



Original Research Article

Green synthesis of titanium dioxide nanoparticles with *Glycyrrhiza glabra* and their photocatalytic activity

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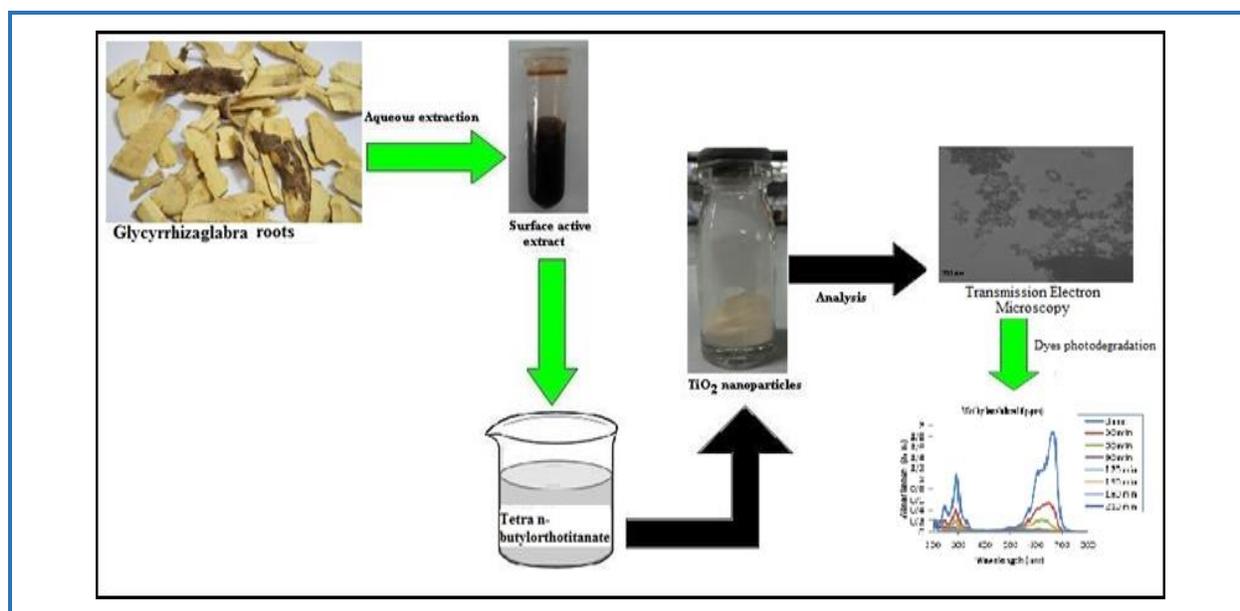
Photocatalytic activity

ABSTRACT

Green synthesis of nanoparticles using plant extracts is a new method to develop environmentally safe nanoparticles, which can be used in numerous applications. In this study, TiO₂ nanoparticles were synthesized from tetra-*n*-butyl orthotitanate using the vegetal surface active substances extracted from *Glycyrrhiza glabra* plant via sol-gel method. The synthesized nanoparticles were characterized using X-ray diffraction (XRD), UV-vis diffuse reflectance spectroscopy (UV/DRS), and Fourier-transform infrared spectroscopy (FT-IR). The morphology of the TiO₂ powder was characterized using transmission electron microscopy (TEM) and the results indicated that TiO₂ particles were nanospheres with a diameter of 60-70 nm. The photocatalytic activity of titania was investigated using the photodegradation of methylene blue, and acid red 88 and coumarin 30 solutions under UV irradiation. The results indicated that the photocatalytic activity of the TiO₂ nanoparticles that was carried out by the degradation of MB solution was higher than AR 88 and coumarin 30. Moreover, the same photocatalytic effects on different dyes was not observed for the same size titania nanoparticles.

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Graphical Abstract



Introduction

Photocatalytic activities make the titanium dioxide appealing to a wide range of industrial applications such as environmental purification, gas sensors, dielectric ceramics, pigments, high efficiency dye-sensitized solar cells, cosmetics, inorganic membranes, and catalysis [1].

Three common polymorphs have been identified for naturally occurring crystalline TiO_2 : rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic) [1]. Rutile showed thermodynamically stable form, whereas anatase and brookite are metastable [2]. Physical properties such as refractive index chemical reactivity and photochemical activity are different for distinct crystallographic forms of TiO_2 and hence they are appropriate for different application fields. Rutile TiO_2 has eminent stability in different pH environments, high dielectric constant, and photo-absorption invisible spectrum (>400 nm), whereas anatase structure has a slightly higher Fermi level and a higher degree of surface hydroxylation caused to better activity for photo-degradation of many pollutants in water and air [2].

Furthermore, nano-sized TiO_2 has been reported for photocatalysis in wastewater treatment, and UV screening agent in cosmetics, plastic, silicone resins and lacquers, where in nano-sized particles caused desirable transparency [3]. Many research studies have been conducted on synthesis of nanosized TiO_2 with different morphologies such as nanospheres, nanostructured thin films, nanotubes, nanowires, nanofibers, and mesoporous structures [1]. Besides, to improve the

photocatalytic activity of TiO₂, the crystalline phase, crystal size, and specific surface area (small size and high crystallinity of nanoparticles) have been evaluated [2].

Various techniques including, sol-gel, hydrothermal/solvothermal, reverse-micellar and emulsion precipitation [1] have been used to synthesize the nano-TiO₂. Sol-gel is the most used technology due to the producing homogenous molecules, different choices for precursor, controlling over microstructure, needing to low reagent purity, low temperature, and low cost [4].

