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Production and evaluation of floating photocatalytic composite particles formed using Pickering emulsions and membrane emulsification

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Abstract

Floating photocatalytic composite particles were created by injecting a lipid (sunflower oil or liquefied cocoa butter) into an aqueous suspension of TiO₂ nanoparticles using the process of membrane emulsification to control the (Pickering) emulsion size. The composite particle median diameters were controlled in a range from 80 to 300 µm. The composite particles floated in water and possessed photocatalytic activity, which was further enhanced by chemically incorporating silver particles into the TiO₂ shell. The cocoa butter-based composite particles proved more robust, and were not affected by the UV photocatalytic process. Using a combination of cocoa butter and hexane, for the core of the particles, it was possible to generate composite TiO₂ and lipid particles with 36 mg TiO₂ per gram of particle. Optimal dye decolourization was achieved with a particle surface coverage of between 60 and 80%. Complete surface coverage resulted in a reduced reaction rate due possibly to reflection of the UV light.

1. Introduction

The photocatalytic potential of the semi-conductor, titanium dioxide (TiO_2) has been described at length, and many reviews of its wide-ranging uses have been published; a recent example being that of Gaya and Abdullah¹. In essence, when the anatase crystalline form of TiO_2 is irradiated with UV light at wavelengths in the vicinity of 365 nm, electrons are promoted from the valence to the conduction band. Both the energised electrons and the positive holes created thereby can undergo reactions that lead to the formation of a number of free radical species (Figure 1). These highly oxidizing species have the ability to completely mineralize organic matter². Many applications of TiO_2 relate to the remediation of aqueous environments and there are a number of different ways by which TiO_2 could be employed to achieve this. In some studies the TiO_2 nanoparticles have been incorporated into a larger polymer matrix, to facilitate easier solid-liquid separation by sedimentation³. An alternative is to incorporate the TiO_2 nanoparticles into an easily floating species. It has been shown that such particles are able to receive sufficient solar, or artificial, irradiance to be able to produce free radicals⁴. One early application of this concept was to coat hollow glass beads with TiO_2 for the treatment of oil slicks at sea^{4,5}. More recently, high surface-area exfoliated vermiculite has been used to support TiO_2 for water decontamination⁶ whilst Magalhaes and Lago⁷ grafted TiO_2 onto expanded polystyrene beads. Syoufian and Nakashima⁸ took a different approach, and succeeded in manufacturing submicrometer sized hollow spheres from TiO_2 itself that floated on the surface of water. Recently, detailed chemical formulation has been described to form TiO_2 on the surface of hollow glass spheres, which are then used as floating photocatalysts⁹.

If the concept of using floating catalytic particles were ever to become a viable alternative to conventional advanced oxidation methods for water remediation, an efficient method of mass producing particles having the desired characteristics would be required. In the particular context described above, buoyancy and particle size are key parameters. If the particles are to be separated and recycled to a UV contactor then they need to possess a physical property that facilitates solid-liquid separation, and particles that float easily would be beneficial. The position of the particles at the air-water interface will also be important; it is likely that there is an optimum position at the interface to maximise the use of the incident UV light, together with the water and oxygen that is present. Hence controlling the particle size, and its buoyancy, is an important consideration. One means of producing particles of uniform and controllable size is to employ membrane emulsification¹⁰. This is a much-studied process by which a liquid (the dispersed phase) is forced through the pores of a microfiltration membrane into another immiscible liquid – the continuous phase. Stabilisation of the particles formed conventionally requires the use of emulsifiers or stabilisers. However, it is possible to stabilize such particles using finely divided solids, and emulsions stabilized in this way are known as ‘Pickering Emulsions’ and do not require the use of any additional emulsifying agent¹¹. Emulsions stabilized by proteins and food colloids are widely used commercially, and fine clays were historically used for stabilization in what is known as ‘suspension polymerisation’. The work presented here describes the production, and testing, of composite particles formed by coating lipids - sunflower oil and cocoa butter - with nanoparticulate TiO₂. As used here, the finely dispersed TiO₂ both stabilizes the dispersed phase oil drops as well as providing photocatalytic reaction sites at the surface of the particles, see Figure 1. In this work, the photocatalytic

potential of such particles was demonstrated by bringing about the decolourization of aqueous solutions of the dye indigo carmine. Apart from using the dye as a convenient assay for photocatalytic reactivity, there is interest in photocatalytic oxidation of dyes using TiO_2 ¹². Other potential uses of photocatalyst particles includes the ability to 'split' water into hydrogen and oxygen¹³. In all these photocatalyst applications it is beneficial to have the catalyst close to the liquid surface, to minimise the UV light attenuated within the liquid.

2. Experimental

2.1 Materials

TiO_2 , P25 (Aeroxide) was purchased from Lawrence Industries (Tamworth, UK). sunflower oil was purchased from a local supermarket and cocoa butter from Keylink UK. Citric acid, lanthanum nitrate and sodium nitrate were supplied by Fisher Scientific. Indigo carmine [3,3-dioxo-1,3,1,3-tetrahydro-[2,2]-bi-indolylidene-5,5-disulfonic acid disodium salt], hexane, silver nitrate and oxalic acid were supplied by Sigma Aldrich.

2.2 Generation of Pickering Emulsions

Pickering emulsions were generated using a Dispersion Cell (150 mL volume), supplied by Micropore Technologies Ltd (Loughborough, UK), for membrane emulsification, using membranes with pore sizes of 5 or 14 μm . A comprehensive description of the device, and its use, can be found elsewhere¹⁰. The shear rate at the membrane surface was varied by altering the speed of rotation of a paddle-blade stirrer mounted above the membrane. The dispersed phase (liquid lipid) was injected

by means of a syringe pump, and a peristaltic pump, through the membrane pores at a rate of up to 10 mL/min into the Dispersion Cell. The drops formed during emulsification were sized approximately using an optical microscope and the volume distribution and particle size of the Pickering emulsions were obtained using a Malvern Mastersizer Model S (Malvern, UK). The primary particle size of the TiO₂ was determined from surface area measurements made using the BET method with an ASAP 2020 instrument (Micromeritics (UK) Ltd., Dunstable). Particle density measurements were made using a helium pycnometer (Micromeritics (UK) Ltd.)

Initially, suspensions of TiO₂, ranging in solids content from 2 to 8.5% w/w, were prepared by mixing TiO₂ in a solution comprising 1mM sodium nitrate, 3 mM lanthanum nitrate or 0.5% w/w citric acid in deionized water. The multivalent aqueous cation solutions were used as they were previously reported to have enhanced the stability of particle stabilised emulsions¹⁴. The citric acid was used as it has been shown¹⁵ that mildly acidic conditions promotes weak flocculation of the TiO₂, which are the conditions required for stabilising an emulsion¹⁴. The Pickering emulsion thus formed was then decanted from the Dispersion Cell and replaced with fresh TiO₂ suspension to generate further floating TiO₂ particles. The influence of stirrer speed settings on particle size was investigated. In the case of the melted cocoa butter, the Dispersion Cell was placed in a water bath at 40°C, as was the cocoa butter for injection. A further formulation was tested using a mixture of cocoa butter and hexane. In this case the liquid was mobile at room temperature and the injection was performed under room temperature conditions.

After formation, the emulsion was stirred for 30 min at 3 Volts (205 to 222 rpm) in an ice-cooled beaker for a conditioning stage, to allow the lipid to set and the particles to stabilise. The Pickering emulsions were then left to settle for approximately 2 hours. This resulted in a three-layered mixture comprising a settled suspension of TiO₂ particles, a clear aqueous phase layer and a creamy emulsion top layer containing floating TiO₂ coated lipid particles (i.e. a Pickering emulsion). The Pickering emulsion was removed by pipetting and then washed in 100 mL of continuous phase solution (this stage will be referred to as the 'washing stage' later in this paper). For the washing stage, the drops were mixed using the paddle bladed stirrer at a gentle rotation speed of 558 rpm for 10 minutes and then allowed to settle again. The washing stage removed any entrapped TiO₂ particles not firmly fixed to the floating lipid-TiO₂ composite particle. The volume distribution and size of the TiO₂ coated lipid particles generated in the Dispersion Cell were determined from: (i) the Pickering emulsion after 10 mL lipid had been injected; and (ii) the Pickering emulsion after the washing stage, using the Malvern Mastersizer. For size analysis, or for use in the photocatalytic tests, the TiO₂ stabilised lipids were pipetted into a Petri dish (diameter 130 mm) which contained only water and dye (100 mL volume used); i.e. there was no further necessity for salts or citric acid as the post-washed TiO₂ stabilised lipids were stable in water and the salts and citric acid were only used during the initial composite particle formation stage.

