Alternative natural dyes in water purification: Anthocyanin as TiO$_2$-sensitizer in methyl orange photo-degradation

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**Abstract**

Natural molecular dye, anthocyanin, is described here as safe sensitizer for TiO$_2$ particles in photo-degradation of organic contaminants in water. The dye is a promising replacement for the more costly and hazardous heavy metal based systems, such as CdS particles and Ru-compounds. TiO$_2$/anthocyanin effectively catalyzed the photo-degradation of methyl orange contaminant under solar simulator radiation. The new TiO$_2$/anthocyanin catalyst showed comparable efficiency to earlier systems, while avoiding their hazardous nature. When supported onto activated carbon (AC) particles, the resulting AC/TiO$_2$/anthocyanin system showed enhanced efficiency and ease of recovery from the catalytic reaction mixture. The natural dye molecules showed the tendency to degrade under photo-degradation conditions, just like earlier hazardous sensitizers. However, complete mineralization of anthocyanin occurred leaving no traces of organic species in solution. Sensitizer degradation caused deactivation of the supported catalyst on recovery. Such a shortcoming was overcome by re-treatment of the recovered catalysts with fresh dye.

Effects of different reaction parameters on the catalyst efficiency were studied. A mechanism, similar to earlier CdS-sensitized catalyst systems, is proposed for the TiO$_2$/anthocyanin catalyst.

1. Introduction

In our search for safe processes to purify contaminated waters, complete mineralization of organic contaminants has been approached [1–4]. This strategy could be achieved by a number of techniques, the most economic of which is solar-based degradation. The simplest technique is to mix powders of suitable catalysts in the contaminated water and expose the system to direct solar light. Different catalyst systems were suggested. Due to its chemical stability, robustness, non-toxic nature and low cost, the TiO$_2$ is the best photo-degradation catalyst system. However, its wide band gap ($\sim 3.1$ eV) limits its use to UV radiations only. Therefore, only small portions of direct solar light can be used in case of pristine TiO$_2$ catalysts. In order to function under solar radiations, TiO$_2$ can be sensitized with attached dye molecules or particles. Different types of dyes are reported as sensitizers for TiO$_2$ system, such as ruthenium complex molecules, CdS particles and others [5–8].

Such sensitizers were effectively used in Graetzel type solar cells and in water purification.

Natural dyes extracted from plants were widely reported as sensitizers for TiO$_2$ particles in Graetzel type solar cells. Examples of such dyes are chlorophyll derivatives, natural porphyrines and anthocyanins which are molecular in nature [9–13]. Unlike the case with solar cells, natural dyes have limited use as sensitizers in water purification studies [14].

In a recent study [1] we critically assessed using heavy metal based sensitizers such as CdS particles, and demonstrated that such hazardous systems should be avoided in water purification strategies. We also highlighted the need to either stabilize such dyes or replace them with safer sensitizers. A well-known natural dye, anthocyanin (also spelled as anthocyannin), will be investigated here as a safe alternative sensitizer in photo-degradation of organic water contaminant catalyzed by TiO$_2$ particles. Methyl orange (MO), I, is an irritant hazardous contaminant, as observed from its MSDS, and was chosen here as a model contaminant. Anthocyanin dye is responsible for several colors in the red–blue range depending on pH value. The red anthocyanin absorbs at 530 nm (band gap 2.3 eV). This pigment occurs in fruits, flowers and plant...
leaves. The structural formula for anthocyanin, II, is shown below. The pigment was extracted from flowers of a plant called Karkade (Hibiscus). Karkade is commonly abundant at market-places, and is used as a safe low cost beverage in different Middle East regions. As sensitizers themselves may degrade under photo-degradation experiments yielding hazardous species, CdS is one example, the tendency of anthocyanin to degrade will also be investigated here.

Sensitization with natural molecular dyes follows similar ratio-
nale to sensitization by CdS semiconducting particles [15,16]. The valence band – conduction band formalism used in CdS particles is paralleled with HOMO/LUMO formalism in molecular dye sensitiza-
tion. When a dye molecule is excited by a visible light photon, one electron jumps from HOMO to LUMO, leaving a positive charge (hole) in the HOMO. The resulting hole is responsible for contami-
nant molecule oxidation. On the other hand, the excited electron travels from the dye molecule LUMO to the TiO2 particle conduction band, and consequently reduces other species, such as O2 molecules.

