O 2. A COMPARATIVE STUDY TO ENHANCE THE PHOTOCATALYTIC ACTIVITY OF PICKERING EMULSIONS STABILIZED WITH DIFFERENT SURFACE-MODIFIED TITANIUM DIOXIDES VIA MEMBRANE EMULSIFICATION WAY

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ABSTRACT: This study is based on the application of surface-modified TiO2 to stabilize Pickering emulsions (PE) and then to be used in photocatalytic system for degradation of indigo carmine dye. Number of the reactive sites on the TiO2 surface plays an important role on the performance of photocatalytic degradation. Due to this theory, the aim must be to increase the amount of TiO2 nanoparticles adsorbed on the water/oil interface thereby creating stabilization of PE. In this regard, TiO2 were modified using various types of organic acids such as salicylic, benzoic, and citric acids to investigate their effects on photocatalytic reaction efficiency and kinetics. Instead of conventional emulsification technologies, membrane emulsification method was used to prepare PE which enables the homogeneous particle size distribution. The bonding structure and surface properties of the particles along with the degradation efficiency of indigo carmine dye were investigated to assess the effect of the surface modification of TiO2 on the photocatalytic activity of the PE-based system in terms of types of oil phase and organic acid. Additionally, the efficiencies of PE and bare surface-modified TiO2 were compared to understand the advantage of PE. Characterization of surface modified TiO2 was performed using TGA, BET, DSC, FTIR, XRD, and SEM analyses. It is found that surface modified particles help to achieve better degradation percentages rather than bare TiO2. According to the results, olive oil based composite particles stabilized with salicylic acid-TiO2 provided the best promising result as a 78% dye removal.

***Keywords**: Pickering Emulsion, Surface Modification, Dye Decolorization, Water Treatment, Photocatalytic Degradation.*

1. INTRODUCTION

Decrement in water resources and increase in the amount of wastewater generated by various industrial activities have become an environmental problem that has become very important in recent years. The accumulation of the textile dyes is increasing day by day with the industrial growth in the last century. It has significance to treat wastewater containing harmful substances for human health like carcinogenicity, toxicity and bioaccumulation. Especially textile industry causes the accumulation of some of major contaminants as polycyclic aromatic hydrocarbons. There are many treatment methods for decolorization of wastewater. Among these methods, photocatalytic degradation makes possible the dye to be discolored by sunlight or UV light. Indigo Carmine (IC) Dye is one of used textile azo dye in the industry which has serious environmental concern. Up to 30% of the used dye is released in wastewater effluents, and a large portion of the consumed dyes are azo dyes which are generally as a highly toxic class of IC (Harrache, et al., 2019).

TiO_2 has ability to degrade the organic and inorganic pollutants from water by photodegradation. The properties of TiO_2 which make it an attractive and effective photocatalyst are non-toxicity, desirable thermal and chemical stability, chemical and biological inertness, high photosensitivity, and relatively low cost production (Chattopadhyay et al., 2012; Mekprasart et al., 2012; Atar et al., 2014; Nawaz et al., 2017). Large surface area of TiO_2 causes increment in adsorption-desorption sites of catalyst which enables effective transport channels for reactant molecules. Furthermore, crystallinity, provides generation of electron hole pairs in the bulk and surface of TiO_2. That is why, it can be concluded that, crystal nanostructure which has large surface area is wanted combination for the process (Nawaz et al., 2017). Photocatalytic degradation using TiO_2 is used to degrade organic contaminants due to the leading extremely active reactive oxygen types as photo- generated hole (h+) and hydroxyl radicals ($\cdot OH$) under irradiation of solar light as demonstrated in Figure 1. Photocatalytic degradation owns a lot of benefits counted as minimum cost, straightforward operation, superior catalytic yield, full oxidation performance, low energy consumption, and no secondary contaminants formation after degradation (Ding et al., 2016; Katsumata et al., 2013).

