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Modification and characterization of C-doped TiO_2 photocatalysts for photodegradation of reactive red (RR4)

W.I. Nawawi[a,b,*], A.Y. Ani[b], M.A.M. Ishak[b], A. Ramli[b], M.S. Azami[b,c], F. Zaid[b], F. Bakar[b,c], R. Zaharudin[b,c]

[a]*Department of Chemistry, University of York, Heslington, York YO10 5DD, UK, Tel. +60 49882570, Fax +6049882026, email: wi_nawawi@perlis.uitm.edu.my, wi.nawawi@york.ac.uk (W.I. Nawawi),*
[b]*Photocatalysis laboratory, FSG, Universiti Teknologi MARA, 02600 Arau, Perlis, Malaysia, Tel. +60 49882812, email: asnida933@perlis.uitm.edu.my (A.Y. Ani), Tel. +60 49882273, email: azlanishak@perlis.uitm.edu.my (M.A.M. Ishak), Tel. +60 167603950, email: saifulddinazami@gmail.com (M.S. Azami), Tel. +60175100311, email: aniesfarha27@gmail.com (F. Zaid)*
[c]*Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia, Tel. +60 103767209, email: faezah_bakar@ymail.com (F. Bakar), Tel. +60 196954776, email: nurraihanzaharudin@gmail.com (R. Zaharudin)*

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ABSTRACT

Carbon doped TiO_2 (C-doped TiO_2) photocatalyst was prepared by using polyethylene glycol (PEG) as carbon precursor under calcination process using muffle furnace. The modified C-doped was immobilized onto a glass plate by using brush and DSAT method with the optimum C-doped TiO_2 was measured by the highest photoactivity detected from photodegradation of reactive red 4 (RR4) dye. The optimum condition of C-doped TiO_2 denoted as C2 consist of 0.1 g of PEG in 6.5 g TiO_2 was found where the photodegradation rate of C2 was *ca* 0.1545 min^{-1} and it is 2.5 times faster as compared with unmodified TiO_2. The presence of C-C bond represented as carbon element was detected in all C-doped TiO_2 samples analyzed by Fourier Transform Infrared (FTIR) spectra at 933 nm. No bandgap energy of C-doped TiO_2 samples changes was recorded by UV-vis DRS spectroscopy, all C-doped TiO_2 except C1 have shown higher photocatalyic activity as compared with unmodified TiO_2 due to the presence of carbon in which acts as electron scavenger. No significant changes in term of surface morphology between C-doped TiO_2 and unmodified TiO_2 sample observed by SEM images. The C-doped TiO_2 immobilized sample produces a fine surface with a smooth coating, excellent photodegradation of RR4 dye and can be used in wide range solar applications.

Keywords: Carbon doping; Muffle furnace; Polyethylene glycol; Photocatalysis; Reactive red 4 dye

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1. Introduction

Water is the main source of every living life; it is covered 71% in the entire earth while the rest is land. As human population continuously increases, people are putting continuous threat to the earth's that pollute the water resources and harm the ecosystem. An increasing of industrial sectors produce a large amount of toxic chemicals and pollutants that might harm and damage the environment and human health [1,2]. These pollutants normally in suspended solids in water will change the characteristics of clean and green environment.

The pollution in the environments will affect the future's young generation. The water pollution is known as the change of water quality due to its chemical, physical and biological properties [3]. Almost every human activity will change the composition of water and thus result unsuitable for domestic, industrial, agriculture and for the survival of aquatic life. The water pollutant is known as an agent affecting aesthetic due to its organic properties that might alter the purity of water [4].

The increasing of the textile industry in the production of saris, jeans and batik give a serious threat to the ecosystem and the aquatic life. Most of the materials used in dyes come from the non-biodegradable organic material. The non-biodegradable is defined as contaminant materials

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*Corresponding author.

in water that cannot be brake down by its microorganism. Thus, several methods were developed in treating the dyes like biological, physical and chemical methods [2–4].

One of the ways to treat the organic pollutants is by using advanced oxidation process (AOPs) which under a chemical method [5]. Photocatalysis is one of the famously applied processes in advanced oxidation. Titanium dioxide (TiO_2) becoming a great potential material to use in wastewater treatment due to its ability to act as cleaning agent [6]. However, the uses of TiO_2 technology is limited due to its band gap energy that requires of photocatalysis process only active under ultraviolet (UV) spectrum which consisted only 5% from the solar spectrum of the sun [6–8]. Efforts have been made to make this photocatalyst active under visible light solar spectrum by modifying TiO_2 photocatalyst.