It is believed that the electron transfer from anthocyanin to TiO2 particles occurs through chemical bonds that bridge them together, as shown in III below. Such bonds occur by virtue of surface hydroxyl groups on TiO2 particles and on dye molecules [10,11,15–20].

2. Materials and methods

2.1. General

All common solvents and reagents used were of analytical grade and were purchased from Aldrich, Riedel or Merck. Activated carbon, with measured surface area 850 m2/g, was purchased from Aldrich. Anatase TiO2 powder, with particle size less than 5 µm, was purchased from Aldrich. The XRD spectrum for TiO2 was measured in the powder form on a Philips X'Pert PRO diffractometer with Cu Kα (λ = 1.5418 Å) as a source, at ICMCB, University of Bordeaux. The XRD lines were identified by comparing the measured diffraction patterns to JCPDS data cards. Fig. 1 indicates that the TiO2 was in the anatase form.

2.1.1. Extraction of anthocyanin pigment

Dry dark red Karkade flowers were crushed in a juice mixer. The resulting finely ground powder (10.00 g) was soaked in a 250 ml Erlenmeyer flask with 100.00 ml ethanol. The mixture was magnetically stirred gently at 60 °C for 20 min. The mixture was then cooled, for 20 min, and filtered. Electronic absorption spectra were measured for the resulting pigment solution, on a Shimadzu UV-1601 spectrophotometer. The solution was stored in the dark and refrigerated for further applications.

2.1.2. Preparation of TiO2/anthocyanin catalyst

Anatase TiO2 powder (10.00 g) was refluxed for half an hour with 30 ml of anthocyanin ethanolic extract and 30 ml deionized distilled water (5 × 10−4 M anthocyanin). The mixture was then left to cool to room temperature. It was then chilled in ice for 15 min. The resulting TiO2/anthocyanin solid was suction-filtered through sintered glass, collected and washed with cold water. The solid was left to dry under air in dark and stored in the dark for further use. Adsorption of anthocyanin on the surface of TiO2 occurred readily, as reported earlier in Refs. [21,22].

2.1.3. Preparation of AC/TiO2/anthocyanin catalyst

The preparation was a two-step process, starting with AC/TiO2 preparation, followed by attaching anthocyanin. TiO2 (20.00 g) and AC (4.00 g) were thoroughly stirred magnetically in water (40 ml) for an hour. The mixture was then suction-filtered. The composite AC/TiO2 solid, 2:10 by mass, were dried at 130 °C for 2 h. Attachment of anthocyanin was then conducted as follows: The AC/TiO2 composite (10.00 g) was magnetically stirred in 100.00 ml of ethanolic anthocyanin solution (5 × 10−4 M) for 1 h, before suction-filteration through sintered glass. The solid was left to dry under air in dark two days and was kept in the dark for further use.

Fig. 1. XRD pattern measured for commercial TiO2 particles in the anatase form.
2.2. Materials characterization

The electronic absorption spectrum for the extracted anthocyanin in ethanol is shown in Fig. 2a. The spectrum shows the typical absorption band ($\lambda_{\text{max}}$ 540 nm) as reported earlier in Refs. [23–25].

Electron absorption spectra, measured for the reddish TiO$_2$/anthocyanin particles suspended in toluene, are shown in Fig. 2b. The band at $\lambda_{\text{max}}$ 550 nm is attributed to the supported anthocyanin. Fig. 2a–b shows a 10 nm red shift in the spectrum of the supported anthocyanin molecules, compared to solution molecules. The shift indicates a chemical reaction between the dye molecules and the TiO$_2$ surface, as described above.

TGA data for the AC/TiO$_2$/anthocyanin (measured on a TA 2950HR V5-3 TGA apparatus, at ICMCB, University of Bordeaux) showed ~80% weight remaining after 500 °C, which is attributed to TiO$_2$ (Fig. 3). The percent is parallel to catalyst nominal composition, which contained 83% TiO$_2$.

TGA study of TiO$_2$/anthocyanin was inconclusive. This is due to the fact that anthocyanin, attached at the surface, exists in only small percentage. Loss of anthocyanin did not appear in the TGA study.