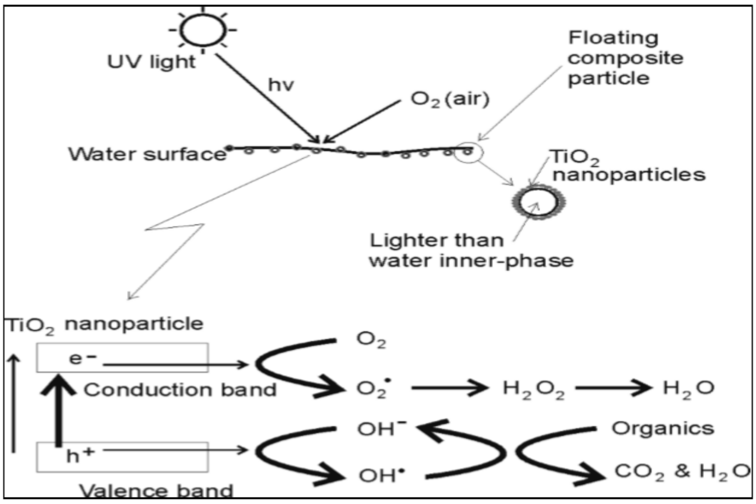

Figure 1. Schematic of composite TiO_2 forming free radicals to decompose organic matter (Holdich et al., 2012).

In this study, Pickering emulsions which are stabilized using fine solid particles were produced applying membrane emulsification method. This technique is a relatively new technique attempting to improve on traditional emulsification methods by producing each droplet singly, as required. There are lots of advantages which are required less energy, no necessary any additional chemical materials, high effectiveness of separation, enlarging easily and constant operation. By using the membrane emulsification method, emulsions of the desired size are achieved by passing the dispersed phase through the pores of a microporous membrane into the continuous phase with the aid of pressure (Drioli and Giorno, 2009). Stabilization of interface between two immiscible phases by solid colloidal particles, such as TiO_2 decreases and eliminates synthetically surfactants (Kasiri & Fathi, 2018).
The purpose of this study was to stabilize the surface of the oil droplets by surface modified TiO_2 nanoparticles. To achieve this adsorption at the surface, TiO_2 nanoparticles were modified using salicylic, benzoic, citric acids. The resulting nanoparticles were applied to generate Pickering emulsions by membrane emulsification. The photocatalytic assessment of those composite particles was investigated as a function of weak acid and oil types.

2. MATERIAL AND METHOD

2.1 Materials

The anatase TiO_2 powder (Degussa P25) was obtained from Sigma-Aldrich, that owns mean particle size of 21 nm, more than 99.5% purity on trace metal basis, 50 m^2/g surface area. Olive oil (Local Market; Migros) and safflower oil (Feliz) were bought from local markets. Oleic acid was purchased from Sigma Aldrich (>99% purity GC). Surface Modification of TiO_2 was carried out using salicylic acid (SA) (Merck), benzoic acid (BA) (Merck), and citric acid (CA) (Merck ≥99.5%). indigo carmine dye (Sigma Aldrich), acetone (Merck, analysis grade), and ethanol (Merck, analysis grade) were also used for the tests.

2.2 Surface Modification of TiO_2

The procedure explained by Nawaz et al., 2017 was followed for the surface modification of TiO_2. The obtained solution was filtered through a filter paper. After that filter cake was washed with water repeatedly until pH reaches to 5.5-6.5 and then heat-treated at 105°C for 30 min.

2.3 Characterization of Surface Modified TiO_2 Nano Particles

The morphologies of nanoparticles were investigated by scanning electron microscopy (SEM) (Jeol 6510, Japan). The BET surface areas were obtained using Quantachrome Autosorb IQ2 instrument

(Quantochrome, USA). X-Ray diffraction (XRD) was utilized to determine the crystallinity of the pure TiO_2 and BA-TiO_2 composite nanoparticles using Rigaku Smart lab, Japan with Cu Kβ radiation and a scanning range of 10-80˚.

