



TiO₂ modified by salicylic acid as a photocatalyst for the degradation of monochlorobenzene via Pickering emulsion way

Mohamed Faouzi Nsib^{a,b,*}, Asma Maayoufi^a, Noomen Moussa^b, Najah Tarhouni^b, Abdelghani Massouri^b, Ammar Houas^a, Yves Chevalier^c

^a URCMEP (UR11ES85), Faculty of Sciences, University of Gabès, 6029 Gabès, Tunisia

^b National School of Engineers (ENIG), University of Gabès, 6029 Gabès, Tunisia

^c Laboratoire d'Automatique et de Génie des Procédés, UMR 5007, CNRS, Université Claude Bernard Lyon 1, 69622 Villeurbanne, France

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ABSTRACT

Pickering emulsion could be a new way for the enhancement of the photocatalysis process efficiency, in particular when applied to degrade non-soluble organic pollutants. To validate this idea, Pickering emulsions were prepared by using monochlorobenzene (MCB) as a model organic contaminant of low solubility in water and TiO₂ modified by salicylic acid (SA) as stabilizer. XRD, TEM, TGA, XPS and FTIR were used to characterize the fine solid particles of TiO₂-SA. Electrical conductivity and optical microscopy were used to characterize emulsions. We focused to prepare emulsions of small drop size by varying the pH of continuous phase (water), the weight fraction of solid particles and the emulsification process. The as-prepared emulsions were photocatalytically degraded under visible radiation. The removal rate of MCB was measured by UV/vis spectroscopy. The results proved that use of a Pickering emulsion stabilized by TiO₂-SA nanoparticles provides an effective and novel way to intensify the photocatalytic degradation of the organic contaminant.

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1. Introduction

Many non-biodegradable aromatic organics (oil, grease, hydrocarbons, solvents, and tars) exist in wastewaters coming from industrial sectors such as production of cosmetics, insecticides and pesticides, refinery and petrochemicals, various organic syntheses, automotive and mechanical industry [1]. These organic products are a significant source of pollution that has harmful effects on natural environment. Besides their toxicity, these products constitute an insoluble liquid phase floating on the surface of the water which causes a reduction in the transfer of atmospheric oxygen. This has an impact on the biological quality of surface water. Given their very low solubility in water, many of these aromatic products exist as emulsions of oil in water (O/W) and are therefore difficult to treat.

Typically, the conventional unit operations of treatment may be a gravity separation, dissolved air flotation, emulsion breaking or incineration. However, most of these operations have drawbacks and are only partially effective. Photocatalysis as a method of treating polluted water, widely applied for the degradation of organic

contaminants [2,3], represents an extremely promising alternative, but its efficiency generally decreases greatly when the concentration of the contaminant on the surface of the photocatalyst becomes weak, i.e., when the hydrophobic organic contaminant has a reduced tendency to locate on the hydrophilic surface of the photocatalyst. Consequently, it can be expected that the improvement of the contact area between the aromatic pollutant and the photocatalyst increases the photocatalytic activity and thus enhances the efficiency of the process. Despite the large number of publications on the application of photocatalysis as a process of degradation of soluble pollutants in water [4–7], the bibliography is very poor in publications dealing with poorly soluble organic pollutants [8]. Hence, the innovative idea is to emulsify these pollutants in water and stabilize the obtained emulsion by fine solid particles having photocatalytic properties.

More than a century ago, Pickering [9] found that colloidal particles situated at the oil–water interface could stabilize emulsions, henceforth called “Pickering emulsions”. The adsorption of colloidal particles at the oil/water interface is a crucial factor for preparing stable Pickering emulsions. By reducing the fluid–fluid interfacial energy, the colloidal particles play an effective role of surfactant [10]. It has been reported in the literature that the preferential localization of solid nanoparticles to O/W interface is maximized when the solid particles have a three-phase contact angle θ equal to 90° [11]. However, this threshold value of contact

* Corresponding author at: National School of Engineers (ENIG), University of Gabès, 6029 Gabès, Tunisia. Tel.: +216 97770192; fax: +216 75392190.

E-mail address: Mohamed.faouzi.ncib@gmail.com (M.F. Nsib).

angle probably depends on the nature and size of solid particles and the organic chain grafted to their surface for controlling the hydrophilic/hydrophobic balance [11]. Stable emulsions could only be prepared with particles of intermediate hydrophobicity because of the high affinity of particles to the O/W interface when θ is close to 90° [12]. On the contrary, the particles that are completely wet by one of two liquid phases are dispersed in this phase and do not stabilize emulsions. Emulsion stability tends to be high for weakly charged surfaces and non-flocculated particles [13].

The Pickering emulsions have many interests compared to conventional emulsions. Indeed, the use of solid particles as emulsifiers gives reproducible formulations, reduces the formation of foam, and reduces the toxicity and cost of treatment. Moreover, the Pickering emulsion is generally stable even if changing some physicochemical parameters such as pH of the continuous phase (water), temperature and composition of the oil phase [14]. These characteristics have allowed Pickering emulsions to find many applications especially in pharmaceutical, food and cosmetics industries [15–17]. The feasibility of such emulsions has also been used to synthesize inorganic hollow spherical particles [18], inorganic/organic hybrids [19] and polymer microspheres [20]. Moreover, Pickering emulsions using modified titania as stabilizer and photocatalyst for the surface-initiated photocatalytic polymerization were used to prepare Polystyrene microspheres [21–24].

However, the literature is very poor in studies of Pickering emulsions as a way to intensify the photocatalytic degradation of organic contaminants [8]. The solid particles chosen to stabilize emulsions must, here, meet three essential criteria:

- A good photocatalytic activity.
- A partial wettability ($\Theta_{\text{water}} \leq 90^\circ$) to be adsorbed at the oil–water interface.
- A nanoscale size to avoid sedimentation.