2.3. Photo-catalytic experiments

Catalytic experiments were conducted in a magnetically stirred 100 mL glass beaker equipped with a thermostated jacket. The outside walls were covered with aluminum foil to reflect back stray radiations. Known amounts of catalyst systems were loaded into the reactor. Aqueous solution (50.00 mL) of known contaminant (MO) nominal concentration was then placed, in the dark. The pH was controlled by adding a few drops of NaOH or HCl dilute solutions. Direct visible irradiation using, a solar simulator halogen spot lamp was then directly placed above the photo-catalytic solution, which was left open to air. The spot lamp spectrum resembles solar light spectrum [26]. Light intensity at the top of the solution surface was directly measured with a Lutron LX-102 light meter and a 407 A Spectrophysics wattmeter. The measured light intensity was 0.0212 W/cm$^2$.

The reaction progress was followed with time, starting immediately after exposure to radiation. Aliquots of reaction mixture were syringed out and immediately centrifuged (5000 rounds/min for 5 min) in the dark. The liquid supernatant was then spectroscopically (480 nm) analyzed using pre-constructed calibration curves.

Different control experiments were conducted for different purposes. Experiments with no catalysts, conducted at constant pH, showed no contaminant concentration loss, after 90 min exposure to radiation.

To check if contaminant loss occurred by adsorption onto solid systems, control experiments were conducted by adding known amounts of catalyst, to the reaction mixture, in the dark. No significant contaminant adsorption occurred on the TiO$_2$ or TiO$_2$/anthocyanin systems. The AC/TiO$_2$/anthocyanin showed significant contaminant adsorption in the dark. Such adsorption was accounted for in photo-catalytic experiments, by using higher contaminant concentrations, as described later.

To check for dye sensitizing effect in the visible region, control experiments were conducted using catalysts under solar simulator radiations with a cut-off filter. The filter was placed between the light source and the reaction mixture to block wavelengths of 400 nm or shorter.

The reaction rate was measured based on analyzing remaining contaminant concentration with time. Values of turnover number (contaminant reaction moles per nominal TiO$_2$ mole after 60 min) and quantum yield (contaminant reacted molecules per incident photon) were also calculated and used for efficiency comparison.

Complete mineralization of the degraded methyl orange was confirmed by decrease in absorbance band between 200 and 400 nm. Such a band is typical for the aromatic ring derivative. The spectral analysis showed no traces of any new organic species, such as alcohols, carboxylic acids, ketones, aldehydes, appearing in the reaction mixtures. Moreover, the azo group of methyl orange, with absorption band at 480 nm decreased with time. The results indicate complete mineralization of the degraded methyl orange.
Evidence in favor of complete mineralization of degraded methyl orange was obtained by polarographic analysis of its catalytic reaction mixture (AC/TiO2/anthocyanin) at different reaction times. Anodic stripping differential pulse polarography (ADDP) was conducted for this purpose, using an MDE150 dropping mercury electrode on a PC-controlled POL150 Polarograph. The hanging mercury drop electrode (HMDE) method was followed. As reaction progressed, both S2O2−3 and SO42− continued to appear, as evidenced from their growing signals at −0.15 and −1.2 V (vs. Ag/AgCl) respectively, Fig. 4. Methyl orange is the only source for the ions S2O2−3 and SO42−. The analysis showed no traces of any new organic compounds, in the reaction mixture. Combined together, the results provide solid evidence in favor of mineralization of degraded methyl orange.

The continued appearance of the nitrate ions with time, as evidenced by polarographic analysis, Fig. 5, is another indication of mineralization. The azo group in the methyl orange is normally converted into nitrogen gas or into nitrate ions under other similar photo-degradation experiments [1,27].

3. Results and discussions

The systems TiO2/anthocyanins, AC/TiO2/anthocyanins, and naked TiO2 were attempted as catalysts for Methyl Orange photo-degradation, under solar simulator radiations. The focal object was to study feasibility of anthocyanin as a safe sensitizer for TiO2 and AC/TiO2 systems, compared to other earlier hazardous CdS systems. The catalyst efficiency was studied in terms of initial reaction rates, turnover number and quantum yield values, and the results were compared to earlier systems.

3.1. Control experiment results

Control experiments indicated no contaminant degradation reaction in the absence of catalyst systems. TiO2 did not exhibit significant methyl orange adsorption, as observed from dark experiments. The AC/TiO2/anthocyanin showed relatively high adsorption of methyl orange in the dark. Experiments conducted using different methyl orange concentrations showed an equilibrium adsorption uptake of 0.25 mg/0.12 g solid, after 60 min stirring. These results were considered while designing photo-degradation experiments using the AC/TiO2/anthocyanin catalysts, viz. higher contaminant concentrations were used to account for contaminant adsorption.