As proposed by Devi and Reddy¹⁶, silver-deposited P25 TiO₂ was prepared by the addition of oxalic acid and 0.1 M solution of AgNO₃ to 1000 mL of distilled water to give resulting concentrations of 5x10⁻³ M of oxalic acid and 4x10⁻⁴ M, of AgNO₃. The pH of the AgNO₃ – oxalic solution was adjusted¹⁶ and 4 g TiO₂ was added to the

solution. The resulting suspension was irradiated under UV- light ($\lambda = 365 \text{ nm}$) for 1 hour under vigorous agitation using a magnetic stirrer. After irradiation the suspension was left to settle overnight. After settling, 900 g of the clear supernatant water was carefully pumped out of the container avoiding re-suspension of the settled solids. The remaining suspension was tipped into the Dispersion Cell and 10 mL of mobile lipid was injected through the membrane. According to the cited literature^{16,17} the application of UV light to the silver nitrate – oxalate mixture results in the adsorption of silver onto the TiO_2 composite particles resulting in an enhanced photocatalytic species.

2.3 Assessment of Photocatalytic Activity

Solutions (100 mL) of indigo carmine having an absorption of approximately 1.0 when measured at a wavelength of 620 nm (A_{620}), were dispensed into disposable plastic Petri dishes and then placed uncovered beneath a tubular 'black light blue' source (20 WT12 BLB ISL, Philips (UK) Ltd., Croydon) emitting principally at 365 nm. The intensity directly below the source was measured using a radiometer (Model UVX, UVP, Cambridge) fitted with a sensor having peak sensitivity at 365 nm and measurements of light intensity were taken at various positions under the lamp. The dishes were positioned at fixed locations and experiments were conducted in duplicate, or even more replicates. Two Petri dishes could be accommodated under the lamp, receiving almost identical average light intensities of 0.68 mW/cm^2 . Various masses of composite particles were added by pipetting the composite particle suspension onto the surface of the dye in the Petri dishes to initiate dye decolourization. The actual mass of particles used was determined after the

experiment was completed, by filtering the suspension and drying the remaining particles at room temperature. After drying and weighing, the amount of TiO₂ used was checked by 'ashing' the sample by heating in a muffle furnace at 550 degrees Celsius to burn off all the organic materials and leave the TiO₂ for weighing after cooling. During the dye decolourisation tests, samples of aqueous dye (4 mL) were taken periodically in such a way as to avoid removing photocatalytic particles from the system, filtered through a 0.2 µm Millipore nitro-cellulose membrane in order to remove any turbidity and then placed in 2 mL cuvettes for A₆₂₀ determination using a spectrophotometer, Model 1201, Shimadzu (UK) Ltd., Milton Keynes. Approximate values of surface coverage of the floating particles was determined at the start of the experiment by photographing the surface of the Petri dish containing the particles and dye solution and using bit map editing software with adjustable grey scale thresholds to determine the fraction of the total surface covered by the floating particles.

3. Results and discussion

The techniques described above using the Dispersion Cell were capable of producing composite particles that were stable prior to exposure to UV light. The method of size analysis employed, laser light diffraction using a Malvern Mastersizer, involved circulating composite particle suspensions around the instrument's flow cell. This in itself might have caused damage to the particles. However, comparison of size analyses achieved using direct microscopic methods of estimating particle diameter with the results obtained using the Malvern Mastersizer did not reveal any particle disintegration. Comparison of the washed and non-washed particles made

from suspensions of over 3% w/w TiO₂, using sunflower oil demonstrated good floating particle stability, see Table 1: and the median size was the same before and after the washing stage. However, there was evidence of slight degradation after exposure of the sunflower oil core particles to the UV radiation which is discussed later.

Frith and co-workers demonstrated¹⁴ that stabilisation of Pickering emulsions is favoured by an ionic composition that encourages weak flocculation of the particles. Hence, lanthanum nitrate and sodium nitrate were initially used as proposed by these authors to encourage weak flocculation. However, on conducting trials using only citric acid, it was discovered that this compound alone could bring about the stable formation of the oil drop-particle composites. The data of Table 1 was obtained using only citric acid. In the table, the term D10 represents the particle size below which 10% of the distribution occurs, and D90 the size below which 90% of the distribution occurs. The relative span is a measure of how monodisperse a particle size distribution is; it is defined as being the difference between the D90 and D10, divided by the median size (D50). In practical terms a span value of less than 1.0 is taken as being indicative of a monodisperse particulate phase. Hence, the data in Table 1, supported by the information in Figures 2 to 3, indicate that the composite particle distributions are narrow (monodisperse). Also, the particles formed using just the citric acid, at the higher concentrations of TiO₂ used in the slurry (Table 1), are the most monodisperse and appear to be very stable before contact with UV light. Multivalent cation solution was also used, as the continuous phase in the generation of some composite particles with a sunflower oil core, and

the particle size distributions were similar to those illustrated in Figure 3 where simply citric acid was used.

Figure 2 shows particle size distributions achieved using a 14 μm pore diameter membrane at stirrer speeds ranging from 558 to 1085 rpm. The median particle size decreased as the stirrer speed was increased: at 558 rpm it was 230 μm , at 821 rpm 140 μm whilst at 1085 rpm it was 115 μm . It is also evident that the particle size distribution is broader at the lower speeds than at the higher ones. Figure 3 shows similar data obtained using a 5 μm membrane. There is a similar influence of stirrer speed on median particle size to that obtained using the membrane with larger pores, but the effect is less pronounced; at 558 rpm the median was 112 μm , at 821 rpm 98 μm , whilst at 1085 rpm it was 82 μm . The greatest contrast was that the particle size distribution remained relatively narrow, even at the lower stirrer speeds. Figures 2 and 3 demonstrate that it is possible to produce floating composite particles with a size distribution that can be controlled by the pore size of the membrane used, as well as the shear applied during the membrane emulsification.

Figure 4 depicts the results of dye decolourization control tests. These comprised UV-irradiating the dye solution in the absence of photocatalytic particles, contacting dye solution with fully formed composite particles but without UV light (labelled 'TiO₂ in dark') and also with sunflower oil particles devoid of an outer TiO₂ shell, but stabilised by a surfactant (Tween 20), also in the dark. Some dye is evidently taken up by the composite particles even in the dark. This characteristic of the particles is desirable as adsorption constitutes an important step in the degradation of the dye. There has been some conjecture reported in the literature over the mechanism for

dye decolourization using TiO₂ photocatalysis¹⁸: i.e. whether the dye plays an active role in the adsorption of the UV light, helping to facilitate its own destruction. The nature of the work here was not intended to contribute to that field of enquiry, but rather to provide a verified simple method of generation floating photocatalytic composite particles and to demonstrate their utility.

Experiments on dye decolourization conducted using particles stabilized by citric acid, sodium and lanthanum nitrates is shown in Figure 5, which illustrates a compilation of experiments clearly indicating the increasing effectiveness for decolourization with respect to the mass of TiO₂ within the composite particle. With increased TiO₂ loading the particle size distribution will change, and this contributes to the enhancement of the decolourization rate observed at higher loadings. In all cases 1 mL of composite particle stock suspension was used, pipetted into the Petri dish containing 100 mL of dye solution, and giving between 60 and 80% surface coverage of the floating particles. Different masses of TiO₂ were achieved by varying the starting concentrations of TiO₂ that were used at the particle formation stage, and different composite particle sizes were formed, in a similar way to the data illustrated in Figures 2 and 3. However, the correlation of dye decolourization with the mass of TiO₂ present, as determined by the ashing test, is clear.

After exposure to UV radiation it was observed that the composite particles formed using a sunflower oil core had a tendency to shed a small amount of fine solids from their surface whereas those made from cocoa butter maintained their integrity. Filtering the decolourised dye solution through a 0.2 µm pore membrane filter yielded a particle-free filtrate. The presence of these fine particles of TiO₂ points to the

partial destruction of the composite particles during UV exposure when using sunflower oil as the core – a phenomenon that does not occur with composite particles having a core comprising cocoa butter. It is concluded that the cocoa butter particles are more stable. Further conditions that were found to assist in composite particle stability was the size distribution: fairly narrowly sized particles, and at sizes with medians below 100 micrometres were preferable for the production of stable composite particles.

Table 2 provides information on the physical properties of the composite particles formed using cocoa butter as the core, and a mixture of cocoa butter and hexane. From measurements of the specific surface area ($53.2 \text{ m}^2/\text{g}$) and density (4034 kg/m^3) of the TiO_2 it was possible to calculate a primary particle size for the photocatalyst of 28 nm assuming that the particles were spherical. By contrast Figure 6 a Scanning Electron Microscope image of the dry P25 TiO_2 nanoparticles, shows a wide range of particles sizes. The ideal situation would be to have a monolayer coverage of the oil droplets by TiO_2 nanoparticles. However, the nanoparticulate TiO_2 will form clusters in water¹⁵, and whilst this is a desirable characteristic from the perspective of providing composite particles with as high a mass of TiO_2 as possible (as demonstrated in Figure 5), this will be at the cost of a reduced utilization efficiency.