Aggregation of powders through the combination of free hydroxyls by hydrogen bonds on the surface of particles in the process of the sol reaction was previously considered. Various methods such as organic washing, freeze drying, and adding surfactants were proposed to disperse the aggregated powders [5]. However, high cost and great energy consumption are the weak-points of organic washing and freeze drying methods, respectively. Surfactant additions have been introduced as the most economical and efficient approach to prevent the aggregation rigidity of powders [5]. Various surfactants have been used to improve the particle size and distribution of TiO₂ such as CTAB [1], DBS [6], SDS [7], TTAB [8]. On the other hand, biosource surfactants have many advantages over chemical ones such as biodegradability, biocompatibility, low toxicity, high selectivity, tolerating extreme physical conditions like pH and temperature. For these reasons, biosurfactants have been reported to synthesise nano-sized particles [9, 10].

In the present study, nano-sized TiO₂ was synthesized by the sol-gel method using the saponin as a natural surfactant derived from *Glycyrrhiza glabra* plant. Structural features of these particles like particle size of TiO₂ was studied. To evaluate the photocatalytic activities of TiO₂ nanoparticles, methylene blue (MB), and acid red 88 (AR 88) and Coumarin 30 dyes were chosen as azo dyes at different concentration solution and pH ranges.

Experimental

Materials and methods

All chemicals purchased from Merck Co. and used without further purification.

Preparation of plant extract

The collected roots of *Glycyrrhiza glabra* were identified, washed several times with de-ionized water and dried. Then the dried roots of the plant were crashed into small pieces and defatted with acetone and methanol in a Soxhlet apparatus [11]. The air-dried powder was then filled in the thimble and extracted using 100 mL of methanol in the Soxhlet apparatus for 8-10 h and 60 °C. The plant extract (PE) was centrifuged at 15000 rpm for 30 min to remove all unextractable matter that is insoluble in the extraction solvent. The entire extract was concentrated to dryness using rotary flash

evaporator at 60 °C [12]. Then some test such as the index of emulsification (E24) of extracted saponin and so on was also determined [11].

TiO₂ nanoparticle preparation

TiO₂ nanospheres were obtained by the sol-gel method using tetra-*n*-butyl orthotitanate (TBT) as the source of titanium. The synthesis of titania nanospheres was achieved according to obtained critical micelle concentration (CMC) first 55 mL ethanol (96%) and 5 mL ethyl acetoacetate (EAcAc) were mixed and stirred for 5 min. Then the tetra-*n*-butyl orthotitanate was added to the solution and stirred for 30 min. The composition consisted of PE as the surfactant (0.1 gr) and deionized water. The pH was adjusted by adding 2 drops of HNO₃ (65%) solution to obtain pH of 1.5 [8]. The compounds were mixed and stirred for 12 h, and added dropwise into the PE solution while continuously stirring for 6 h. The TiO₂ nanoparticles precipitated were separated by centrifuging at 2000 rpm for 5 min and then washed with ethanol:deionized water (1:1) mixture for 5 times to remove the surfactant. The product was dried at 25 °C in air [1]. In order to complete the removal of the organic materials, the dried samples were calcinated at temperature of 400 °C for 4 h at a rate of 1 °C/min [4].

Analytic methods

The morphology and size of titanium dioxide nanospheres were observed by transmission electron microscopy (TEM, Philips, EM 208). Diffuse reflectance spectroscopy (DRS) were recorded on Shimadzu UV-2501 (Mpc-2200) spectrophotometer. Spectroscopic characterization has been investigated by Fourier-transform infrared (FT-IR), spectra of the samples were recorded using KBr pellets in the range of 4000–400 cm⁻¹ by Shimadzu spectrophotometer (8400 S). X-ray diffraction (XRD, PW 1800, Philips with Cu K α radiation) was used to survey the crystal compositions [13]. The crystallite size was calculated using the Scherrer equation:

$$D = k\lambda / B \cos \theta \quad (1)$$

Where k is the constant equal to 0.94, λ is the X-ray wavelength, B is half-width at half-maximum and θ is the diffraction angle of the phase under investigation [4].

Dyes photo-degradation

The photocatalytic activities of the TiO₂ nanoparticles sample were investigated by measuring the degradation of methylene blue (MB), acid red 88 (AR 88) and coumarin 30 with UV-irradiation, and compared with each other [13]. Degradation experiments were carried out by adding 0.03 gr of TiO₂