The carbon doped TiO_2 become a great potential to overcome the limitation of TiO_2 to enhance photodegradation under visible light irradiation [9–11]. According to Tsumura et al. (2002) the performance of C modified TiO_2 showed high activity in the decomposition of polyvinyl alcohol in water under UV irradiation and it was able to use repeatedly. A recent study proved that adding C precursor into TiO_2 in UV irradiation condition can optimum and accelerates the photocatalytic degradation of dyes [12].

C doped TiO_2 is one of the attract materials studied for the removal of organic compounds such as phenol, duron, 2,4-dichlorophenl, methyl orange and methylene blue dye. Nawawi and Nawi (2013) and Ismail et al. (2015) have reported that C modification can be enhanced the photocatalytic activity of TiO_2 in degradation of various organic pollutants and RR4 dye respectively [13,14]. Nawawi and Nawi (2013) also reported that by adding too much carbon precursor into TiO_2 will reduce the photocatalytic activity under RR4 dye [15].

For instance, C doped TiO_2 prepared by Zhang et al. (2016) shows an active photocatalytic activity under visible light. However, the prepared C doped TiO_2 was done at extremely high temperature with time consuming preparation condition [16]. Hence, this study is to produce C doped TiO_2 with relatively low temperature with fast preparation method.

There is several application techniques used in this process and one of the techniques is using suspension mode [17,18]. However, this method caused treated wastewater becoming slurry and the filtration process is required. Realizing this issue, TiO_2 immobilization technique was implemented onto the support materials such as glass, silica gel and metals to overcome the problems [19,20]. An immobilized TiO_2 technique is implemented to remove the pollutants without filtration process and currently becomes most efficient photodegradation technique in removing dyes from wastewater [21,22]. This method has gained significant interest among the researchers due to its photocatalytic application. Recently, immobilized TiO_2 onto double sided adhesive tape (TiO_2/DSAT) was able to provide a very strong intact between the glass plate and TiO_2 layers and thus better photodegradation activity was observed [20]. A normal immobilization study has used types of binder to increase the adhesiveness of photocatalyst onto the support material such as polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP), polyvinyl chloride (PVC) and polyethylene glycol (PEG). In this study, we have used PEG polymer as a C precursor in order to study the effectiveness of this material science it is rarely reported as the precursor before. The main purpose of this study to produce a visible light active C doped TiO_2 and study of its photoactivity under photocatalytic degradation of RR4 dye using DSAT immobilized technique.

2. Experimental

2.1. Materials

Titanium Dioxide P25-Degussa was provided by Evonic-Aeroxide, polyethyleneglycol (MW:6000) was supplied by Merck Sdn. Bhd., polyvinylalcohol was obtained from R&M Chemicals, reactive red 4 dye (chemical formula: $C_{32}H_{23}ClN_8Na_4O_{14}S_4$, MW: 995.23 g mol^{-1}, λ max: 517 nm) was supplied from Sigma-Aldrich. 55 W fluorescence lamps (Philips model E27 Tornado), commercialize double sided adhesive tape (brand Dr Who),custom made glass cell with dimension 50 mm × 10 mm × 80 mm (L×B×H), glass plate, aquarium pump (model NS750 Guandong Minjiang), 0.45 µm cellulose acetate syringe filter.

2.2. Preparation of C-doped TiO_2

The sample was prepared by adding 6.5 g of titanium dioxide (TiO_2) Degussa P25 powder in 50 mL of ultra-pure water and mixed with various ratio of polyethylene glycol (PEG) (1 mL, 5 mL, 10 mL, 15 mL, 25 mL denoted as C1, C2, C3, C4 and C5, respectively) The sample solution is thoroughly mixed by using magnetic stirrer for 30 min. The formulation was dried in the oven for overnight at 110°C before proceed with calcination process. The calcinations process with 300°C was undergo by replacing a dried sample into special modified glass tubing reactor with quartz wool placed on top of the sample. After the calcinations process, the treated sample was cooled to the room temperature and named as C. The band gap energy of photocatalyst was determined by using Lambda 35 UV-Vis spectrophotometer, from Perkin Elmer equipped with diffuse reflectance attachment at the wavelength of 280–800 nm. Fourier-transform Infrared Spectroscopy (FT-IR) analysis was conducted to investigate the functional groups contained in the photocatalyst recorded in the 4000 to 600 cm^{-1} region. The morphology of C-doped TiO_2 was characterized by using scanning electron microscope (SEM analysis) model JSM-6700F with an accelerating voltage of 5 kV. The electron-hole recombination measurement for unmodified and modified sample was determined by photoluminescence analyzer model Joblin Yvon HR800 UV. Particle size and surface area were measured by using particle Size Analyzer Model PSA1190.