An example, taken by optical microscopy, of composite particles with a cocoa butter core and TiO_2 shell is shown in Figure 7. The image illustrates the two extremes of the composite particle sizes - 50 and 180 microns. The entire distribution lies

between these limits and has a median value of 98 μm (see Table 2 particle type 2), with a coefficient of variation of 38% around this value. That the composite particles are indeed spheres is evident from the image. Knowledge of the densities of cocoa butter and TiO_2 coupled with observations that the TiO_2 forms clusters having dimensions of approximately 5 microns¹⁵, and that the high cluster voidage traps water and reduces the TiO_2 solids concentration to only 3% v/v enabled calculation of the minimum diameter that will be neutrally buoyant by a force balance on the drop (buoyancy against composite particle weight) giving the following equation:

$$d = \frac{6xC\rho_s}{(\rho - \rho_o)}$$

where d is the composite particle diameter, x is the cluster diameter of the TiO_2 , C is the volume concentration of the TiO_2 in the cluster, ρ_s is the density of the TiO_2 , ρ is the water density and ρ_o is the oil density.

The above logic provides a value of approximately 30 μm , or more, for neutrally buoyant composite particles. Particles entirely coated by TiO_2 and smaller than this value will sink, due to the high density of the TiO_2 mineral. Clearly, it is desirable to have small and stable composite particles with a high loading of TiO_2 in the surface shell, and further work to achieve this was performed by mixing the melted cocoa butter with hexane, in a volume ratio of 2/3 lipid to 1/3 alkane. This provided an organic liquid that was mobile at room temperature, and that could be injected through the membrane in the membrane emulsification process in much the same way as the sunflower oil was. During conditioning the hexane evaporated, leaving a solid core of cocoa butter and, during this process, the composite particles shrank in size. Hence, the resulting composite particles were smaller than those produced

without shrinkage, and the resulting concentration of TiO₂ in the shell was higher. The influence of this process on the decolourization is illustrated in Figure 8, where the composite particles including hexane are shown to have considerably greater photocatalytic activity.

Colloidal silver particles were formed at a pH of 2.56 which was determined by the concentration of the oxalic acid used during the preparation of the composite photocatalytic particles. However, in order to encourage the greatest concentration of TiO₂ in the shell of the composite particles membrane emulsification at a pH around the iso-electric point (IEP) may be preferable. Hence, determination of the Zeta potential of the TiO₂ particles in a continuous phase of silver nitrate and oxalic acid was performed. Figure 9, shows that the IEP is close to a pH of 1.0. Further tests in which the composite particles were produced at a pH of 1.0 were performed, with both the 14 and the 5 µm pore size membranes. The intention was to produce composite particles with a median diameter below 100 µm, but with as few as possible particles below 30 µm and with no large particles. The results are summarised in Table 2. For the determination of the amount of TiO₂ in the shell of the composite particles, repeat ash tests were performed over a number of samples. It should be noted that the contribution made by the presence of silver to these weights was negligible. The range of mass of TiO₂ per gram of particle is shown in Table 2 and the mid-values are used in the discussion that follows. The use of hexane clearly significantly increased the amount of TiO₂ trapped in the shell of the composite particles. A maximum value of 35.7 mg TiO₂ per gram of composite particle was achieved when using a pH of 1.0 and the 5 µm pore size membrane for the production of the composite particles. To enable meaningful comparisons to be

made between particles of different diameters, and therefore different surface loadings of TiO_2 , the final column in Table 2 'normalises' the TiO_2 content to a particle diameter of 90 μm : i.e. the value that the TiO_2 loading would take if the particle diameter were 90 μm for each of the different types of particle, based on its current loading and particle size. It is clear that the most effective composite particles are those produced using hexane added to the cocoa butter and injected into a suspension of TiO_2 at a pH of 1.0 with silver nitrate present.

The rate of decolourization of the dye solution using the composite particles based on the cocoa butter particles, doped with silver, appeared to be faster than that obtained from the sunflower oil system. When using 1 gram of composite particles for the decolourization the floating particles completely covered the surface of the Petri dish, providing a layer that may reflect the UV radiation. Therefore, reduced masses of particles were also tested, providing differing levels of surface area coverage. Under these circumstances it was difficult to assess the total mass of composite particles being used before the experiment started, but after it was completed all the particles were removed, filtered and dried at room temperature. Hence, the actual mass used was determined after running the experiment. The results are presented in Figure 10 and Table 3 which shows the first order rate constants. The most rapid rates of decolourization were obtained for 217 and 534 mg of composite particles, i.e. 7.8 and 19 mg of TiO_2 , and all the data was closely modelled using first order kinetics. These masses also provide much faster decolourization than when using lower quantities of particles and, more surprisingly, even when using complete surface coverage (i.e. 100% coverage at 1000 mg of composite particles or 36 mg TiO_2). Hence, it can be concluded that for a static

system (i.e. no forced convection) the most effective surface coverage to be used is in the range of 60 to 80%, and not 100%. A similar result was obtained for the sunflower oil core composite particles, which are described in Table 1.

Additional tests were performed under stirred conditions. For these tests the volume of dye solution was increased to 200 mL, so that a narrow magnetic stirrer could be positioned in the Petri dish. For these tests the mass of composite particles used was increased to 2 g, to maintain the concentration of 1 g per 100 mL of dye solution. The results are illustrated in Figure 11. Stirring definitely led to a more effective use of the photocatalytic composite particles under these particular conditions, with the time for 50% reduction in dye concentration being reduced to about 75 minutes. This is probably due to the dispersion of the particles during stirring, whereas the floating particles remain at the surface where they are most effective (as illustrated in Figure 1). However, it is clearly possible to have too many particles at the surface, leading to reflection of UV light, as illustrated in Figure 10 by the coverage data.

In the work described here the photocatalytic potential of TiO₂ composite particles was demonstrated using the dye indigo carmine even though this compound does not represent a significant threat to the environment. The sorts of recalcitrant compounds increasingly found in bodies of surface water, and in which much current concern is being focussed, are endocrine disrupting compounds such as estradiol, and agrochemicals best typified by atrazine. Both classes of compound have been shown to be oxidizable using TiO₂ in suspensions^{19,20}. The advantage of the composite particles generated by the methods described here is that the composite

floating particles can be separated from the water flow and could be recycled, and the method of production is straightforward and controllable.

In addition to having considerable potential for oxidising a variety of organic chemical species, the particles could be deployed against a variety of water borne organisms. For example it has been shown that TiO_2 is biocidal towards common bacterial contaminants of water²¹ and that the lethality of TiO_2 extends to protozoa²². Another application in which the composite particles described here may prove useful is in photocatalytically induced hydrogen production from water¹³. Other less-dense-than-water materials could be used for the composite particle core, and possibly enhance the buoyancy of the composite particles.

4. Conclusions

TiO_2 has a natural relative density considerably in excess of that of water, and even small particles will aggregate and sink unless treated to prevent this happening. The application of TiO_2 as suggested here in the form of floating photocatalytic composite particles, together with atmospheric oxygen and UV light, provides a viable method of oxidizing organic materials *in-situ*, reducing (or eliminating) the need for exogenous oxidising chemical species which may persist in the aqueous environment much longer than the short-lived species generated at the surface of the TiO_2 .

Pickering emulsions were initially prepared using an ionic composition that had previously been recommended as favouring weak flocculation of the TiO_2 particles

and enhancing the stability of Pickering emulsions. The studies reported here show that, in fact, stabilization of composite particles prepared with sunflower oil as a core, is best achieved using only citric acid, and that the resulting photocatalytic activity is higher in such cases and related to the mass of TiO_2 present in the shell. The lipid is fully enclosed inside a TiO_2 shell, and with future developments it may be possible to reduce the lipid content still further, by introducing air thus forming a foam which would result in particles with even greater buoyancy. For best stability and photocatalytic effect, TiO_2 concentration in the aqueous phase of over 3.5% w/w solids should be used when forming the composite particles, with a minimum 0.5% w/w concentration of citric acid.

The membrane emulsification process was shown here to be a highly effective method of generating floating TiO_2 composite particles. In this process composite particle size can be controlled by the membrane emulsification process and in addition, the method of production is straightforward, requires minimal energy, and generates no waste. Most importantly, it could readily be scaled up²³.

Composite particles made from cocoa butter were considerably more robust than the sunflower oil-stabilised particles. These particles displayed a decreased tendency to shed TiO_2 nanoparticles during contact with the dye, and the kinetics of the dye decolourizations were much faster. The kinetics were shown to be further enhanced by including dispersed silver particles onto the surface of the TiO_2 composite particles. The particles floated readily and could be easily separated from the subnatant water. Hence, engineering a contactor system to use the composite particles under a UV light source and to separate them for recycling and reuse would

be simplified. The incorporation of hexane into the lipid cores of particles provided an additional means of exercising control on the size, and ultimately, on the photoactivity of the composite particles produced. Another finding of operational significance is that total surface coverage by the floating photocatalytic composite particles is not necessary. In fact, 100% surface coverage was found to be detrimental to the photocatalytic effect. It seems likely that albedo effects at high surface coverage reduced the UV at the reaction interface.