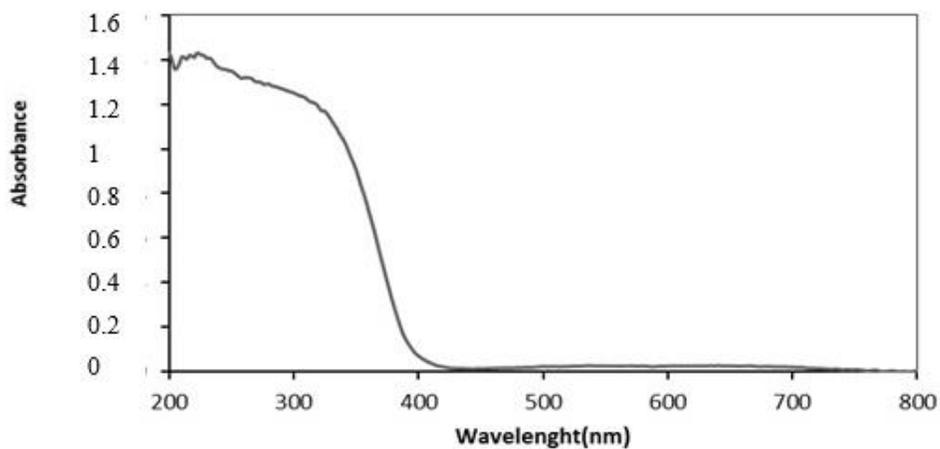


Figure 1. DRS UV-vis spectra of the synthesized TiO₂ nanoparticles

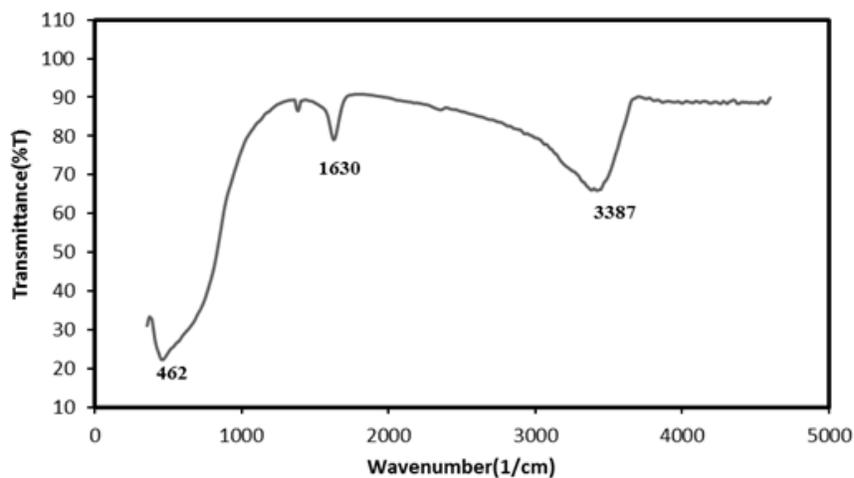


Figure 2. FT-IR spectrum of the synthesized TiO₂ nanoparticles

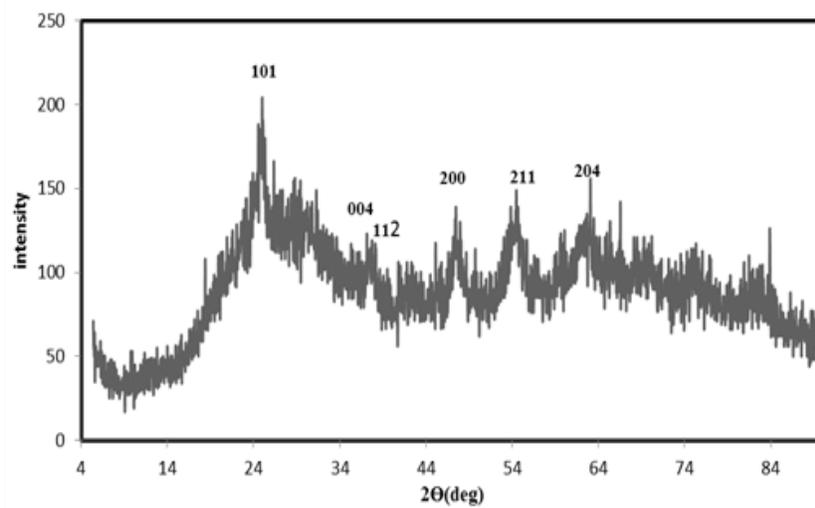


Figure 3. XRD patterns of the synthesized TiO₂ nanoparticles

into 500 mL of 10 mg/L and 20 mg/L aqueous MB, AR 88 and coumarin 30 solution [14]. The mixture was put in ultrasonic for 5 min and it was kept in the dark area under stirring for 30 min to ensure the establishment of adsorption/desorption equilibrium [13]. After 30 min of stirring in dark to attain the adsorption equilibrium, the solution was then irradiated under UV lamp (250 W high pressure Hg lamp) as light sources with continuous magnetic stirring [1]. Then 3.0 mL of solution was drawn out in each 30 min and TiO₂ particles were separated from the suspension by centrifugation at 13000 rpm for 25 min to measure MB, AR 88, coumarin 30 concentration after irradiation [14]. The UV-vis absorption spectra of the taken solutions were obtained using T 80+ UV/vis spectrometer PG instruments Ltd in the range 200-800 nm (λ_{max} =674 nm for methylene blue=507 nm for acid red 88, and 424 nm for coumarin 30) [13]. The same situation was investigated by changing the pH of the three colors (pH=9.5).

Results and Discussion

UV/DRS

The light absorption properties of the TiO₂ nanoparticles were studied by UV-vis/DRS performed under in the wave length range of 200-800 nm. Figure 1 revealed that the absorption spectrum of TiO₂ consists of single broad intense absorption around 400 nm [15].

Fourier-transform infrared spectroscopy (FT-IR)

Figure 2 demonstrates the FT-IR spectra of TiO₂. The peaks at 3387cm⁻¹ and 1630 cm⁻¹ in the spectra are due to the stretching and bending vibration of the -OH group. In the spectrum of pure TiO₂, the peaks at 457 cm⁻¹ show stretching vibration of O-Ti-O [16].