2.3. Photocatalytic activity studies

2.3.1. Immobilization of C-doped TiO_2 photocatalyst

Immobilized C doped TiO_2 was prepared by mixing 6.5 g of C doped TiO_2 with 1 mL of PVA in liquid form as a polymer binder and proceed with the homogenizing procedure by using mechanical stirring process. The formulation was then immobilized by using brush technique on to double sided adhesive tape (DSAT) stacked onto the glass plate support material and dried by using a hot blower for 1 min. The immobilized TiO_2 was transferred into a custom made glass cell with dimension 50 × 10 × 80 mm (L × B × H) containing 25 mL of 30 mg L^{-1} RR4 dye for photodegradation test. This method was continued by using unmodified TiO_2 for comparison study.

2.3.2. Suspension of C-doped TiO_2

In this study, 0.03 g of C modified TiO_2 photocatalyst sample is placed into a glass cell that contained 25 ml of 30 mg L^{-1} RR4. The mixed photocatalyst sample powder and dye was sonicated for 30 seconds to homogenize the suspension. The suspension mode of C doped TiO_2 with RR4 was then transferred into a custom made glass cell with dimension 50 × 10 × 80 mm (L × B × H). The immobilized TiO_2 then irradiated with 55 Watt fluorescence lamp (400–627 nm wavelengths) detected ASD Fieldspec handheld portable spectro-radiometer. The irradiation process was carried out for every 5 min interval until up to 45 min. The treated RR4 dye was collected and the degree of degradation was measured by using spectrophotometer at λ_{max} = 517 nm.

2.3.3. Effect of parameter studies

The effect of parameter studies was conducted in this experiment such as the effect of different model pollutants (photodegradation and mineralization studies), visible light irradiation, grinding and surface coating. For effect of different model pollutant, immobilized C doped TiO_2 was studied by using two different model pollutants which are methyl orange (MO) and RR4 dyes. Both of dye solutions were irradiated under 55 W fluorescence lamps as a source of light while 15 W cold LED is used for photodegradation under visible light irradiation. The comparison of the grinding effect was studied in order to investigate the effect of surface structure of sample toward the photocatalytic activity by using RR4 dye. The effect of surface coating of immobilized C doped TiO_2 was observed between the cracking surface and finely normal surface coating.

3. Results and discussion

3.1. Optimization study C-doped TiO_2

Table 1 shows the percentages of carbon in the prepared samples. The amount percentage of carbon content seems increase with increasing amount of PGE added in the sample with 0.01, 0.25, 1.51, 2.12 and 2.85% for C1, C2, C3, C4 and C5, respectively. Fig. 1 shows the photocatalytic degradation rate of RR4 dye at different amount of carbon. It can be seen that the amount of C loading shows a significant impact in photocatalytic degradation process. All C-doped TiO_2 samples except for C1 show higher photocatalytic degradation rate as compared with unmodified TiO_2. C1 has shown the lowest photocatalytic activity compared with unmodified TiO_2 due to the incomplete process of carbonatization of PEG polymer accumulated on photocatalyst thus reduced the photoctalytic activity of the prepared C1 sample. The optimum loading of C-doped TiO_2 was observed at C2 with 0.1545 min^{-1} where it is 2.5 times faster than unmodified TiO_2 which is *ca.* 0.061 min^{-1}. This observation is due to the carbon presence in C2 acted as electron scavenger thus reduced the electron-hole recombination process. This explanation supported by where they observed that excite electron can be discarded in TiO_2 when carbon combined in C-doped TiO_2 [21–23]. The photocatalytic degradation rate of RR4 is getting decreased beyond the C2 by 0.1247, 0.1149 and 0.118 min^{-1} for C3, C4 and C5 samples respectively. This observation is due to the less penetration of light into the surface of TiO_2 thus decreased the ability of excited electron in modified photocatalysts at high amount of carbon.

3.2. Characterization study of C-doped TiO_2

3.2.1. Fourier transform infrared (FT-IR)

Table 2, shows the spectra presented in unmodified and modified C doped TiO_2 samples. It is observed that all C doped TiO_2 samples containing hydrocarbon group of alkane (C-C and C-H) identified at the range 933–1422 cm^{-1} respectively with strong intensity while no IR peaks spectrum of alkane group is observed in the unmodified TiO_2. The major peak appeared at 3377 and 1688 cm^{-1} in all samples were identified as O-H and H-O-H due to the presence of moisture. The peak at 933 cm^{-1} was observed

Table 1
PEG and carbon compositions, surface area and particle size of bandgap energy unmodified TiO_2 and modified samples

Sample	PEG composition (ml), (g)	Carbon (wt%)	Surface area (mg^2 g^{-1})		Particle size (μm)		Bandgap energy (eV)
			Grind	Without grind	Grind	Without grind	
Unmodified TiO_2	0, 0	0					3.20
C1	1, 0.02	0.01					3.10
C2	5, 0.1	0.25	3.29	0.18	0.78	19.52	3.00
C3	10, 0.2	1.51					2.80
C4	20, 0.3	2.12					2.75
C5	50, 0.5	2.85					2.60