The technique of membrane emulsification, used to generate the particles by the formation of Pickering emulsions, has been demonstrated to be effective in controlling the composite particle size: a Pickering emulsion with a small particle size may produce particles that sink, due to the high density of the TiO₂ mineral. Composite particles that are too large will be less stable and have a relatively low loading of the photocatalyst TiO₂, hence there is a balance and composite particles between 30 and 180 µm appear to be the most effective, when using a common lipid core to form a floating composite particle.

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References

- (1) Gaya, U.I.; Abdullah, A.H. Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems. *J. Photochem. Photobiol. C: Photochem. Rev.* **2008**, *9*, 1-12.
- (2) Shama, G.; Drott, D.W. Photocatalytically induced dye decolourisation in an unsupported thin film reactor. *Chem. Eng. Comm.* **1997**, *158*, 107-122.
- (3) Coutinho, C.A.; Gupta, V.K. Photocatalytic degradation of methyl orange using polymer-titania microcomposites. *J. Colloid Interface Sci.*, **2009**, *333*, 457-464.
- (4) Rosenberg, I.; Brock, J.R.; Heller, A. Collection optics of TiO₂ photocatalyst on hollow glass microbeads floating on oil slicks. *J. Phys. Chem.* **1992**, *96*, 3423-3428.
- (5) Berry, R.J.; Mueller, M.R. Photocatalytic decomposition of crude oil slicks using TiO₂ on a floating substrate. *Microchem. J.* **1994**, *50*, 28-32.
- (6) Machado, L.C.R.; Torchia, C.B.; Lago, R.M. Floating photocatalysts based on TiO₂ supported on high surface area exfoliated vermiculite for water decontamination. *Cat. Comm.* **2006**, *7*, 538-541.
- (7) Magalhaes, F.; Lago, R.M. Floating photocatalysts based on TiO₂ grafted on expanded polystyrene beads for the solar degradation of dyes. *Solar Energy*, **2009**, *83*, 1521-1526.

- (8) Syoufian, A.; Nakashima, K. Degradation of methylene blue in aqueous dispersion of hollow TiO₂ photocatalyst: optimization of reaction by peroxydisulfate electron scavenger. *J. Colloid Interface Sci.*, **2007**, *313*, 213-218.
- (9) Banks, M.R. Process for the Manufacture of Titania Coated Microspheres, PCT Patent Application, WO2009104011A2, **2009**.
- (10) Stillwell, M.T.; Holdich, R.G.; Kosvintsev, S.R.; Gasparini, G.; Cumming, I.W. Stirred cell membrane emulsification and factors influencing dispersion drop size and uniformity. *Ind. Eng. Chem. Res.* **2007**, *46*, 965-972.
- (11) Arditty, S.; Whitby, C.P.; Binks, B.P.; Schmitt, V.; Leal-Calderon, F. Some general features of limited coalescence in solid-stabilized emulsions. *Eur. Phys. J. E.*, **2003**, *11*, 273-281.
- (12) Guettai, N.; Ait Amar, H. Photocatalytic oxidation of methyl orange in presence of titanium dioxide in aqueous suspension. Part II: kinetics study, *Desalination*, **2005** *185*, 439-448.
- (13) Ni, M.; Leung, M.K.H.; Leung, D.Y.C.; Sumathy, K. A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production. *Renewable and Sustainable Energy Reviews*, **2007**, *11*, 401-425.

(14) Frith, W.J.; Pichot, R.; Kirkland, M.; Wolf, B. Formation, stability and rheology of particle stabilized emulsions: influence of multivalent cations. *Ind. Eng. Chem. Res.*, **2008**, *47*, 6434–6444.

(15) Di Giovanni B.A.; Mahdi F.M.; Starov V.M.; Holdich R.G. Particulate clusters and permeability in porous media, *in press*, *Chem. Eng. Res. Des, Part A*, **2011**, <http://dx.doi.org/10.1016/j.cherd.2011.11.019>.

(16) Devi, L.G.; Reddy, K.M. Enhanced photocatalytic activity of silver metallized TiO₂ particles in the degradation of an azo dye methyl orange: Characterization and activity at different pH values. *Applied Surface Science*, **2010**, *256*, 3116–3121.

(17) Szabo-Bardos, E.; Czili, H.; Hovarth, A. Photocatalytic oxidation of oxalic acid enhanced by silver deposition on a TiO₂ surface. *Journal of Photochemistry and Photobiology A: Chemistry*, **2003**, *154*, 195-201.

(18) Wu, T.; Lin, T.; Zhao, J.; Hidaka, H.; Serpone, N. TiO₂ Assisted photodegradation of dyes. 9. Photooxidation of a squarylium cyanine dye in aqueous dispersions under visible light irradiation, *Environ. Sci. Technol.*, **1999**, *33*, 1379-1387.

(19) Farré, M.F.; Franch, M.I.; Malato, S.; Ayllón, J.A.; Peral, J.; Doménech, X. Degradation of some biorecalcitrant pesticides by homogeneous and heterogeneous photocatalytic ozonation. *Chemosphere*, **2005**, *58*, 1127-1133.

- (20) Mai, J.; Sun, W.; Xiong, L.; Liu, Y.; Ni, J. Titanium dioxide mediated photocatalytic degradation of 17 β -estradiol in aqueous solution. *Chemosphere*, **2008**, 73, 600-606.
- (21) Biguzzi, M.; Shama, G. Effect of titanium-dioxide concentration on the survival of *Pseudomonas stutzeri* during irradiation with near-ultraviolet light. *Lett. Appl. Microbiol.*, **1994**, 19, 458-460.
- (22) Sokmen, M.; Degerli, S.; Aslan, A. Photocatalytic disinfection of *Giardia intestinalis* and *Acanthamoeba castellanii* cysts in water. *Exp. Parasitol.*, **2008**, 119, 44-48.
- (23) Holdich, R.G.; Dragosavac, M.M.; Vladisavljevic, G.; Kosvintsev, S.R. Membrane Emulsification with Oscillating and Stationary Membranes. *Ind. Eng. Chem. Res.*, **2010**, 49, 3810-3817.

Table 1 Floating composite TiO₂ particle size distributions and dispersity after formation and after washing when using citric acid and various masses of TiO₂ suspended in water during the emulsification of sunflower oil through a 5 micron membrane

TiO ₂ used in slurry	After formation – before washing				After washing			
	D10	Median size	D90	Span	D10	Median size	D90	Span
w/w %	(µm)	(µm)	(µm)		(µm)	(µm)	(µm)	
2	79	111	152	0.66	70	95	128	0.61
3	84	123	178	0.76	83	117	164	0.69
3.5	73	100	138	0.65	73	100	139	0.66
5.2	73	94	123	0.53	70	94	126	0.60
8.5	68	94	135	0.71	67	95	138	0.75

Table 2 Properties of composite TiO₂ particles when using cocoa butter as the core phase

Conditions under which composite particles were formed	Median particle diameter (µm)	Mass TiO ₂ per gram of composite particles (mg/g)	Surface area of TiO ₂ in composite particle (m ² /g)	Specific surface area per unit volume (µm ⁻¹)	Normalising to a 90 µm particle mass of TiO ₂ (mg/g)
Silver nitrate and oxalic acid at a pH of 2.56, using a 14 µm membrane	330	Range: 5.8 to 6.8; mid value: 6.3	0.34	0.018	24
Citric acid with the addition of hexane at a pH of 2.1, using a 14 µm membrane	98	Range: 9.4 to 12.8; mid value: 11.2	0.59	0.061	12
Silver nitrate with the addition of hexane and oxalic acid at a pH of 2.56, using a 14 µm membrane	90	Range: 10.3 to 14.5; mid value: 12.4	0.66	0.067	13
Silver nitrate with the addition of hexane and oxalic acid at a pH of 1.0, using a 14 µm membrane	86	Range: 16.7 to 17.1; mid value: 16.9	0.9	0.070	16
Silver nitrate with the addition of hexane and oxalic acid at a pH of 1.0, using a 5 µm membrane	76	Range: 33.6 to 37.7; mid value: 35.7	1.9	0.079	30

Table 3 First order rate constants for decolourization of dye solution with composite particles prepared using cocoa butter with hexane, silver nitrate and TiO₂

Mass of Composite Particles (mg)	Rate Constant (min⁻¹)	Correlation Coefficient (R²)
48	0.0057	0.9301
69	0.0031	0.9893
217	0.0254	0.9898
534	0.0531	0.9572
1000	0.0052	0.9952

Figure Captions

- Fig. 1. Schematic diagram of floating composite TiO₂ composite particles and their action forming free radicals to decompose organic matter
- Fig. 2. Floating composite particle size distribution formed using three shear rates at the membrane surface and a 14 micron pore sized membrane: sunflower oil is the composite particle core
- Fig. 3. Floating composite particle size distribution formed using three shear rates at the membrane surface and a 5 micron pore sized membrane: sunflower oil is the composite particle core
- Fig. 4. Control tests: minimal dye decolourization using sunflower oil as the composite particle core in the absence of UV light and any composite particles
- Fig. 5. Decolourisation of blue dye using floating composite TiO₂ particles made using a TiO₂ suspension with sodium and lanthanum nitrates and citric acid present at different surface coverage of the particles: sunflower oil is the composite particle core; the mass of TiO₂ recovered at the end of the experiment is included in the key
- Fig. 6. Scanning electron microscope image of P25 titanium dioxide
- Fig. 7. Optical microscope image of the size range of composite particles

produced (50 to 180 microns) and illustrating the spherical nature of the composite particles; cocoa butter used as the core material and P25 titanium dioxide as the shell