X-ray diffraction (XRD)

To determine the TiO₂ crystal composition, wide angle X-ray diffraction patterns were measured as shown in Figure 3. In case of mesoporous TiO₂ calcined at 400 °C, the broaden diffraction peak of anatase form are 2 theta: 25.3°, 37°, 47° is observed (JCPDS 21-1272) [2]. The broad nature of the XRD peaks indicates a small crystallite size of the particle. The average crystallite size of the particles obtained from the X-ray line broadening studies of the (101) reflection was found to be 24 nm [1].

Transmission electron microscopy (TEM)

The structure and particle size of the nanoparticles were investigated using TEM. Figure 4 shows TEM images of the sample, confirming the formation of the TiO₂ nanoparticle at nano-size. As can be observed, the particle size of nanospheres TiO₂ was found to be at the range of 60-70 nm.

Photocatalytic activity

Before the photocatalytic activity measurement, it is important to distinguish the effect of dye adsorption by TiO_2 nanoparticles from their photocatalytic activities. Figure 5 shows the UV-vis spectrum of different dyes before and after addition of TiO_2 nanoparticles. As can be seen from this figure the adsorption is not the same for different dyes. All the photocatalytic measurements were corrected for this effect [17].

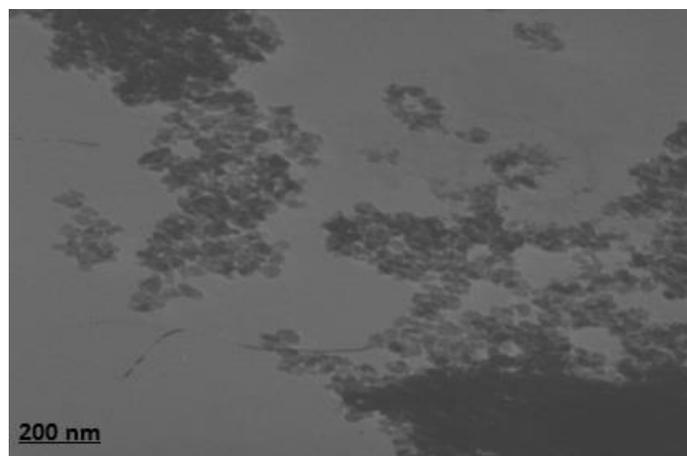
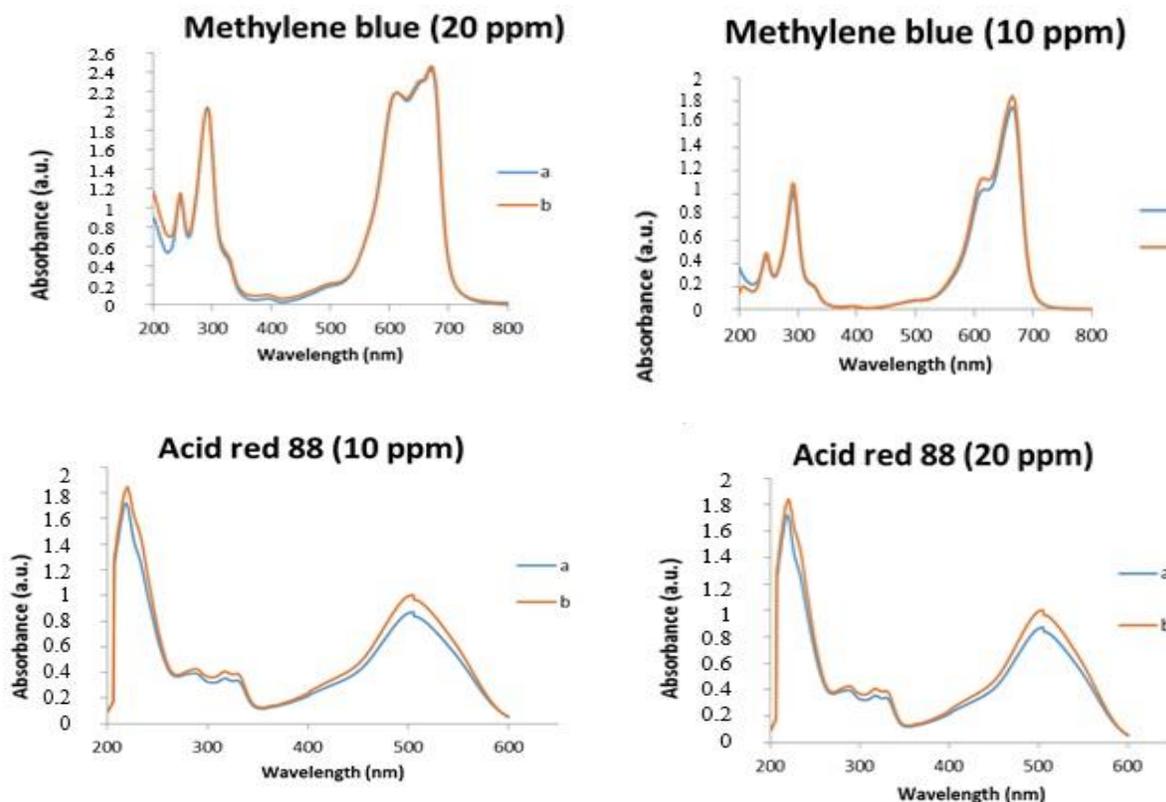