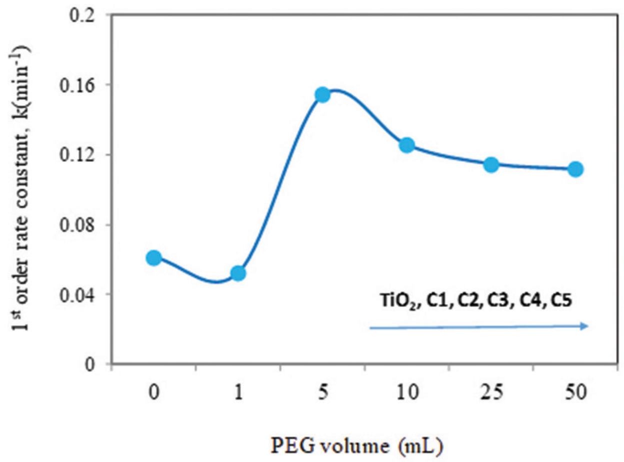

Fig. 1. Plots of degradation rate of 30 mg L^{-1} RR4 under 55 W fluorescent lamp for C-doped TiO_2 samples under suspension at different amount of PEG under 300°C.

Table 2
Major peak of unmodified and modified C-TiO_2 in FTIR Spectra

Hydrocarbon group	IR absorption (cm^{-1})
H-O	3377
H-O-H	1688
C-H	1422
Ti-O-Ti	1290
C-C	933
Ti-O	703

in all C doped TiO_2 sample representing C-C bond and this is clearly showed the presence of carbon in all modified samples. The peak at 1290 cm^{-1} is observed in all sample indicates Ti-O-Ti bond. Apart from that, the peak located in 703 cm^{-1} belongs to oxygen functional group with probably bonded with titania forming Ti-O. No peaks observed in all C doped TiO_2 sample at 703 cm^{-1} as can be seen in Fig. 2 and it looks like no detection peak for TiO_2. However, this observation is due to the overlapping of two peaks (703 and 933 cm^{-1}) thus make the Ti-O peak at all C doped TiO_2 samples not clearly observed.

3.2.2. Scanning electron microscope (SEM)

Figs. 3a and b show the surface morphology for the optimum C-doped TiO_2 sample (C2) and unmodified TiO_2. It can be seen that both samples show the similar sample morphologies which are the spherical shape with hollow pits and spongy structured surface. However, C-doped TiO_2 sample looks more porous surface structure due to the release of volatile matters (from PEG) during the calcinations which resulted increasing the size of the porous structure. This observation in line with several workers who reported the volatile matter from carbon precursor can increase the porosity of the modified sample during calcination [24].

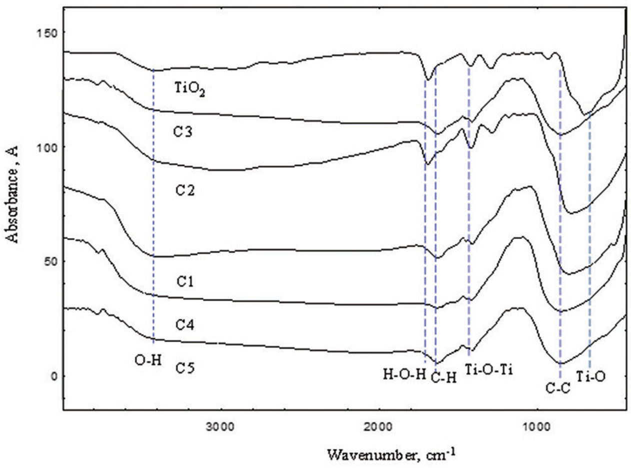

Fig. 2. FT-IR Spectra for unmodified and modified C-TiO_2.