3.2. Effect of pH

Aqueous solutions, pre-contaminated with methyl orange, at different pH values, were prepared. The degradation reaction was conducted under direct solar simulator radiation (0.0212 W/cm²) at room temperature using three different pH values, 4.5, 7.0 and 11. Fig. 6 shows the profiles of TiO2/anthocyanin catalyzed methyl orange degradation reactions at different pH values. The catalyst efficiency was higher in acidic media. The behavior paralleled earlier results observed for contaminant photo-degradation with...
measurements were conducted under direct solar simulator radiation (0.0212 W/cm²).

(b) pH cyanin (0.12 g) stirred inside reaction mixture (50 ml, 5 ppm MO): (a) Neutral, (b) pH = 4.5, (c) pH = 11. Values of T.N. (and Q.Y.) respectively are: (a) 159 × 10⁻⁶ (53 × 10⁻⁶), (b) 268 × 10⁻⁶ (89 × 10⁻⁶) and (c) 160 × 10⁻⁶ (53 × 10⁻⁶). All measurements were conducted under direct solar simulator radiation (0.0212 W/cm²).

TiO₂/CdS systems [1,17,28–30]. Turnover numbers and quantum yield values are comparable in neutral and basic media, but are higher in acidic media. The relatively low efficiency of TiO₂/anthocyanin system, in methyl orange photo-degradation with solar simulator radiation, resembled that of the earlier TiO₂/CdS system [1]. The two systems, however, showed different responses to pH variation. While the TiO₂/anthocyanin showed increased efficiency at lower pH values, the TiO₂/CdS showed lowered value under acidic conditions. The TiO₂/CdS efficiency lowering under acidic conditions was attributed to its higher degradability at low pH. One reason for the increased efficiency of the TiO₂/anthocyanin, at lower pH, is due to its color. Under more acidic conditions, anthocyanin becomes reddish and absorbs in the blue color. This means a higher band gap for the dye. Therefore, the oxidizing power of anthocyanin will be thermodynamically increased at lower pH. Moreover, the stability of anthocyanin is known to increase at lower pH values [24].

It is also known that anthocyanin exhibits higher absorptivity at lower pH values [24,25]. This means that the sensitizer absorbs more radiation at lower pH values, and consequently has higher sensitizing activity.

3.3. Effect of contaminant concentration

Effect of initial methyl orange concentration on its photo-degradation rate, with TiO₂/anthocyanin system, was studied. The results are shown in Fig. 7. Values of quantum yield and turnover number were not significantly affected by contaminant initial concentration. Based on initial rate calculations, the order of the reaction was only 0.37 with respect to contaminant concentration. The TiO₂/anthocyanin resembled earlier CdS-sensitized systems [1,31]. Literature showed that photo-degradation is independent of the contaminant concentration, and in some cases, the rate is lowered with increased initial concentration [31]. Different explanations were proposed, all of which rely on the adsorption of contaminant molecules on the solid surface in a Langmuir-Hinshelwood model. One explanation assumed that at higher contaminant concentration, the contaminant molecules may compete with the adsorbed intermediates and inhibit degradation [1,17,31].

It is argued that the concentration of produced hydroxyl radicals, not the contaminant concentration, determines the rate. Moreover, higher contaminant concentrations may shield the catalytic active sites from the visible light [4,18–22,32,33].

3.4. Effect of catalyst concentration

Fig. 8 shows how methyl orange photo-degradation is affected by TiO₂/anthocyanin amount. The order of the initial reaction rate was 0.35 with respect to total catalyst. Values of quantum yield for (0.05 g, 0.10 g and 0.2 g of catalyst) were 32 × 10⁻⁶, 53 × 10⁻⁶ and 49 × 10⁻⁶ respectively. The turnover number values (196 × 10⁻⁶, 159 × 10⁻⁶ and 74 × 10⁻⁶ respectively) decreased with increasing the catalyst amount. These results resemble earlier reports where light screening occurred by increased catalyst concentrations [1,4,31].