2.4 Preparation of Pickering Emulsion

The floating photocatalytic composite particles stabilized with SA-TiO_2, BA-TiO_2 and CA-TiO_2 were prepared by membrane emulsification and Pickering emulsion methods in a stirring cell equipped with the membrane. This system as shown in Figure 2 involves a mechanical stirrer, a glass reservoir with a volume of 150 mL, and a hydrophilic flat nickel porous membrane with a diameter of 3.4 cm and a pore size of 14µm supplied from Micropore Technologies Ltd. (Loughborough, U.K.).

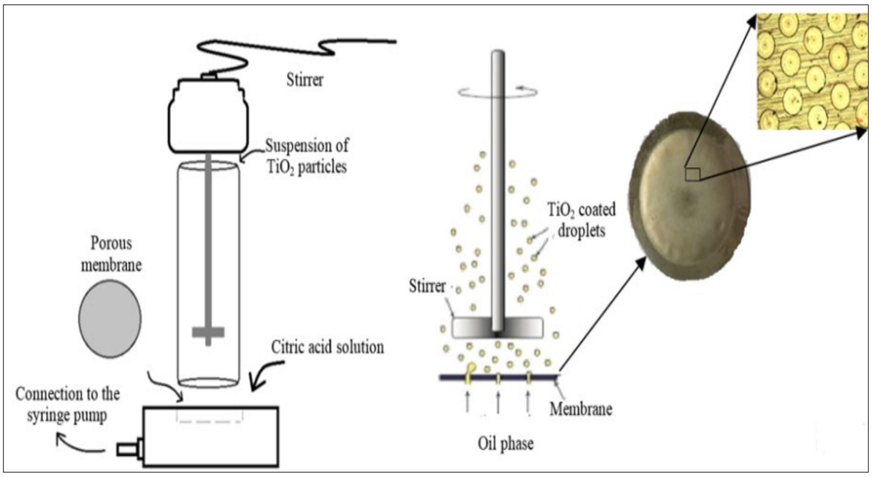

Figure 2. Dispersion cell and nickel porous membrane (Gasparini et al., 2008)

A dispersed phase is injected through a microporous flat membrane by using a syringe pump into a continuous phase, aqueous phase, to obtain floating Pickering. Oil phase which is dispersed as olive oil, oleic acid and safflower oil into the microporous membrane and continuous phase which consist of surface modified TiO_2 particles to able to stabilize the core phase. 10 mL of oil phase were injected at a rate of 5 mL/min through the membrane through the base of the cell using syringe pump. At the second stage, the droplets were conditioned by mixing for 30 min at 2 V to avoid any agglomeration. Finally, Pickering emulsions were left to be settle down for several hours so that three phases were observed as the layer of foating composite particles, aqueous phase, and surface modified TiO_2 nanoparticles.

2.5 Characterization of Pickering Emulsions

To figure out the amount of TiO_2 that was effectively coated on oil droplets, ash test was performed by a stepwise heat treatment in a muffle furnace (Mikrotek). Droplet size measurements of Pickering emulsions were conducted by using a Nikon Eclipse LV150N Optical Microscope.

Photocatalytic Degradation Tests

For each experiment, two duplicates of 200 mL indigo carmine dye solution were located uncovered beneath a tubular “black light blue” source (Philips 18 W/08 BLB ISL), emitting at 365 nm, in order to benefit effectively from the tubular UV. Each experiment was carried out for 180 minutes at room temperature Samples were filtered through 0.2 mM cellulose filter. Once the photocatalyctic degredation experiments were completed, concentration of the samples were determined by a spectrophotometer (Shimadzu, UV 1800 model) at a maximum wavelength of 610 nm.

3. RESEARCH FINDINGS

3.1. Characterization of Composite Particles

The SEM images of BA, SA and CA have showed no difference in morphology. However, SA-TiO_2 and CA-TiO_2 particles were observed bigger comparing to TiO_2 and BA-TiO_2 as illustrated in Figure 3. The BET surface areas, which were obtained using the BJH adsorption-desorption method of BA-TiO_2 and TiO_2

were found as 35.98 m^2/g and 53.2 m^2/g (Holdich et al., 2012) respectively as it is expected. The pore size and pore volume of BA-TiO_2 were found to be 188.64 A° and 0.34 cm^3/g, respectively. Modification of TiO_2 with BA did not affect the crystallinity of TiO_2, and the characteristics peaks for the anatase phase were preserved (Figure 4).