- Fig. 8. Composite particles produced using cocoa butter, silver nitrate, oxalic acid and TiO_2 at a pH of 2.56 and using the 14 μm pore size membrane, with and without hexane usage, 1 g of particles in 100 mL and 10 ppm dye
- Fig. 9. Zeta potential of the TiO_2 composite particles in a continuous phase solution of silver nitrate and oxalic acid similar to what was used in forming the Pickering emulsion
- Fig. 10. Various masses of composite particles used and the apparent surface coverage of the floating particles: particles produced using cocoa butter with hexane, silver nitrate, oxalic acid and TiO_2 at a pH of 1 and the 5 μm pore size membrane, 1 g of particles in 100 mL and 10 ppm dye
- Fig. 11. Influence of stirring when decolourising 200 mL of dye at 10 ppm using 2 g of composite particles using cocoa butter with hexane, silver nitrate, oxalic acid and TiO_2 at a pH of 1 and the 5 μm pore size membrane

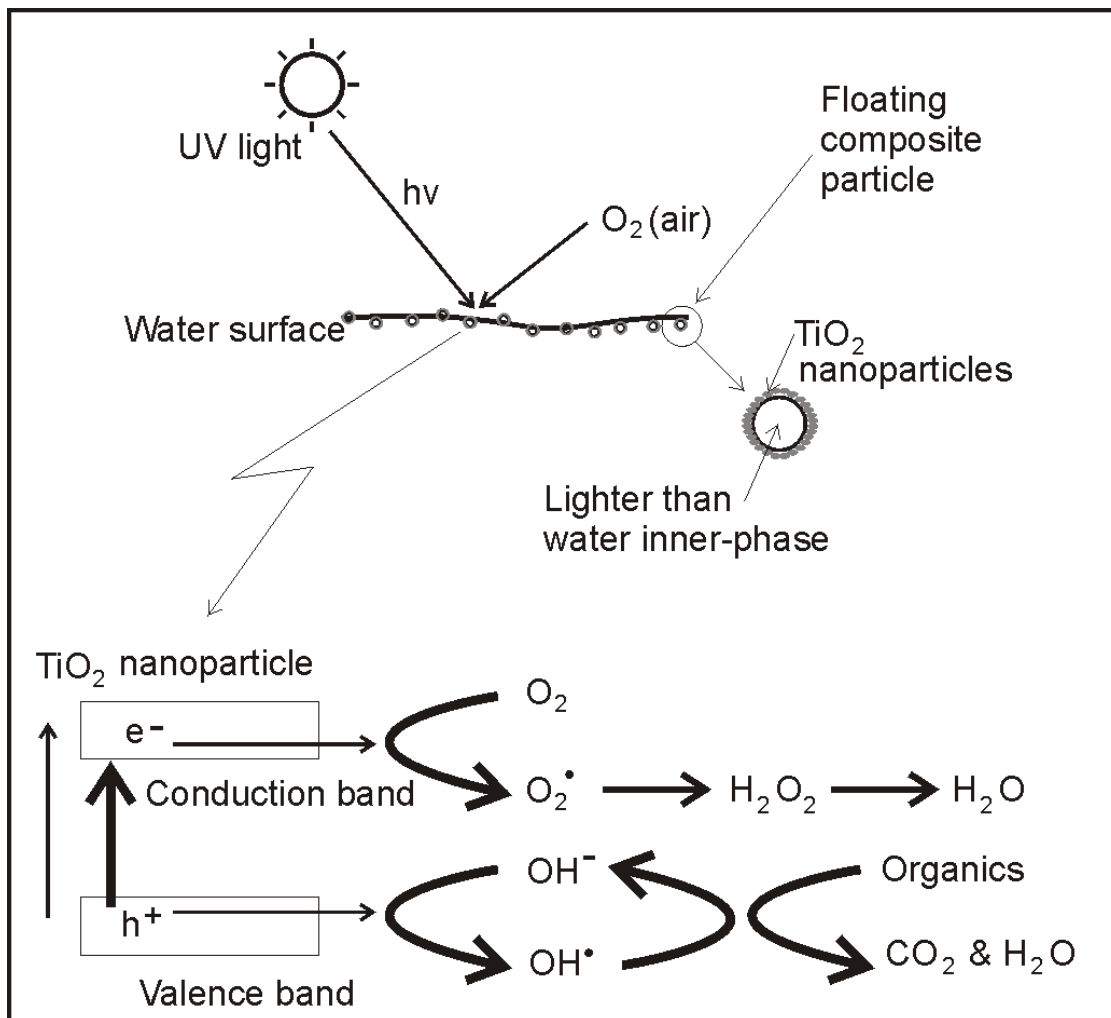


Fig. 1. Schematic diagram of floating composite TiO₂ particles and their action forming free radicals to decompose organic matter

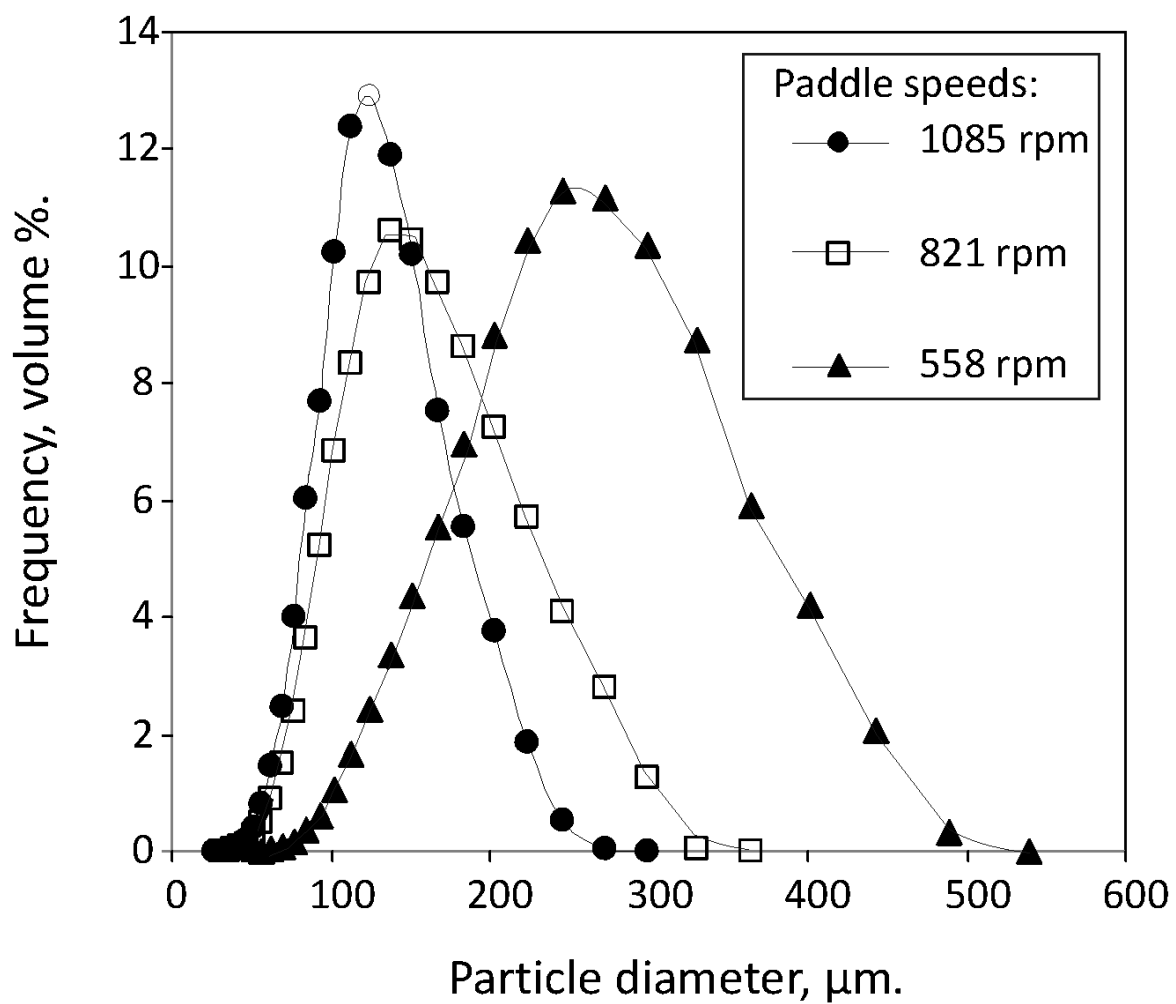


Fig. 2. Floating composite particle size distribution formed using three shear rates at the membrane surface and a 14 micron pore sized membrane: sunflower oil is the composite particle core