3.5. Effect of activated carbon support

The TiO₂/anthocyanin system showed a promising non-hazardous catalyst in methyl orange photo-degradation processes, as compared to other hazardous systems such as TiO₂/CdS. However, the TiO₂/anthocyanin must satisfy two other features in order to be considered for future water purification studies, namely: high catalytic efficiency and ease of recovery after reaction cessation. The TiO₂/anthocyanin catalyst efficiency was not high enough, showing up to 40% degradation of contaminant under ambient conditions, Figs. 5–8. Moreover, the small particles of the catalyst system made it difficult to recover by simple filtration. For these reasons, more work was needed to overcome such shortcomings. The AC/TiO₂/anthocyanin system was thus used.

![Fig. 6. Effect of pH on methyl orange photo-degradation rate using 0.1 g TiO₂/anthocyanin (0.12 g) stirred inside reaction mixture (50 ml, 5 ppm MO): (a) Neutral, (b) pH = 4.5, (c) pH = 11. Values of T.N. (and Q.Y.) respectively are: (a) 159 × 10⁻⁶ (53 × 10⁻⁶), (b) 268 × 10⁻⁶ (89 × 10⁻⁶) and (c) 160 × 10⁻⁶ (53 × 10⁻⁶). All measurements were conducted under direct solar simulator radiation (0.0212 W/cm²).](image1)

![Fig. 7. Effect of methyl orange initial concentration on its photo-degradation reaction rate. (a) 5 ppm (b) 7.5 ppm (c) 10 ppm.](image2)

![Fig. 8. Effect of TiO₂/anthocyanin amount on photo-degradation of methyl orange (50 ml solution of 5.0 ppm Methyl Orange). Nominal catalyst amounts (a) 0.05 g (b) 0.1 g (c) 0.2 g. Calculated n = 0.35. Calculated values of Q.Y and (T.N) (a) 32 × 10⁻⁶ (196 × 10⁻⁶) (b) 53 × 10⁻⁶ (159 × 10⁻⁶) (d) 49 × 10⁻⁶ (74 × 10⁻⁶).](image3)
Under acidic conditions, the AC/TiO2/anthocyanin showed higher methyl orange photo-degradation was faster at lower pH, Fig. 9. Moreover, the supported system was easy to recover at pH lower than 5, complete degradation of methyl orange occurred within 40 min. Furthermore, the supported system was easy to recover by simple filtration.

As in TiO2/anthocyanin system, the AC/TiO2/anthocyanin system caused complete mineralization of the reacted methyl orange. Fig. 10 shows the continued disappearance of absorption bands of both phenyl and azo groups as the photo-degradation reaction progressed with time. Complete mineralization occurred in less than 40 min, as appears from Fig. 10. Polarographic analysis of the resulting reaction mixture showed partial increase in concentrations of nitrate, sulfate and sulfite ions. Total resulting ions could not be measured due to their tendency to adsorb onto activated carbon surface. Although control experiments showed possible adsorption of methyl orange onto AC (with 0.25 mg/0.12 g AC) the disappearance of methyl orange beyond that amount is due to mineralization. Complete mineralization of organic contaminants observed here is consistent with earlier reports in Refs. [1–4,34].

The higher efficiency of AC/TiO2/anthocyanin, compared to TiO2/anthocyanin, at lower pH, is due to adsorption of contaminant molecules onto AC surface. In acidic media the methyl orange molecules undergo protonation [4,11,17]. The protonated molecules adsorb better on AC, and become in close proximity to the TiO2/anthocyanin catalytic sites. The ability of solid supports, such as AC, to enhance efficiency of catalysts in photo-degradation systems has been documented in earlier literature [17,31,35]. The results highlight future feasibility of AC/TiO2/anthocyanin in more future photo-degradation study.

Like other sensitizers, anthocyanin itself is not immune to photo-degradation. However, it does not yield hazardous species on degradation. Fig. 10 shows that if anthocyanin dye happens to degrade, concurrently with methyl orange degradation, it may undergo complete mineralization. Thus no hazardous organic products resulted from anthocyanin possible photo-degradation itself. The lack of any resulting organic compounds in the reaction mixture, as evidenced from spectral and polarographic analyses after reaction completion, is an indication for this result.