Oxides frequently used in photocatalysis as TiO_2 and ZnO have very hydrophilic surfaces and therefore will settle in the aqueous phase. Different functionalities such as silanes, titanates, fluorocarbons and salicylic acid [25–27] have been grafted onto oxide surfaces to improve their adsorption properties at the oil–water interface. The affinity between the catalyst TiO_2 and pollutants is an important factor in enhancing the photodegradation efficiency. Shun-Xing et al. [28] established that aromatic carboxylic acid such as salicylic acid is used as surface modifier for five purposes: (a) to enhance the surface coverage of aromatic pollutants on TiO_2 by phenyl group interaction; (b) to develop a simply and fast surface modified technology, using chemical adsorption by TiO_2 through an ester-like bond between $-\text{COOH}$ group and the surface $-\text{OH}$ groups of TiO_2 ; (c) to improve the dispersive capacity for TiO_2 powder in polar and non-polar solvent by hydrophilic groups $-\text{COOH}$, $-\text{OH}$, and hydrophobic group $-\text{phenyl}$; (d) to accelerate the migration rate of pollutant to the surface of TiO_2 ; (e) to expand the wavelength response range.

However, the chemical modification should be: (i) stable to UV/Vis irradiation used in photocatalysis to ensure the stability of O/W emulsion during the photocatalytic process, and (ii) not screen the photocatalyst/contaminant interaction. Prospective research to meet these criteria is therefore essential to formulate functional Pickering emulsions.

In this paper, a Pickering emulsion was prepared by using monochlorobenzene (MCB) as model organic contaminant of low solubility in water and TiO_2 modified by salicylic acid (SA) as stabilizer. The as-prepared emulsion was first photo-catalytically degraded under visible radiation, and then separated by centrifugation to decrease the amount of MCB in water. We focus to prepare emulsions of small drop size by varying the pH of continuous phase (water) and the emulsification process. This is expected to improve

the contact area between the organic contaminant and the photocatalyst and to intensify the photocatalytic degradation of MCB via the Pickering emulsion way.

2. Experimental

2.1. Preparation of TiO_2 photocatalyst

The TiO_2 photocatalyst was prepared through the sol–gel process. The two precursor solutions, here denoted as precursors A and B, were prepared as follows. Precursor A: $(\text{C}_4\text{H}_9\text{O})_4\text{Ti}$ (40 ml), $\text{C}_2\text{H}_5\text{OH}$ (50 ml) and CH_3COOH (3.0 ml). Precursor B: H_2O (7.0 ml) and $\text{C}_2\text{H}_5\text{OH}$ (50 ml). Each precursor was stirred for 10 min at room temperature. Afterwards, the precursor B was added to the precursor A drop wise with vigorous stirring. The resultant mixture was further stirred for 20 min. The sol solution was placed in a culture dish for 1.0 day to finish the sol–gel transition and filtered. Filter residue was rinsed with water repeatedly, and then dried at 110°C for 24 h to get a dried gel. The dried gel was ground and heat treated at 400°C for 2.0 h to get a stable TiO_2 photocatalyst. 400°C was selected after preliminary tests (not shown here) on the photodegradation of MCB in aqueous solution. Powders of prepared TiO_2 calcined at 400°C showed higher activity than those calcined at 300, 500, 600 and 700°C respectively.

2.2. Surface modification

Surface modification was carried out through adding 1 g of the TiO_2 nanoparticles into 50 ml of saturated solution of SA. A constant magnetic stirring was conducted for 30 min at room temperature until the adsorption equilibrium, resulting in a light yellow coloration of the surface of TiO_2 , inferring that a chemical reaction took place (chemisorption) between SA and TiO_2 . After filtered, the surface-modified titania nanoparticles ($\text{TiO}_2\text{--SA}$) were washed with water three times and heat treated for 30 min at 105°C . The obtained powder was then grinded to get fine particles.

2.3. Catalyst characterization

The X-ray diffraction (XRD) patterns obtained on a D5000X-ray diffractometer (German Bruker) using $\text{Cu K}\alpha$ radiation at a scan rate of 0.02°s^{-1} were used to decide the crystallite size and identity of TiO_2 powders. The average crystallite size was determined according to Scherrer's equation:

$$d = \frac{k\lambda}{\beta \cos \theta}$$

where k is the shape factor of particles equal to 0.89, β is the peak width at half maximum (in radians), λ is the X-ray wavelength (0.15418 nm), and θ is the Bragg angle. The transmission electron micrograph (TEM) was recorded with a JEM-3010 (JEOL Company, Japan) electron microscope and was used for observing the shape of prepared particles and estimating the particle size.

TGA experiments of SA, prepared pure TiO_2 and $\text{TiO}_2\text{--SA}$ composite were performed with a Perkin-Elmer Diamond thermobalance, in the temperature range of $25\text{--}300^\circ\text{C}$, under a dynamic atmosphere of nitrogen. Samples were put into platinum crucibles, at a heating rate of 5°C min^{-1} .

ESCALAB-210 spectrometer (VG Scientific) was used for X-ray photoelectron spectroscopy (XPS) measurements, the $\text{Al K}\alpha$ X-ray source operated at 300 W (15 kV, 20 mA). The surface properties of the $\text{TiO}_2\text{--SA}$ sample were analyzed by recording the C 1s XPS spectra.

The modifying effect of TiO_2 nanoparticles with salicylic acid and its stability during photocatalysis were characterized by a Perkin-Elmer SPECTRUM 1000 Fourier transform infrared (FTIR)

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