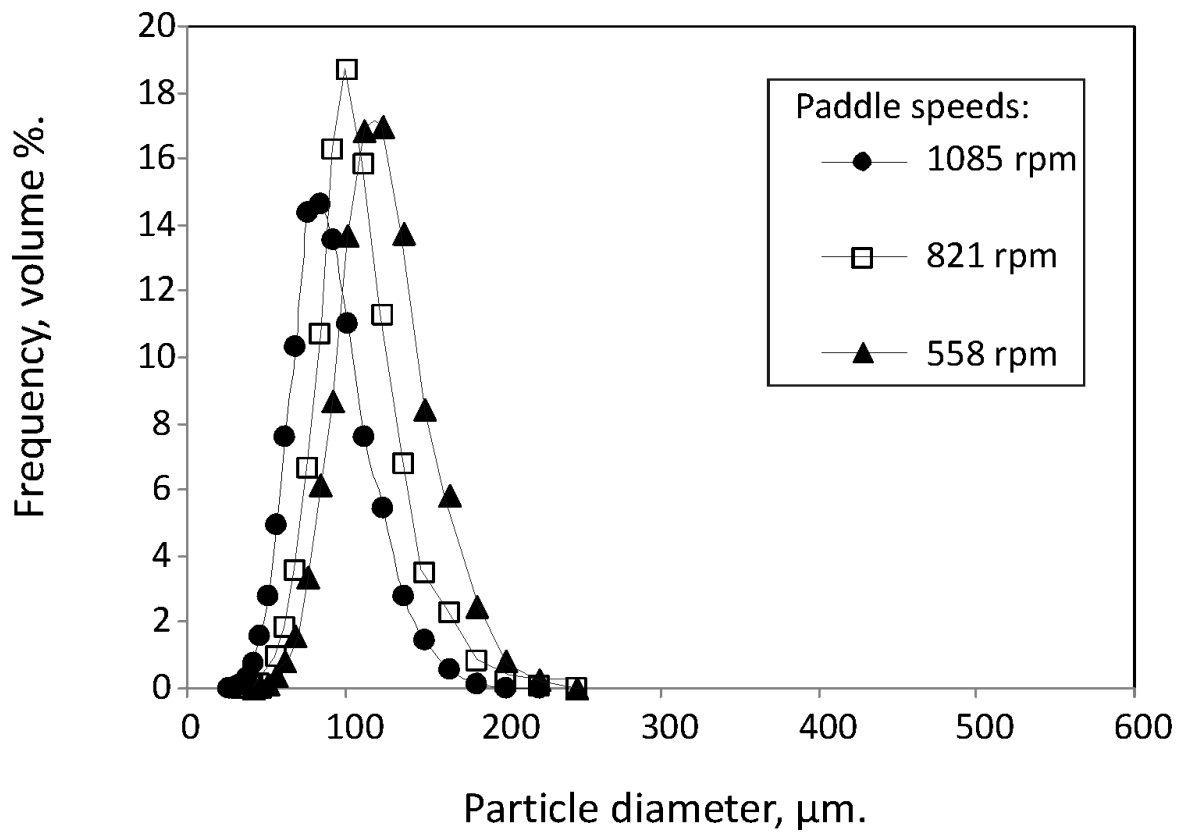


Fig. 3. Floating composite particle size distribution formed using three shear rates at the membrane surface and a 5 micron pore sized membrane: sunflower oil is the composite particle core

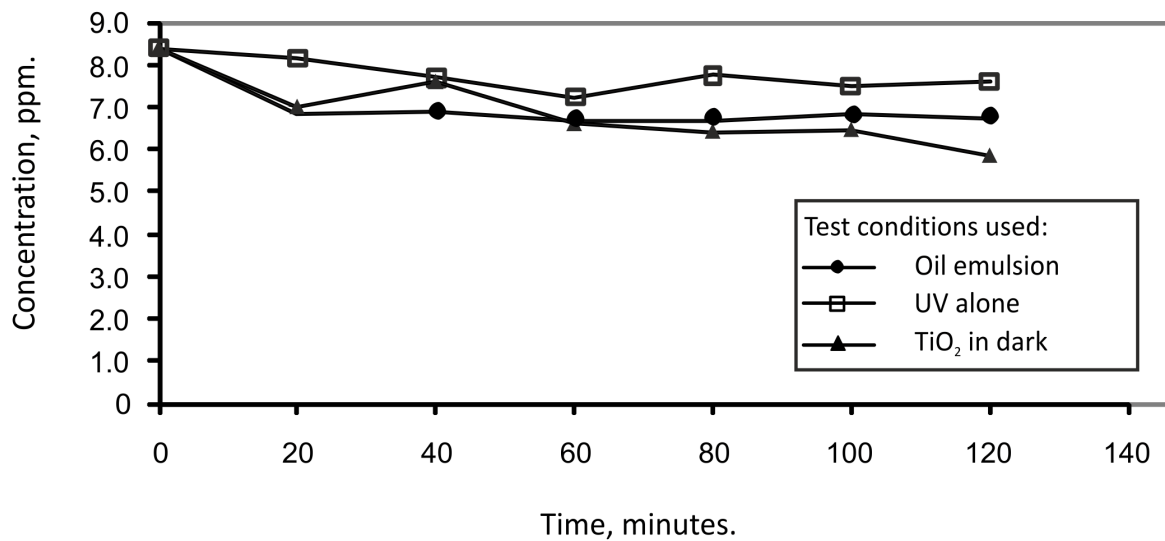


Fig. 4. Control tests: minimal dye decolourization using sunflower oil as the composite particle core in the absence of UV light and any composite particles

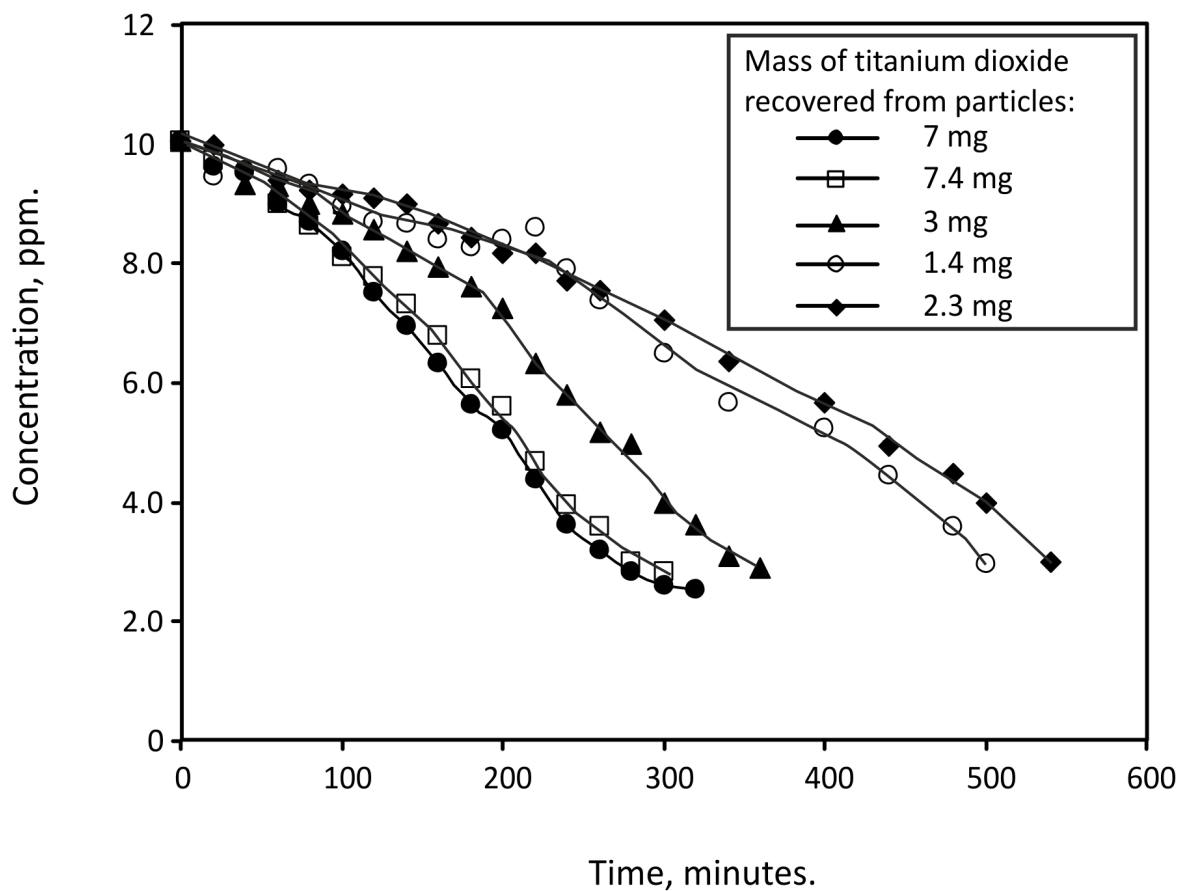


Fig. 5. Decolourisation of blue dye using floating composite TiO_2 particles made using a TiO_2 suspension with sodium and lanthanum nitrates and citric acid present at different surface coverage of the particles: sunflower oil is the composite particle core; the mass of TiO_2 recovered at the end of the experiment is included in the key