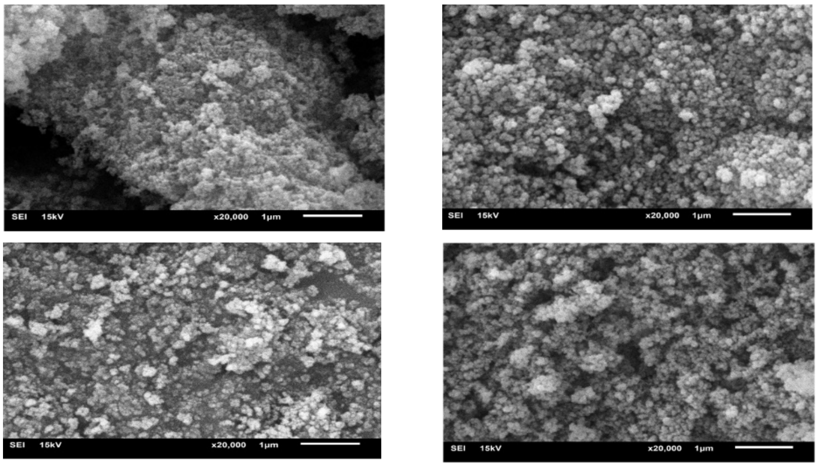

Figure 3. SEM images of (A) BA-TiO_2, (B) SA-TiO_2, (C) CA-TiO_2 and (D) pure TiO_2

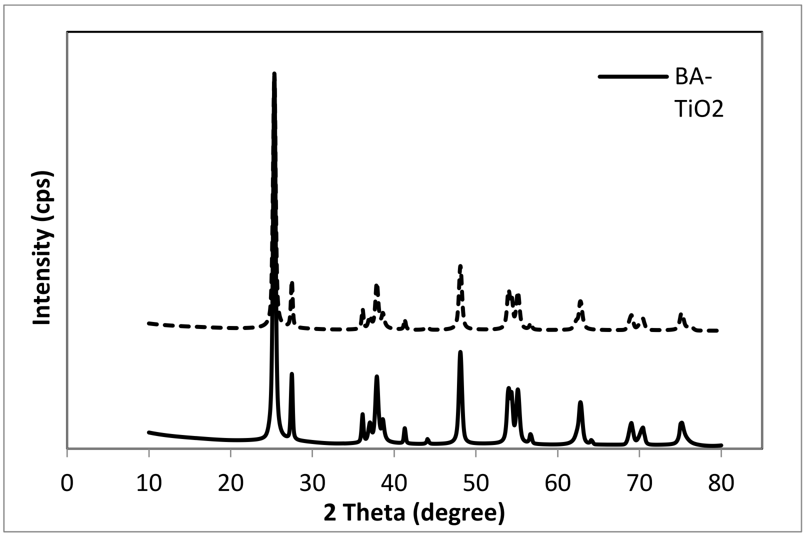

Figure 4. X-Ray diffraction pattern of TiO_2

3.2 Evaluation of Pickering Emulsions

Floating composite particles were generated using membrane emulsification and Pickering emulsions ways to obtain the droplets with homogeneous size distribution. The highest amount of TiO_2 adsorbed on TiO_2 surface was achived using oleic acid due to the highest amount of oleic acid among the other oils.

Table 1. Properties of surface modified TiO_2 coated composite particles

Core Phase	**Continuous Phase**	**CompositeParticle Median Diameter (µm)**	**TiO_2 Coated (mg/g)**
Oleic Acid	0.5 g BA-TiO_2- 2 g CA	77	13.43
Safflower Oil	0.5 g BA-TiO_2- 2 g CA	126	11.05
Olive Oil	0.5 g BA-TiO_2- 2 g CA	126	5.69

3.3 Assessment of Photocatalytic Degradation

To observe the effect of weak acid type SA, BA, and CA were used for surface modification of TiO_2. Figure 5 illustrates all weak acid types enable dye removal percentage as 78 % and 65 % for SA and BA, respectively. It can be said that, due to having more coated TiO_2 SA provided higher percentage compared to others.