Figure 4. TEM image of the synthesized TiO_2 nanoparticles



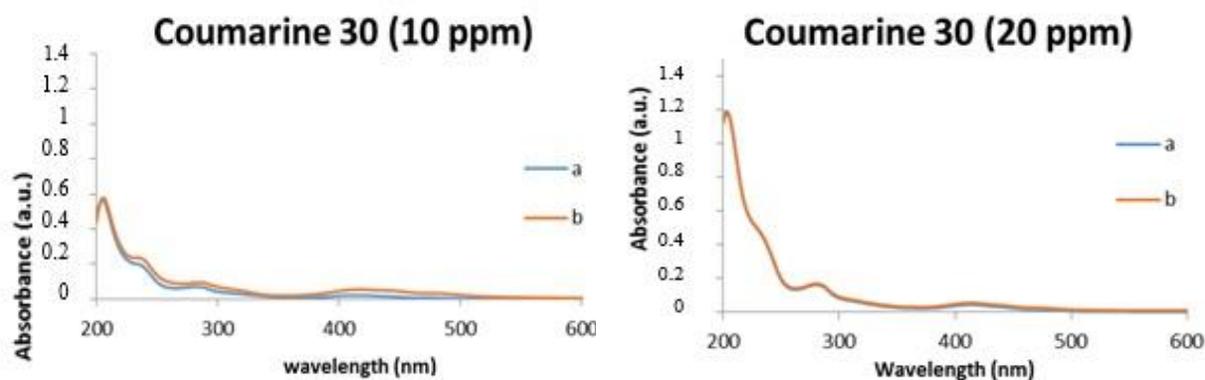
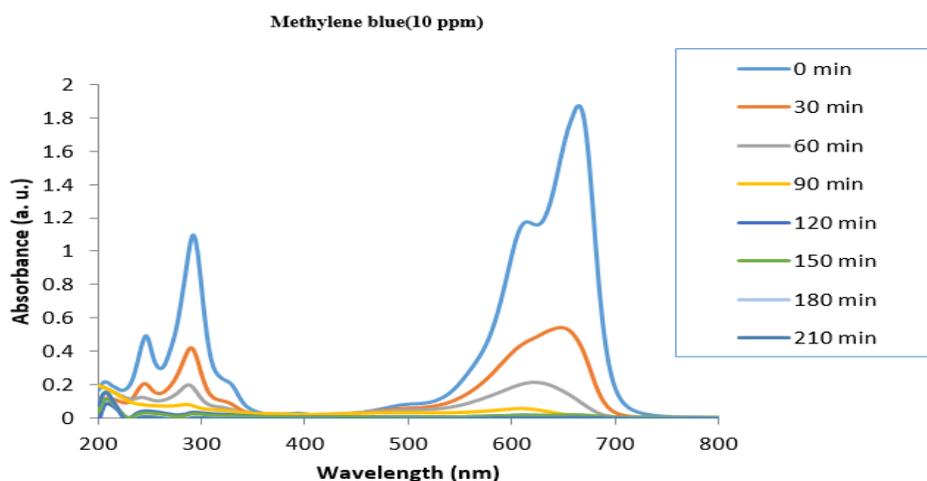
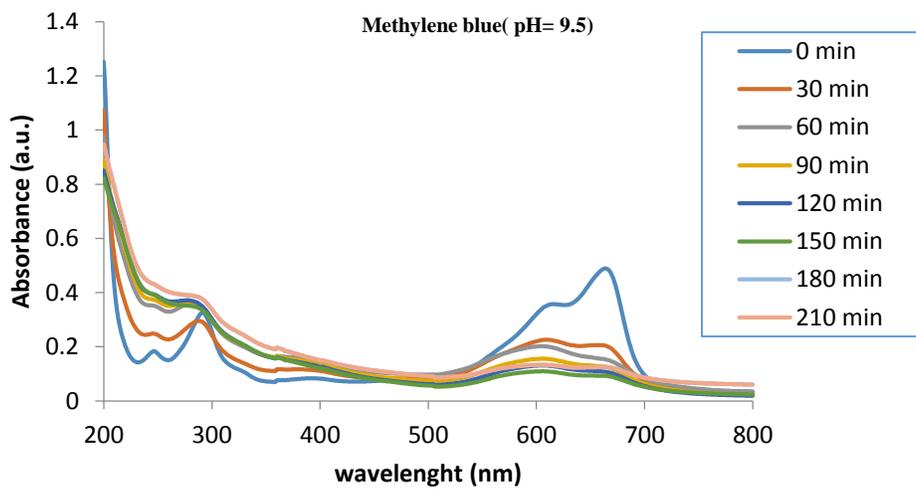
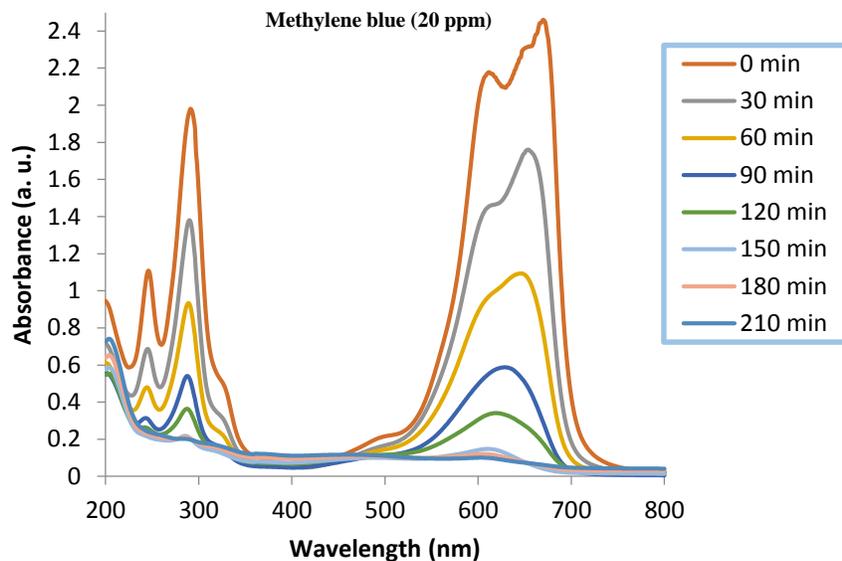