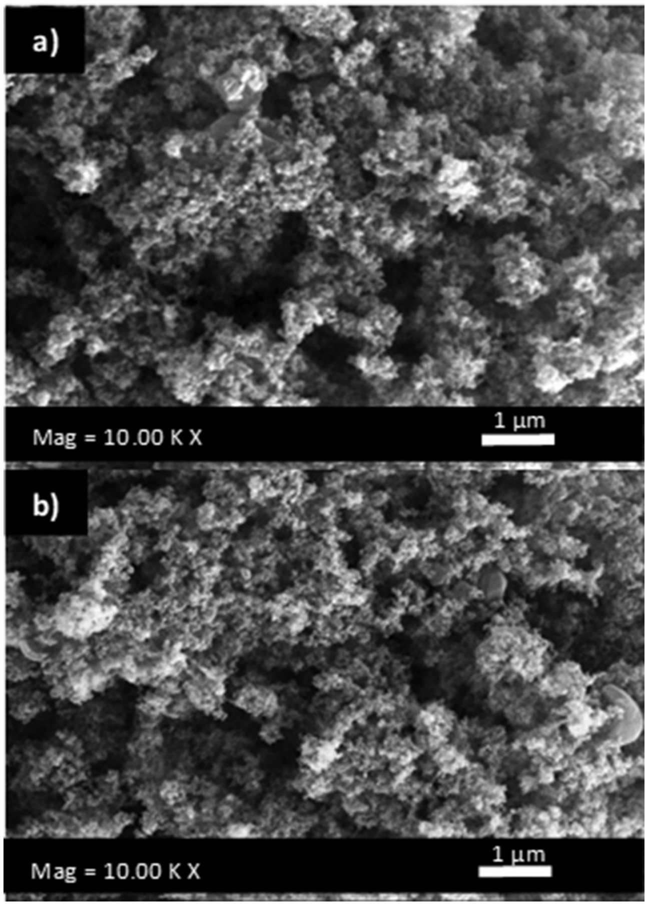

Fig. 3. SEM images of a) C-doped TiO_2 and b) unmodified TiO_2.

3.2.3. UV-Vis diffuse reflactance spectroscopy (UV-Vis DRS)

The UV-Vis Diffuse Reflactance Spectroscopy (UV-Vis DRS) is used to identify the bandgap energy of unmodified and modified TiO_2 samples, also can predict the amount of carbon content in the samples by comparison. Based on Fig. 4, the absorption edge of unmodified TiO_2 is around 380 nm while for C-doped TiO_2 is around 410 nm. It was observed that the carbon content is depending upon the loading of PEG as can be seen in Fig. 1. The higher PEG loading the higher amount of carbon will be in the sample. Bandgap energy can be determined by plank equation as $E = 1240/\lambda$ where λ is determined by the slope extrapolation of the sample spectrum [25].

Table 1 shows the bandgap energy values of unmodified and modified TiO_2 samples base on the calculation of plank equation with λ value of each sample is taken from UV-vis/DRS spectrums. It was clearly observed that high amount of PEG can produce the lowest bandgap energy. It means that C5 has lowest bandgap energy and it should be provide the highest photoactivity. However, it doesn't show that C5 is the highest since k value is 0.118 min^{-1} whereas optimum C2 has higher k value 0.1545 min^{-1} as compared with C5. This is due to the several factors like less penetration of light for high amount of carbon as a shield of light. Another contributing factor is that the value of λ for high carbon content is not exactly true since there is an overlapping of 2 peaks (carbon and TiO_2) thus, the bandgap energy determination of theses treated samples are cannot be considered for this case.

3.2.4. Photoluminescence study

Fig. 5 shows the photoluminescence (PL) spectra for unmodified TiO_2 and C2 samples. Photoluminescence is the result of electron hole recombination emission, the high photoluminescence spectra are results the high of electron hole recombination occurred in the photocatalyst. In Fig. 5, C2 sample shows lower PL intensity compared with unmodified TiO_2 with the maximum peaks intensity were 3200 and 5350, respectively. This means that electron-hole recombination of the excited electron has able to be inhibited by carbon in C2, hence the free and active hole (h^+) is able to react with water forming hydroxyl radical for oxidation.

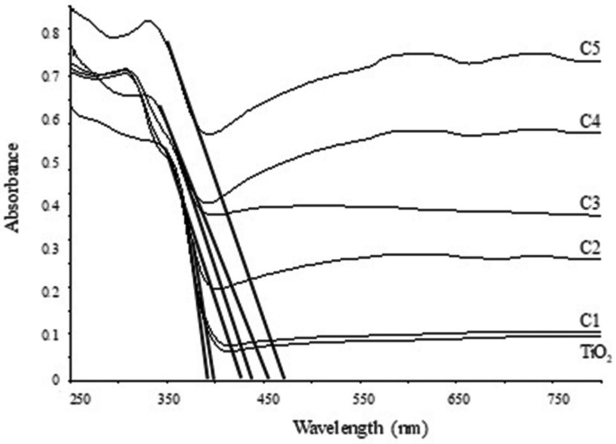

Fig. 4. UV-Vis/DRS spectrum of unmodified and C-doped TiO_2 samples.