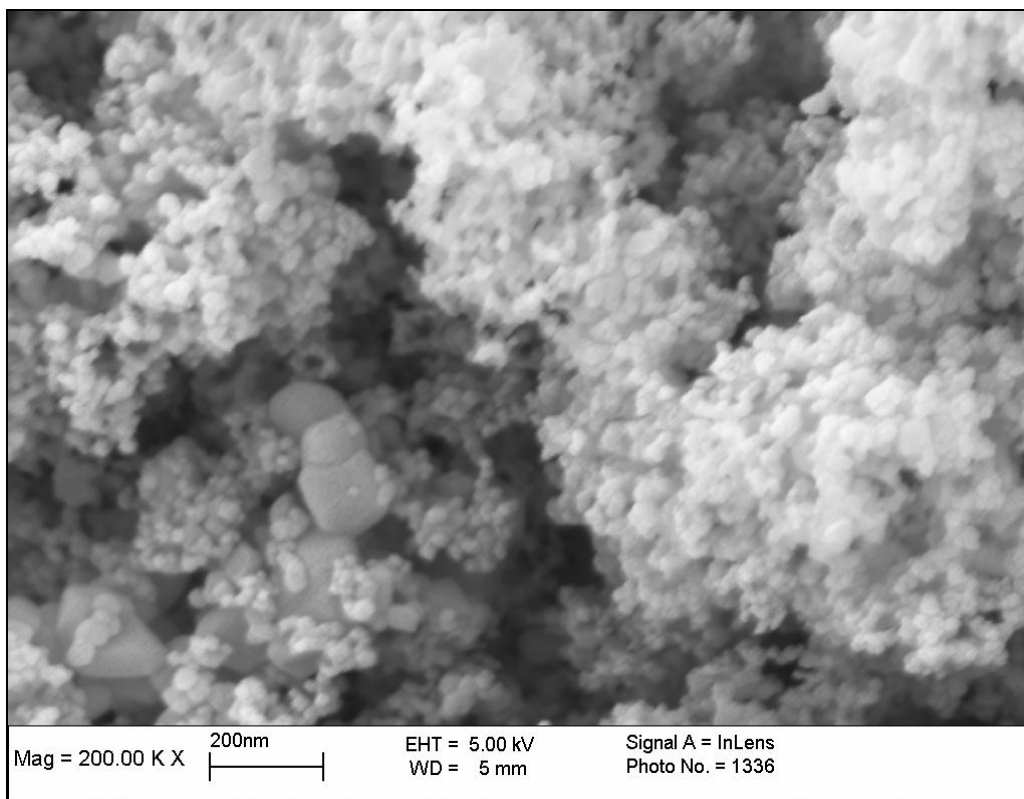


Fig. 6 Scanning electron microscope image of P25 titanium dioxide

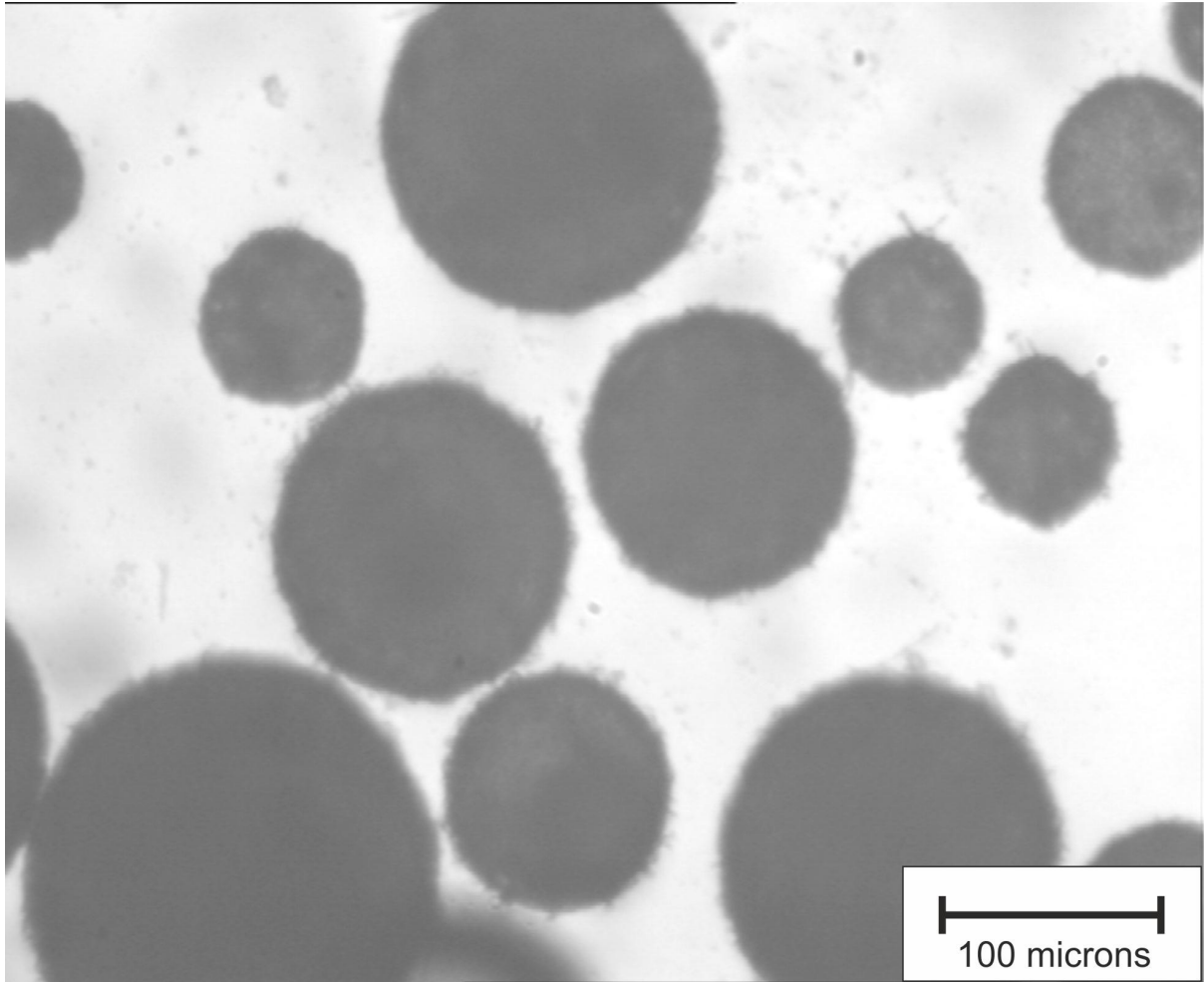


Fig. 7. Optical microscope image of the size range of composite particles produced (50 to 180 microns) and illustrating the spherical nature of the composite particles; cocoa butter used as the core material and P25 titanium dioxide as the shell

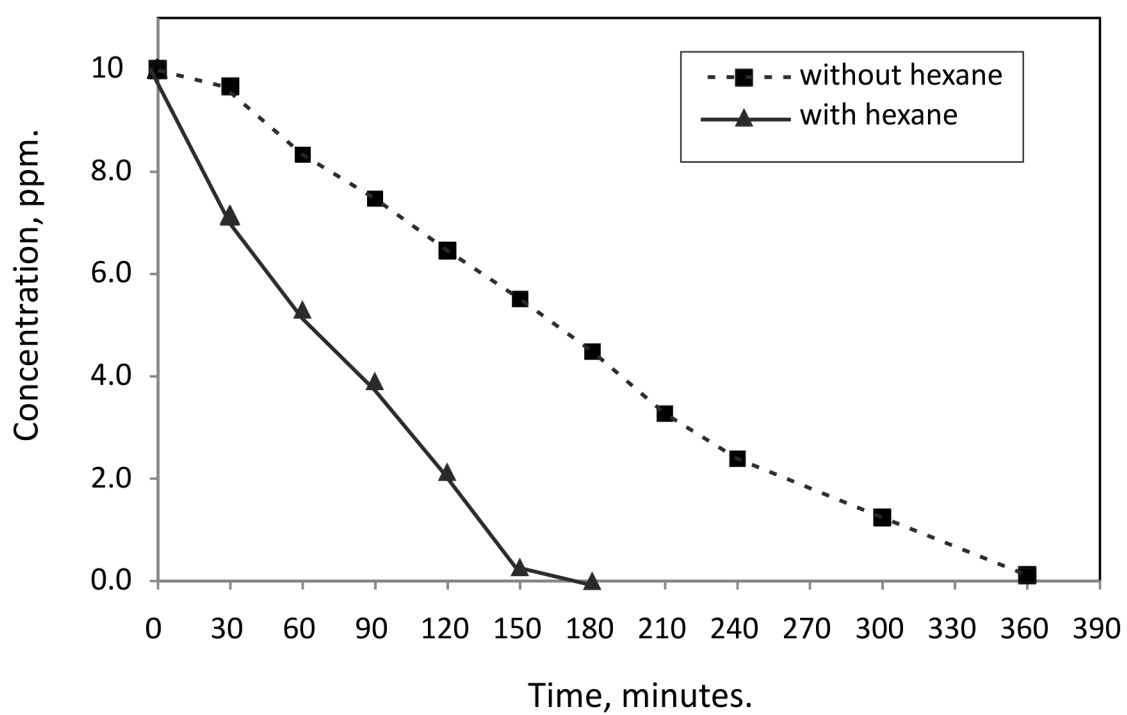


Fig. 8. Composite particles produced using cocoa butter, silver nitrate, oxalic acid and TiO_2 at a pH of 2.56 and using the 14 μm pore size membrane, with and without hexane usage, 1 g of particles in 100 mL and 10 ppm dye