Figure 5. UV-vis spectrum of different dyes before a) and after b) addition of nanoparticles

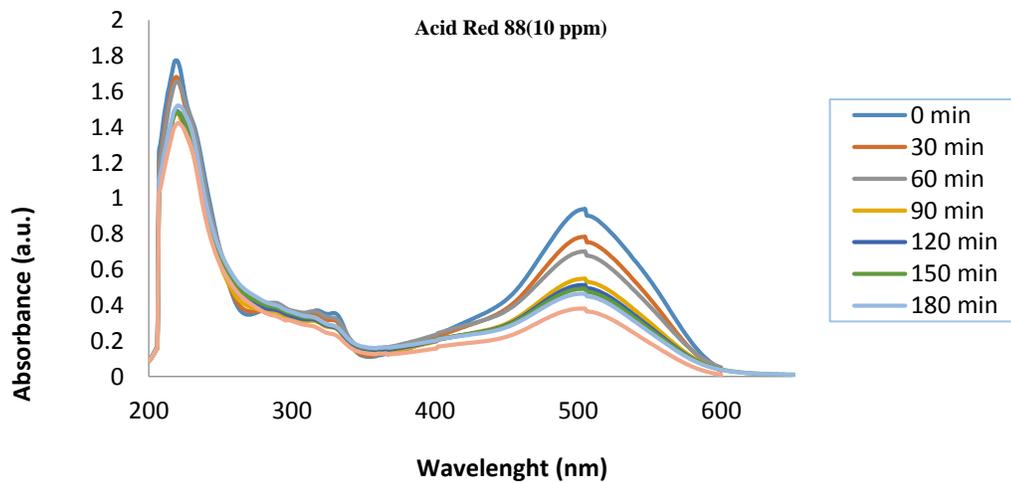
Photocatalytic activities were evaluated following the degradation of aqueous dye solutions under UV irradiation [18]. Figures 6a, 6b, and 6c illustrate the photocatalytic degradation of MB, AR 88, and coumarin 30 at different time intervals using TiO₂ catalyst, respectively. These figures show the different effects of TiO₂ nanoparticles of the same size on different dyes. By increasing the UV illumination time, the absorbance is reduced. This means that the dye concentration in the solutions has been reduced due to decomposition of the dye by TiO₂ nanoparticles [17].