Anthocyanin tendency to degrade is evident, as the recovered AC/TiO2/anthocyanin system showed less intense color than the fresh ones. The band at 550 nm, observed in Fig. 2b for fresh systems, was difficult to observe for recovered catalyst system. The recovered system also showed lowered (only ~15%) photo-catalytic efficiency compared to fresh samples. However, when the recovered catalyst was regenerated by treatment with fresh anthocyanin solution, as described in section 2.1 above, the system regained 80% of its efficiency. Fig. 11 explains this observation.

Preliminary study on the AC/TiO2/anthocyanin showed that methyl orange photo-degradation was faster at lower pH, Fig. 9. Under acidic conditions, the AC/TiO2/anthocyanin showed higher efficiency, as exhibited by values of calculated turnover number and quantum yield, compared to the TiO2/anthocyanin system. At pH lower than 5, complete degradation of methyl orange occurred within 40 min. Moreover, the supported system was easy to recover by simple filtration.

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**Fig. 9.** Effect of medium acidity on photo-degradation rate of methyl orange (50 ml 15 ppm) using 0.12 g AC/TiO2/anthocyanin. The pH values were: (a) 7, (b) 3, (c) 4.5, (d) 9.2 and (e) 11. Values of turnover number (and quantum yields) were: (a) 306 × 10−6 (101 × 10−6); (b) 1589 × 10−6 (527 × 10−6); (c) 1688 × 10−6 (560 × 10−6); (d) 196 × 10−6 (65 × 10−6); (e) 12 × 10−6 (4 × 10−6).

**Fig. 10.** Electronic absorption spectra showing continued mineralization of methyl orange under photo-degradation conditions using AC/TiO2/anthocyanin under acidic conditions. Both the phenyl group (in the range 200–400 nm) and azo group (480 nm) continued to disappear with time. Measurements were taken (a) after 0 min, (b) after 10 min, (c) after 20 min, and (d) after 30 min.

**Fig. 11.** Photo-degradation profiles of methyl orange with time, under solar simulator radiation, (a) using fresh AC/TiO2/anthocyanin catalyst, and (b) using regenerated AC/TiO2/anthocyanin after re-treatment with anthocyanin. Reactions were conducted at room temperature using 50 mL of methyl orange (20 ppm), pH 4.5, and 0.12 g gross catalyst amount.
tendency of anthocyanin to degrade is thus compensated for by its low cost, and its ability to regenerate the recovered supported catalyst. Anthocyanin is thus a good alternative to other hazardous heavy metal based sensitizers in TiO$_2$ catalysis.

### 3.6. Proposed mechanism

The mode of action of anthocyanin in sensitizing TiO$_2$ essentially resembles earlier models commonly used in Graetzel solar cells [9–11,18]. Scheme 1 summarizes these processes. The Scheme also explains how anthocyanin sensitizes TiO$_2$ in photo-degradation of methyl orange. Earlier mechanisms used for organic contaminant photo-degradation with dye-sensitized TiO$_2$ are thus applicable here. This is because the kinetics resembled earlier literature [1–4,14,31]. Therefore, a mechanism was proposed for the TiO$_2$/anthocyanin catalyst system based on earlier ones.

As the anthocyanin molecules absorb the visible light, electrons are excited from HOMO to LUMO, electron-hole formation occurs. The excited electrons are then injected into the TiO$_2$ conduction band and travel to the opposite end of the particle where they reduce O$_2$ to superoxide O$_2^-$ ions. On the other end, the holes oxidize contaminant molecules, either directly or indirectly [17–19]. The holes may also oxidize OH$^-$ or H$_2$O to form OH radicals [2,31]. The resulting radicals assist oxidation of contaminant molecules. Scheme 2 shows how TiO$_2$/anthocyanin catalyzes photo-degradation of methyl orange based on earlier Chatterjee’s mechanism [14].

### 4. Conclusion

Complete mineralization reactions of methyl orange, can be effectively photo-catalyzed by anthocyanin-sensitized TiO$_2$ (anatase) particles under solar simulator radiations. Unlike other earlier synthetic dyes (such as Cds and Ru-compounds), the low cost natural dye, anthocyanin, is non-hazardous, as it yields no toxic organic products on degradation. The TiO$_2$/anthocyanin catalyst system showed similar efficiency and kinetics to earlier systems. Catalytic efficiency was further enhanced by supporting TiO$_2$/anthocyanin onto activated carbon. The supported system has the added value of being easy to recover and to regenerate by re-treatment with fresh dye solution. This makes it potentially useful in future water purification.

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