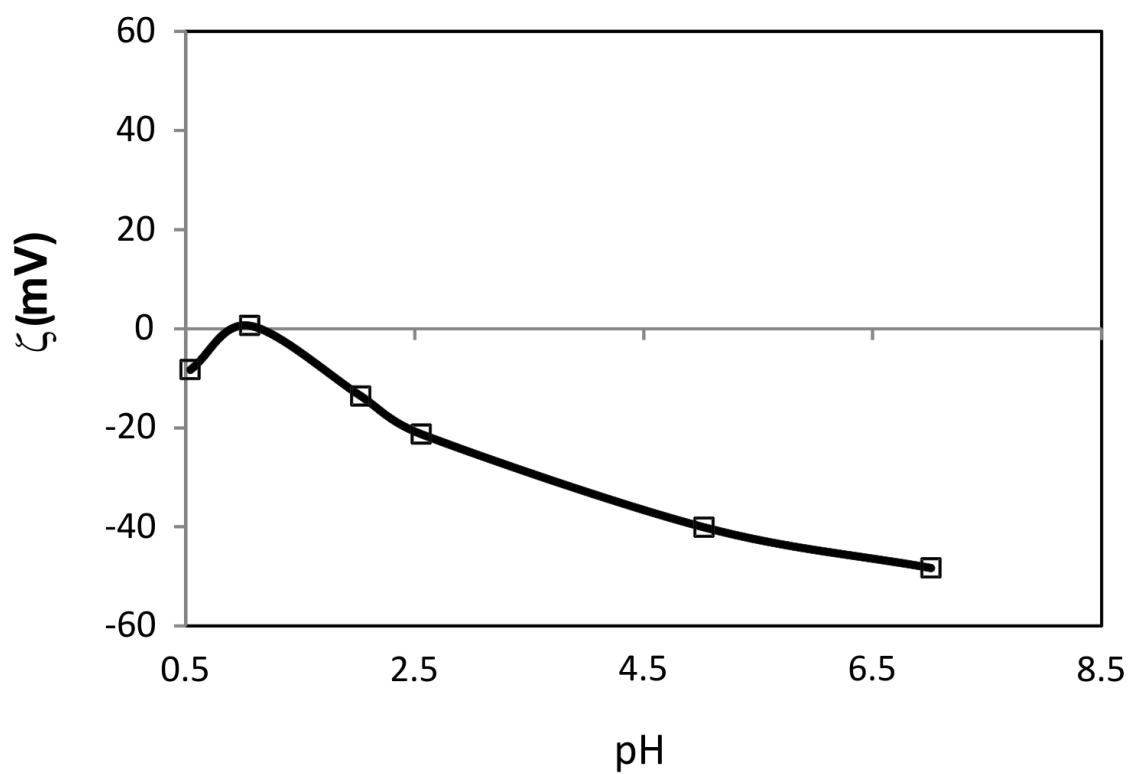


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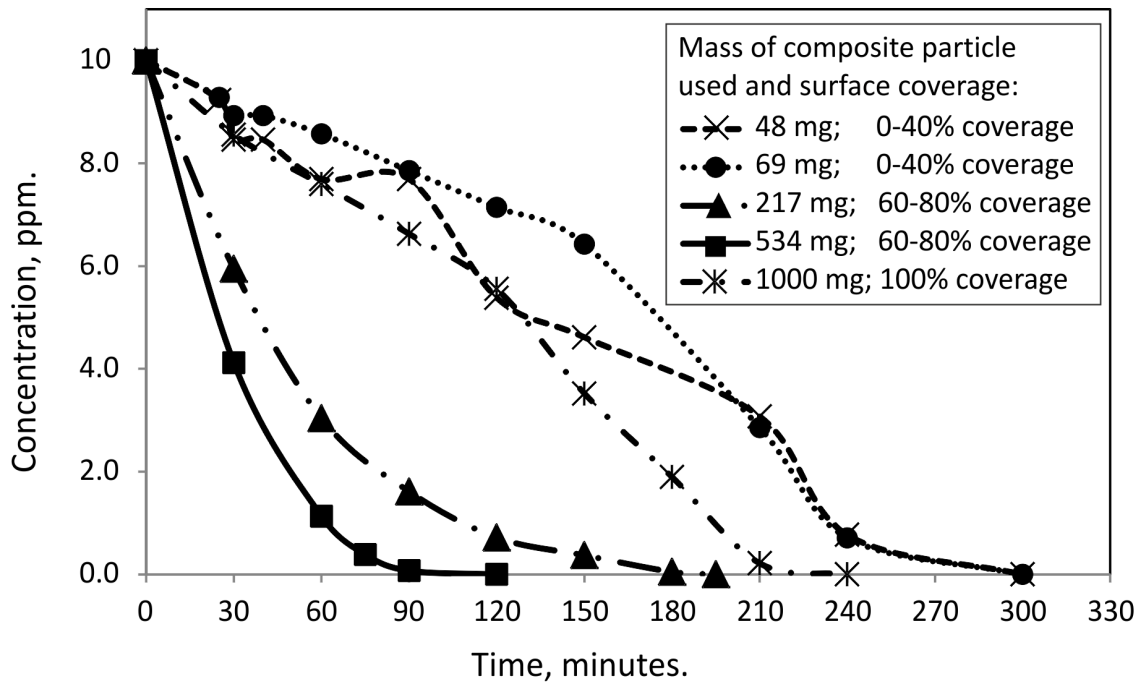


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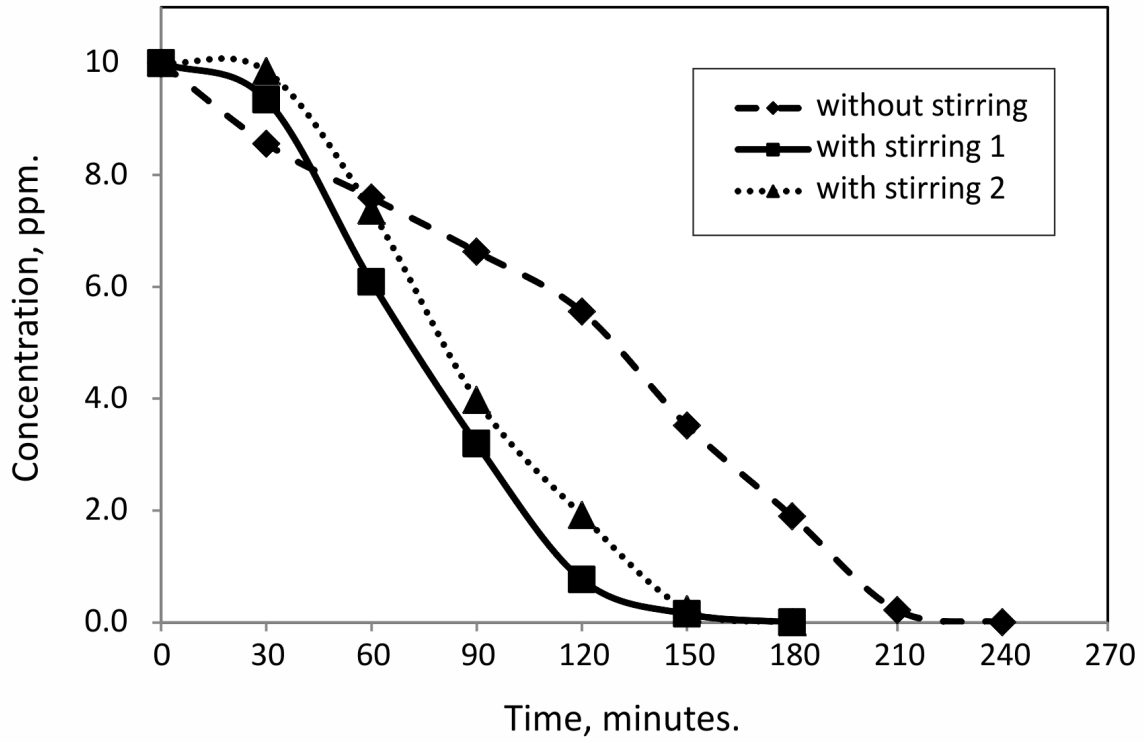


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