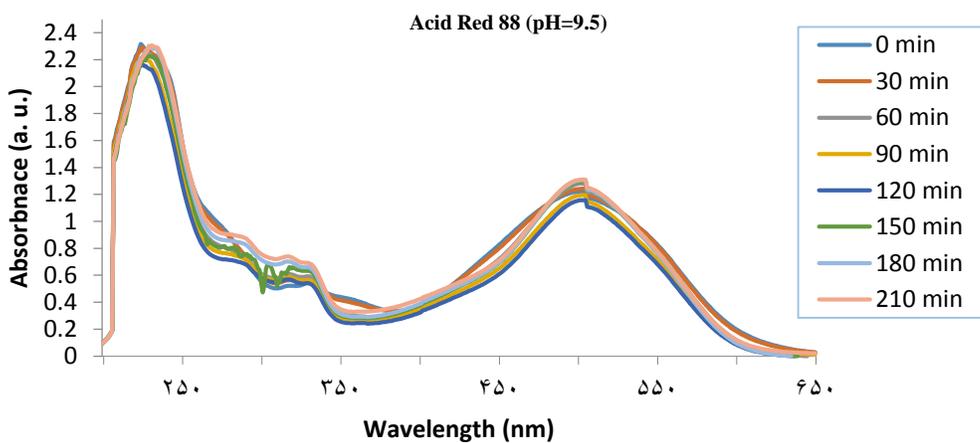
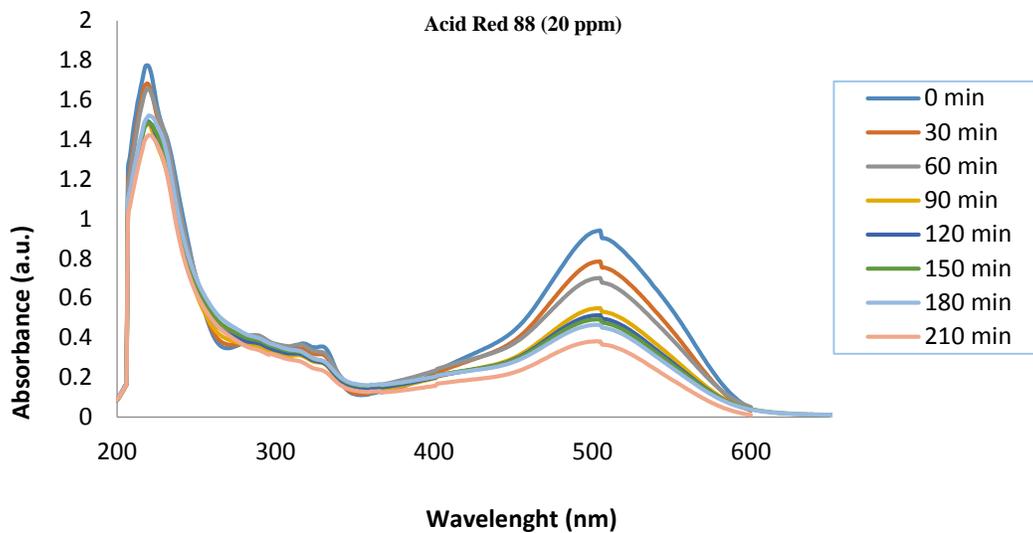
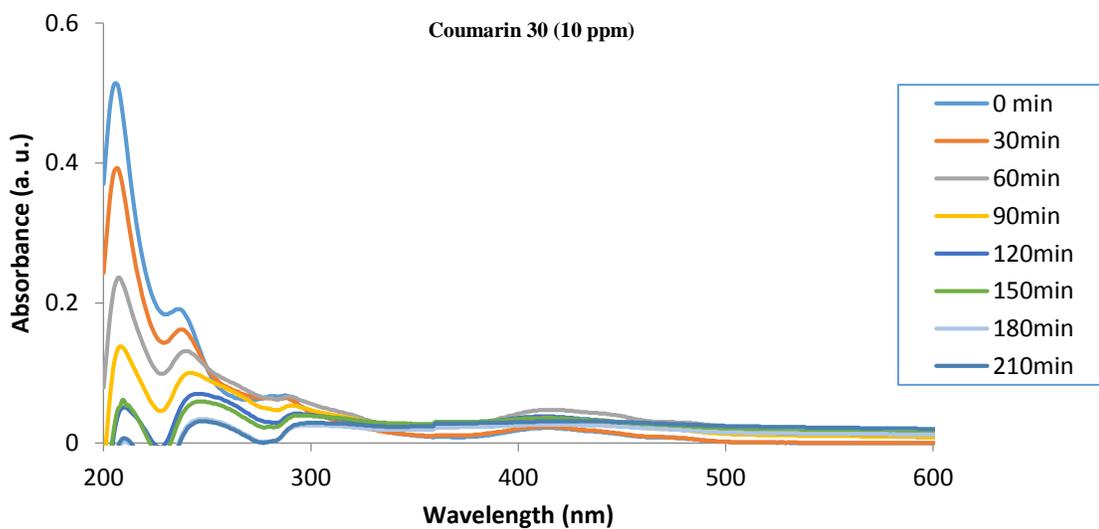
Figure 7 depicts the comparison of the photocatalytic degradation of different dyes using the same sized TiO₂ nanoparticles. In Figure 7, C₀ is the initial concentration of dyes, and C is the concentration of them after visible light irradiation. According to the literature the photoactivity of TiO₂ depends on the morphology, crystallization of the sample and surface area of the photocatalysts [17]. According to the results in Figure 7, one can observe that the photocatalytic efficiency is not the same for different dyes.

