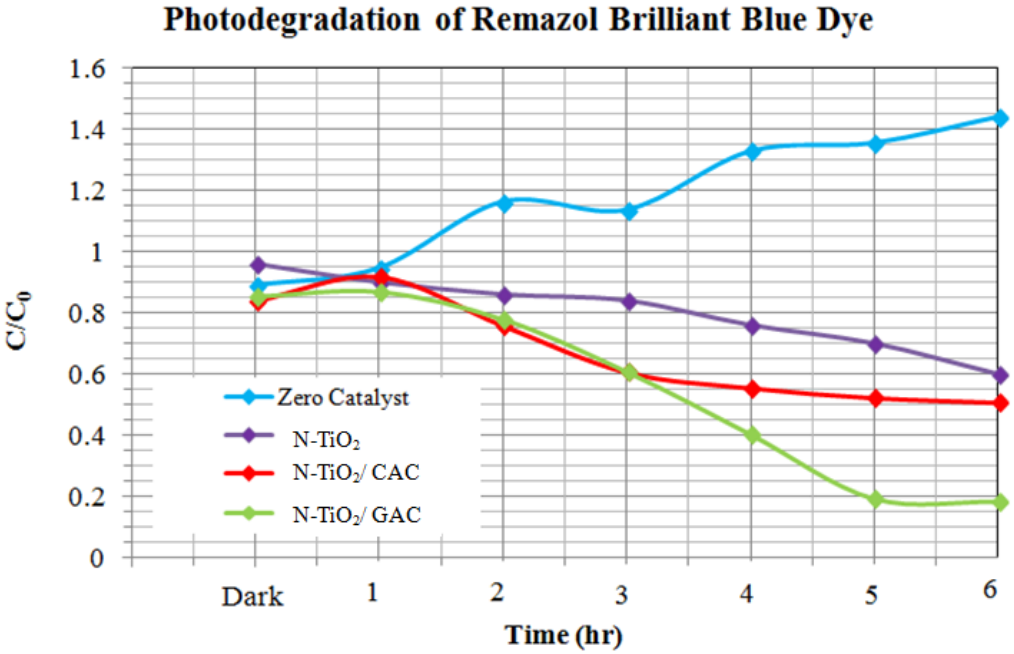

Figure 3. Synergetic adsorption-photocatalytic oxidation of the prepared photocatalysts.

The N-TiO_2/CAC resulted with a maximum removal efficiency of ~ 80%; while N-TiO_2/GAC resulted with ~45% degradation within 6 h of illumination. It is evident that both prepared synergized photocatalysts played an exclusive role in degrading the RBB dye. The carbon derived from the AC played a crucial role for the enhancement of the photocatalytic activity by decreasing the band gap energy and increased the adsorption process compared to N. A low removal efficiency of RBB dye was observed for N-TiO_2/GAC photocatalyst was attributed due to the large condensation of N-TiO_2 on the pores on AC. However for the better removal of RBB dye, the adsorption phenomenon driven by the synergization had its major contribution in comparison to the photocatalysis.

4. Conclusion

The synergetic N-TiO_2/AC composites have been successfully synthesized. The prepared photocatalysts had a better absorbance towards the visible region ensuring the utilization of the solar irradiation. The synergetic effect was also well observed in terms of adsorption and contributed for the better removal of RBB dye. Thus shows the significance of the developed synergized photocatalysts. On the whole the prepared N-TiO_2/AC exhibited its vibrant applicability towards wastewater treatment by incorporating both the sorption and photocatalytic effect.

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