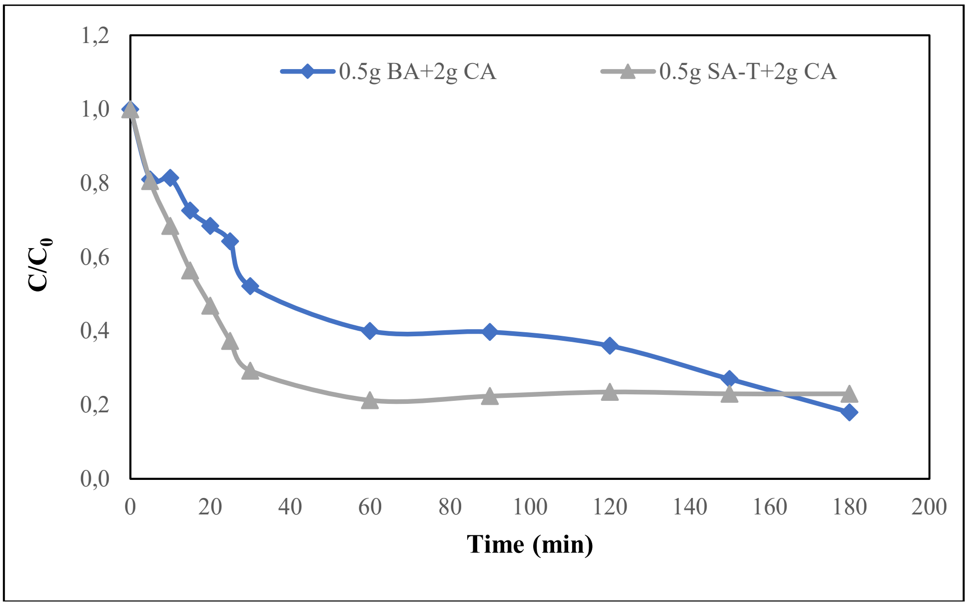

Figure 5. Effect of modifying agents (Dispersed phase: olive oil)

The effect of particle cores on photocatalytic degradation of IC is illustrated in Figure 6. According to the results, the maximum degradation of dye was reached with the safflower oil /BA-TiO_2 composite particle due to the high amount of TiO_2 coated. The less degradation was obtained for oleic acid. It is expected that, amount of higher coated TiO_2 results grater degreadation results as observed for safflower oil.