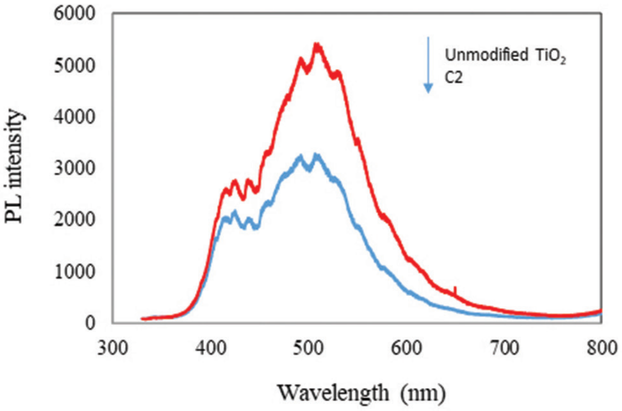

Fig. 5. Photoluminescence spectra of unmodified TiO_2 and C2 samples.

3.3. Photodegradation study of C-doped TiO_2

3.3.1. Photodegradation study of immobilized TiO_2/DSAT by using brush coating method

In this study, titanium dioxide (TiO_2) photocatalyst is immobilized onto glass plate by using brush coating method and stack together by using a technique known as double sided adhesive tape (DSAT) which has been reported before [20,26,27] and it has the ability to enhance the adhesiveness if the immobilized TiO_2 with a less of polymer binder used, It also able to immobilize TiO_2 without polymer and can be reused up to 30 times. The performance of immobilized TiO_2/DSAT was observed under degradation of RR4 dyes with 55 W fluorescence lamp as source of light irradiation. The rate of photodegradation was determined based on pseudo first order rate constant as shown in Eqs. (1)–(3).

$$r = \frac{dc}{dt} = \frac{k'KC}{1 + KC} \tag{1}$$

$$r = k'KC = kC \tag{2}$$

$$ln\frac{Co}{C} = kt \tag{3}$$

where k represents the first order rate constant of the reaction (min^{-1}); C_0 is the initial concentration of the dye (mg L^{-1}), C is the concentration of the dye at time t (mg L^{-1}); and t is the irradiation time (min). By plotting ln (C_o/C) vs. t of equation 3 yields a straight line whose slope is k. The rate constant, k was determined for each photocatalyst sample and used as a measure of the photoactivity of the sample. Fig. 6 shows the rate constant values for unmodified TiO_2 and C2 sample. It shows that C2 was slightly higher than unmodified TiO_2 with $K = 0.091$ and 0.0865 min^{-1} respectively.

3.3.2. Effect of different model pollutants and mineralization study

The effect of different model pollutants is studied on methyl orange (MO) and RR4 dyes. Figs. 7a and b show the photodegradation and rate percent remaining of MO

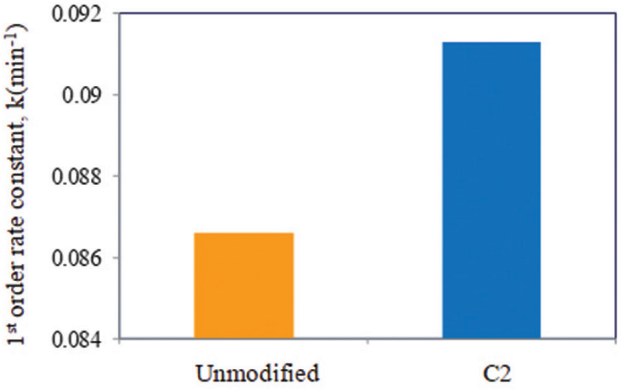

Fig. 6. Photocatalytic degradation rate of RR4 under immobilized TiO_2/DSAT between unmodified TiO_2 and C2 samples.

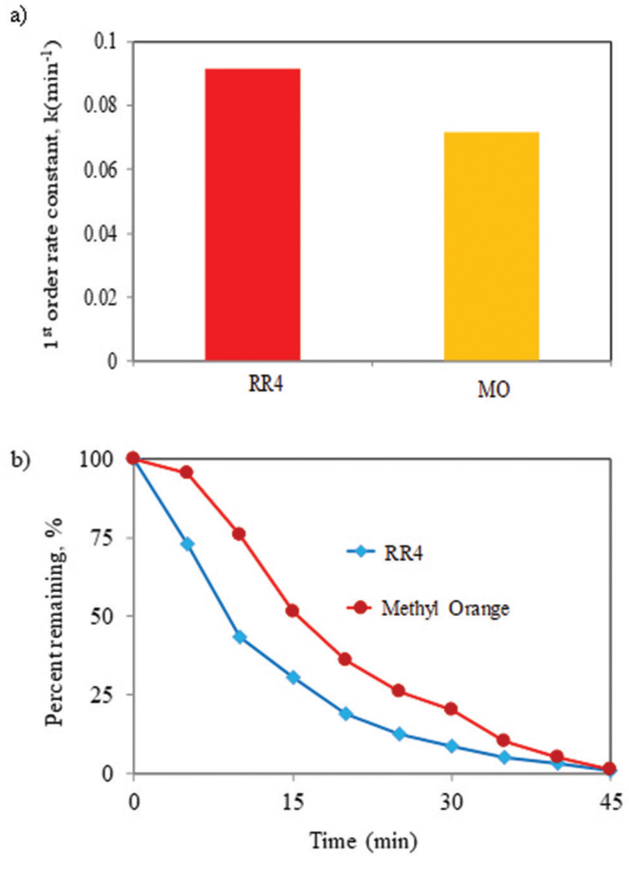

Fig. 7. Photocatalytic degradation of MO and RR4 dyes under immobilized C2 sample calculated based on a) pseudo first order rate constant and b) percent remaining.