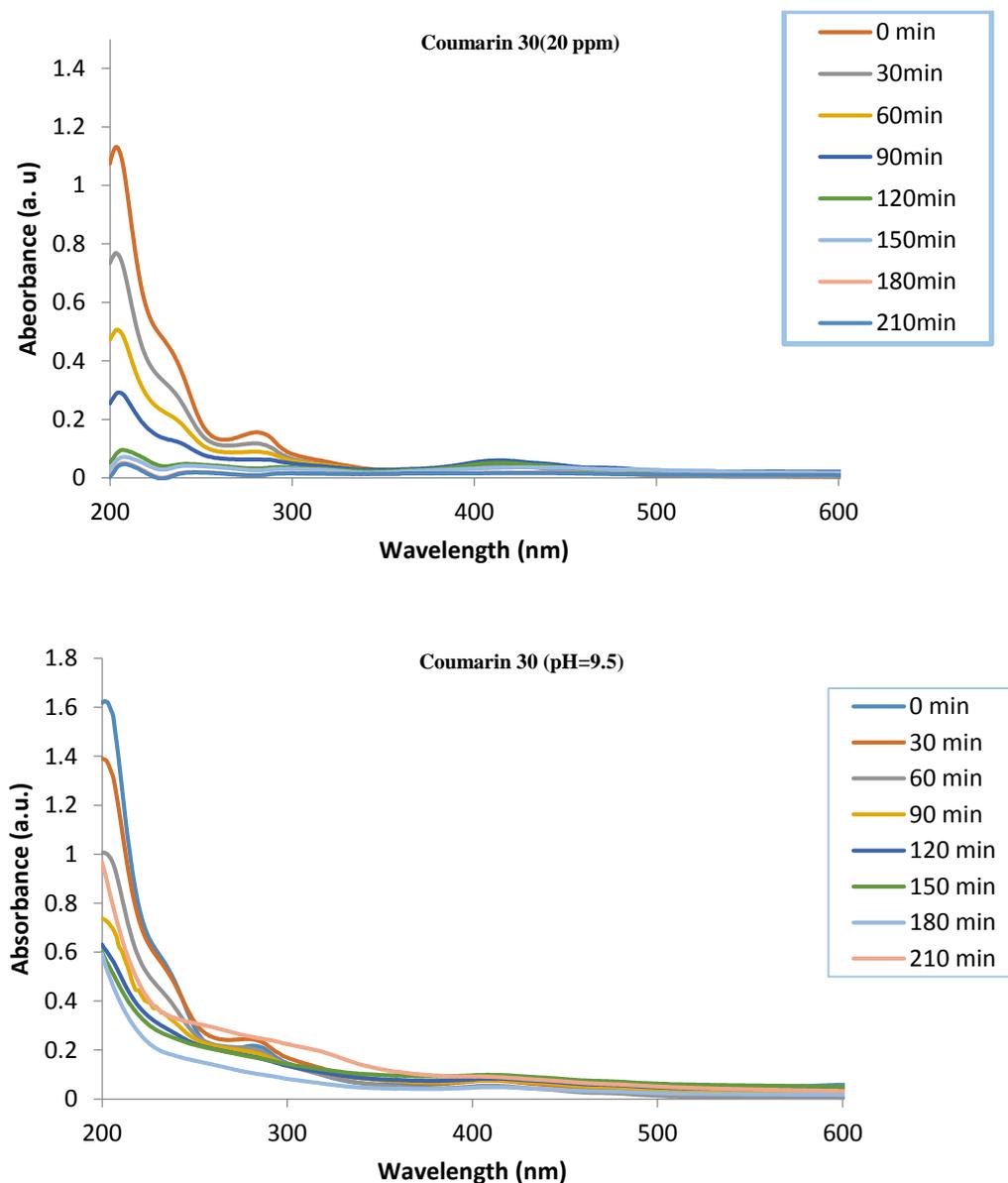




a



**b**



c

Figure 6. UV-vis spectrum of a) MB, b) AR 88, c) Coumarin 30 dyes solutions

Photocatalytic activity of methylene blue is better than the other two colors. For the TiO_2 , the methylene blue was almost all degraded within 60 min under UV-irradiation, whereas the degradation time of AR 88 took about 90-120 min for a less percent degradation, and the rate of degradation for coumarin 30. The pigment of methylene blue is a cationic dye. Thus the electrostatic gravity on the catalyst surface (TiO_2) and dye caused to attract better and then saw a better result for degradation in the acidity and in particular alkalinity condition.

Conclusions

This study showed that, PE as a natural surfactant can be extracted from the *Glycyrrhiza glabra*. Sol-gel technique was utilized to synthesize TiO₂ nano-particles from a mixture of PE and tetra-*n*-butyl orthotitanate precursor in aqueous solution. The TiO₂ nano powders were characterized using UV/DRS, XRD, FTIR, and TEM. The results of the TEM analysis revealed the uniform morphology of the nanosphere TiO₂ particles. The XRD spectra showed that, the main phase of TiO₂ nanopowders were anatase with a crystal size of 24 nm. The TiO₂ nanoparticles were found to exhibit higher photocatalytic activities in the degradations of azo dye MB than the azo dye AR 88 and fluorescent dye coumarin 30, indicating that the TiO₂ can be effectively used as a photocatalyst.

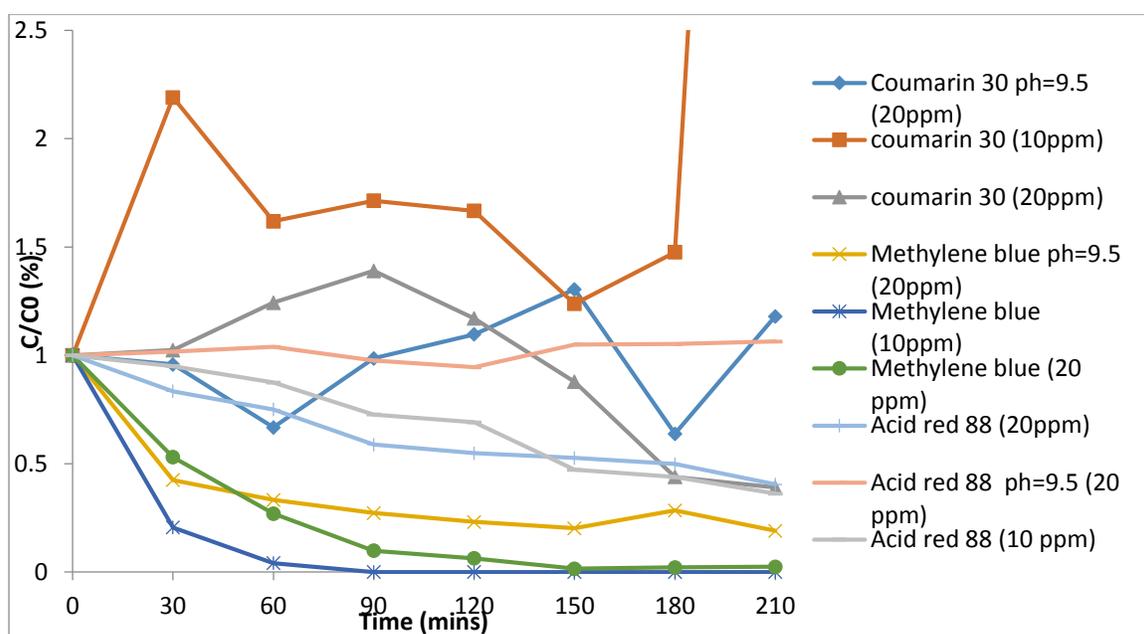


Figure 7. Photodegradation of MB, AR 88 and Coumarin 30 by TiO₂ catalysts under visible light irradiation

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Disclosure Statement

No potential conflict of interest was reported by the authors.

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