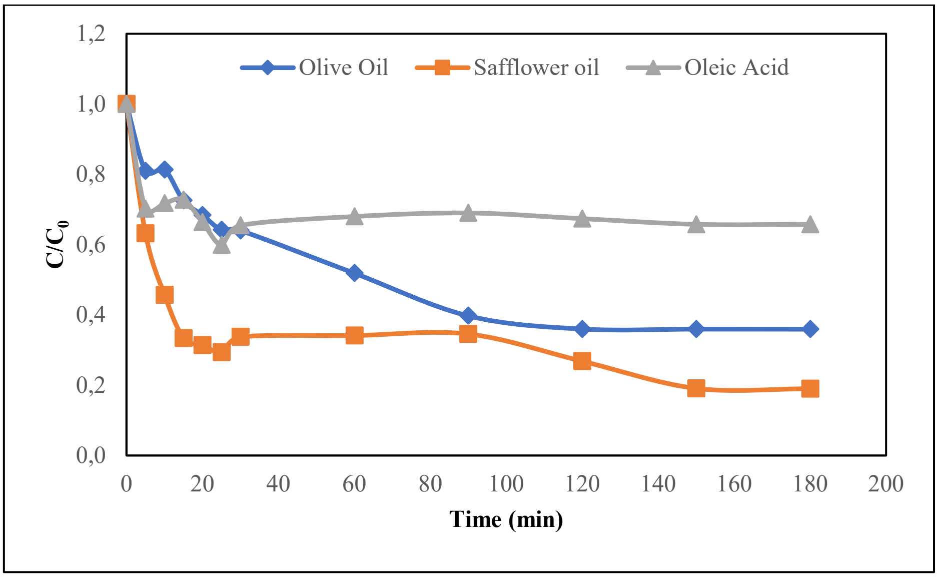

Figure 7. Effect of oil type (Conditions: 0.5 BA-TiO_2 + 2g CA)

4. CONCLUSIONS AND DISCUSSION

Surface modification of TiO_2 leads increment of the photocatalytic efficiency of composite nanoparticles. The amount of TiO2 getting higher leads the degradation of IC dye improvement. It is proved that surface modification leads greater amount of coated TiO_2 . Best dye removal was obtained for 0.5 g SA-TiO2+ 2g CA as 78 %. Regarding results and acids characteristics, higher OH numbers leads higher coated TiO_2 amount and this enables greater dye removal percentage.

REFERENCES

Atar, N., Eren, T., and Yola, M., 2014, Novel efficient photocatalyst based on TiO2 nanoparticles involved boron enrichment waste for photocatalyctic degradation of atrazine, *Chemical Engineering Journal,* 250, 288-294.

Chattopadhyay, K., Maiti , S., Maiti, U., Rana, T., and Thapa, R., 2012, Anatase titanium dioxide nanoparticles synthesis via simple hydrothermal route: Degradation of Orange II, Methyl Orange and Rhodamine B, *Journal of Molecular Catalysis A: Chemical*, 363, 223-229.

Ding, Y., Zhou, P., and Tang, H., 2016, Visible-light photocatalyctic degradation of bisphenol A $NaBiO_3$ nanosheets in a wide pH range: a synergistic effect between photocatalyctic oxidation and chemical oxidation. *Chemical Engineering Journal*, 291, 149-160.

Drioli, A., and Giorno, L., 2009, *Membrane Operations Wiley VCH*, 463-488.

Gasparini, G., Holdich, R., and Kostvintsev, S., 2008, Membrane emulsification: droplet size and uniformity in the absence of surface shear, *Journal of Membrane Science,* 312, 182-189.

Harrache, Z., Abbas, M., Aksil , T., and Trari, M., 2019, Thermodynamic and kinetic studies on adsorption of Indigo Carmine from aqueous solution by activated carbon, 144, 180-189.

Holdich, R., İpek, İ., Lazrigh, M., and Shama, G., 2012, Production and evaluation of floating photocatalytic composite particles formed using pickering emulsions and membrane emulsification, *Industrial and Engineering Chemistry Research* , 51, 12509-12516.

Kasiri , N., and Fathi, M., 2018, Production of cellulose nanocrystals from pistachio shells and their application for stabilizing Pickering emulsions, *International Journal of Biological Macromolecules*, 106,1023-1031.

Katsumata, H., Taniguchi, M., Kaneco, S., and Suzuki, T., 2013. Photocatalyctic degradation of bisphenol A by Ag3PO4 under visible light, *Catalysis Communications,* 34, 30-34.

Mekprasat, W., Pecharapa, W., and Vittayakorni, N., 2012, Ball-milled CuPc/TiO2 hybrid nanocomposite and its photocatalyctic degradation of aqueous Rhodamine B, *Materials Research Bulletin*, 47, 3114-3119.

Nawaz, M., Miran, W., Jang, J., and Sung Lee, D., 2017, Stabilization of Pickering emulsion with surface-modified titanium dioxide for enhanced photocatalytic degradation of Direct Red 80, *Catalysis Today*, 282:38-47.

Spyropoulos, F., Hancocks, R. D., and Norton , I. T., 2011, Food-grade emulsions prepared by membrane emulsification techniques, *Procedia Food Science*, 1:920-926.