and RR4 dyes by using immobilized C2 respectively. It can be seen that the pattern of photodegradation for MO is quite similar with RR4 but RR4 dye shows a slightly better photocatalytic activity compared to MO where the degradation rate was *ca.* 0.091 and 0.072 min^{-1} under immobilized C2. This might be due to the several factors such as the absorbance of peak maximum for MO dye is near to UV light region (465 nm) thus it could make some difficulty of photocatalysts to degrade MO dye and this is proved by a very high publication of photocatalysts papers for MO as model pollutant [28]. Another factor that might be influent for difficulties of MO to degrade is due to the consequences of semiconductor photosensitizers is the direct oxidation of sensitizer molecule. This self-sensitized oxidation has an advantage for the degradation of colored pollutant [29]. The heterogeneous photocatalytic process usually involves partial or complete mineralization of the organic substances into CO_2 and H_2O by the oxidizing species that exist on the surface of titanium oxide [30], mineralization was applied to determine how long the irradiation time is taken in completing the degradation of MO and RR4 dyes. Fig. 8 shows the mineralization of MO and RR4 dyes by using C2 sample as photocatalyst. AS can be seen, it took more than 8 h to perform a complete mineralization for both dyes. This is about 11 and 15 times slower as compared with decolorization of RR4 and MO dye respectively. This is due to the oxidation process of both organic dye may turn into intermediates prior to complete oxidation (CO_2 and H_2O). Fig. 9 shows the percentage remaining of RR4 and MO dyes using C2 sample under visible light irradiation. The process was kept in the dark condition for 30 min prior visible light irradiation for adsorption equilibrium [31,32]. I was found that there is no photodegradation was occur for both dyes, meaning that C2 sample has not active under visible light condition. This observation supported UV-Vis spectra that discussed earlier where there no bandgap energy decreasing on C2 sample.

3.3.3. Effect of grinding

The effect of grinding is studied based on photocatalytic activity of before and after grinding. The purpose is only to show how the effect of surface structure and pores of sample influence the result. Interestingly, the size of structure does give an effect toward photocatalytic activity. Based on Fig. 10, it is proven that after grinding the sample, the photodegradation activity was 5 min faster before grinding. This observation is due to the high surface area

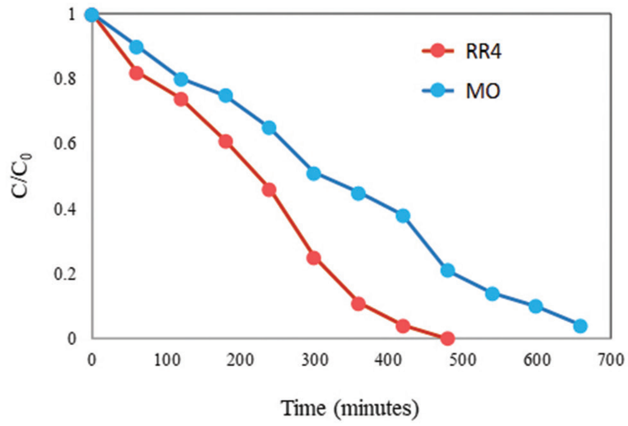

Fig. 8. Mineralization study (COD values) for RR4 and MO dyes using C1 sample as photocatalyst.

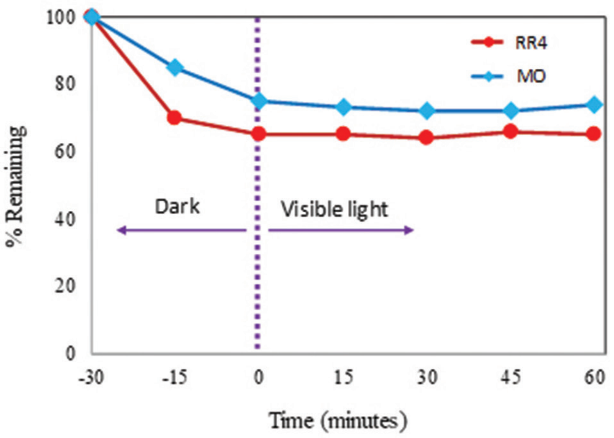

Fig. 9. Photocatalytic degradation of RR4 and MO dyes of C1 sample under visible light irradiation.

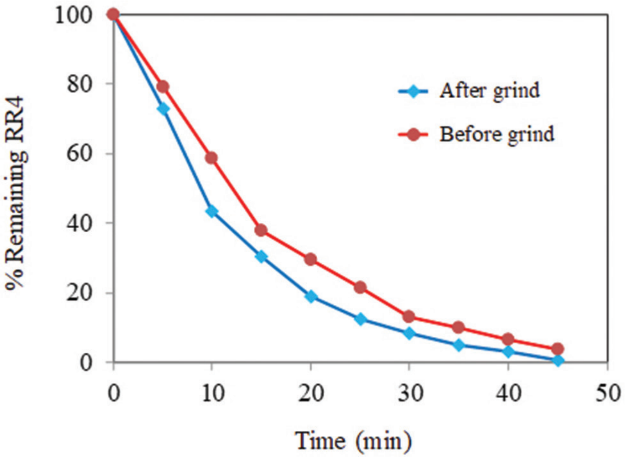

Fig. 10. Percent remaining of MO after and before grinding.

for the ground sample since it is reduced the particle size. Table 1 shows the particle size for grinding and without grinding samples as well as surface area where the surface is influenced by particle size. Particle size for C2 sample under grinding condition was 0.78 µm with 3.29 $m^2 g^{-1}$ of surface area and it showed smaller particle size than sample without grinding where it was 19.5 µm and 0.18 $m^2 g^{-1}$. It seems that the bigger particle size, the smaller surface it would be and the more surface is exposed to the light, it means that more hydroxyl radical will be produced and more surface contact of this hydroxyl radical with RR4 dye for degradation.

3.3.4. *Effect of surface coating*

Fig. 11 shows the images of immobilized unmodified TiO_2 and immobilized C2 samples. It is observed that immobilized unmodified TiO_2 has uneven surface coating with crack formation while immobilized C2 has much better of surface coating. This observation is due to the presence of carbon that plays an important role in surface coating process where it is in line with Azami et al. [33] where they found that immobilized with commercially available C doped TiO_2 known as Kronos has a good surface coating as compared with immobilized P25.

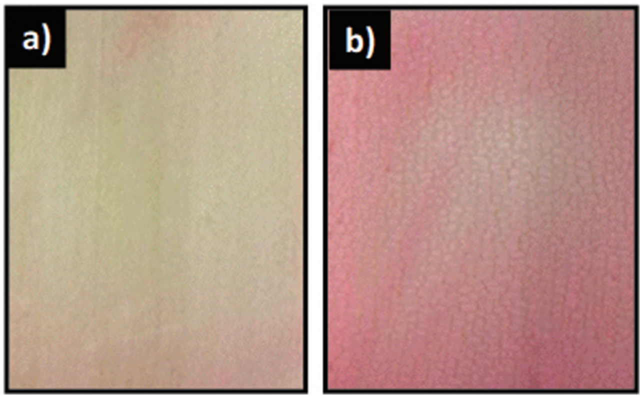

Fig. 11. The image of a) immobilized coating using C2 and b) unmodified TiO_2.

4. Conclusion

The modified C doped TiO_2 was successfully modified by using PEG as carbon precursor. The optimum of C doped TiO_2 was found at 0.1 g (5 ml) of PEG in 6.5 g TiO_2 named as C2 where it is 2.5 times faster as compared with unmodified TiO_2 under photodegradation of RR4 dye. It was found that presence C-C bonding was found in all C doped TiO_2 samples where it refers to C doping on TiO_2. No significant changes in term of surface morphology between C2 and unmodified TiO_2 where both samples have the spherical shape with hollow pits and spongy structured surface observed in SEM analysis. UV-vis/DRS shows the absorption increment at visible light region corresponding to the increments of carbon in C doped TiO_2 samples and the value of λ for high carbon content (beyond C2) is not exactly true since there is an overlapping of 2 peaks (carbon and TiO_2) thus it cannot be used for determination of bandgap energy. In immobilization study, C2 sample shows slightly higher photocatalytic activity as compared with immobilized unmodified TiO_2. RR4 dye was found to be faster to degrade as compared with MO dye, grinding and smooth surface coating effects have proven can increase the photocatalytic activity.

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Author contributions

The experimental work and drafting of the manuscript were carried out by F. and assisted by W.I. and M.S., A.Y., A., R., and F. participated in the interpretation of the scientific results, characterizations, manuscript revision and the preparation of the manuscript. W.I., M.A.M, supported the work and cooperation between UiTM Perlis and UiTM Shah Alam, supervised the experimental work, commented and approved the manuscript. The manuscript was written through comments and contributions of all authors. All authors have given approval to the final version of the manuscript.

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