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Original Research Paper

The relationship between iron and Ilmenite for photocatalyst degradation

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ABSTRACT

Photocatalytic degradation of organic compounds is a key target for the development of sustainable environmental pollution management system. The use of pre-treated Ilmenite with low concentration of Fe ions via single step of chloride process is essential to generate a highly effective photocatalyst. In the present study, comprehensive investigations on Fe concentrations in Ilmenite has been conducted. Based on the findings, pre-treated Ilmenite with low Fe content (0.76–7.15 at%) was successfully synthesized through a single step chloride process by using 15–35 v/v% of HCl. Interestingly, Ilmenite with 1.62 at % Fe after pre-treated with 25 v/v% HCl was able to photodegrade 100% of the Reactive Black 5 (RB5) under visible light within 30 min. The improvement of photocatalytic degradation efficiency of the pre-treated Ilmenite is mainly attributed to the better photo-induced charge carrier mobility and low recombination losses.

1. Introduction

Today, the increasing awareness of the environmental impacts from pollution and strict requirement on emission regulations has encouraged an alternative route for waste management. The main reason was attributed to the conventional biological processes do not always provide satisfactory results, specifically in industrial wastewater treatment, as many organic substances from various industries are toxic and non-biodegradable [1–4]. Hence, photocatalytic technologies appeared as one of the most feasible option for such biologically persistent wastewater because of their ability in photodegrading aqueous organic pollutants [5]. These technologies are dependent on the in-situ generation of hydroxyl radicals under ambient conditions, which are capable of converting a wide spectrum of toxic organic compounds, such as non-biodegradable substances into relatively innocuous end products like carbon dioxide (CO_2) and water (H_2O) [6–8].

As a matter of fact, the usage of titanium dioxide (TiO_2) in wastewater treatment began during 1970 and 1980s based on Heller's research and knowledge. It turned out that TiO_2 could break down any organic compounds into harmless substances under UV irradiation [9,10]. Since then, many researches on TiO_2 topic in wastewater treatment have gained much attention and has been intensively studied. Indeed, TiO_2 is relatively inexpensive, highly stable chemically and the photo-generated holes are highly oxidizing. However, TiO_2 effectively functions under the UV region ($\lambda <$ 400 nm) and only accounts for about 4–5% of UV rays from our solar energy. Thus, the efficient use of solar energy is essential for effectively degrading organic pollutants. Therefore, considerable efforts have been exerted by modifying TiO_2 with the addition of electron donors, carbonates salts, metal ion doping, and dye sensitization have also been investigated [11]. Several researches have revealed that doped TiO_2 could reduce the valence band in TiO_2, hence reducing the photon energy required to excite electrons and produced hydroxyl radicals [12–17]. Nevertheless, these modifications possess several challenges and drawbacks, including costly production, time-consuming and harmful chemical in use. For instance, titanium (IV) isopropoxide that is frequently been used as the starting material in sol gel method has the negative impact on human health and acute toxic to human and environment.

Over the past few years, there are also a few researches which have been successfully applied a more economical method by using Ilmenite ($FeTiO_3$) or modified Ilmenite to degrade organic compounds [18–20]. Moctezuma et al. [18] showed that the

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Ilmenite was capable to partially break down phenol into carboxyl acid and Pataquiva-Mateus et al. [19] study proved that Ilmenite has the capability to degrade Orange II dye solution completely under acidic condition. Pataquiva-Mateus et al. [19] suggested Fe from Ilmenite dissolved into the solution and thus homogenous Fenton reaction occurred to assist the Orange II dye degradation. On the other hand, Tao et al. [20] synthesised rutile TiO_2 nanorod with low Fe concentration as impurities from Ilmenite. In the study, the rutile TiO_2 nanorod successfully mineralised oxalic acid and the kinetic rate of photo-degradation is better than that of commercial rutile TiO_2. In fact, Ilmenite is a natural source of low titanium content TiO_2 (usually approximately 50–60%). Ilmenite mineral is relatively cheap with a record of 140-165USD/metric tonnes [21] while the market price of pure TiO_2 has reached up to 2000 USD/metric tonnes [22]. Its deposits can be found on all five major continents namely North and South America, Africa, Euro-Asia and Australia. According to recent estimates, the world's total reserves of Ilmenite exceed 680 million tonnes and thus it is sufficient for the preparation of 350–450 million tonnes of TiO_2 [23].

Previously, the use of Ilmenite in photo-degradation under a specific set of environment conditions has been reported [18,19], it is still far from becoming a potential candidate for photo-degradation application because of the high concentration of Fe remains a great challenge. In addition, rapid recombination of charge carriers within the Ilmenite has been limited the wide-spread use of Ilmenite [24]. To the best of our knowledge, the literature regarding to the pre-treated Ilmenite for low Fe concentration through simple chloride process using HCl as the leaching agent is still lacking. The HCl leaching process is more environmental friendly as less waste is generated and could yield TiO_2 with higher purity because $FeCl_2$ and $FeCl_3$ produced are highly soluble in water [25–27]. Therefore, this study aims to optimize the HCl concentration during chloride process to prepare high quality of pre-treated Ilmenite for improving photocatalysis degradation of RB5 dye performance. Such a mechanistic understanding is very important to control the Fe content in Ilmenite, which has potential applications as photocatalyst.

2. Experimental procedures

Natural Ilmenite mineral (Tor Minerals Co., Ltd., Malaysia) was used as the starting material. The sample was crushed and grounded (<45 μm) before subjected to acid leaching experiments. In brief, 2.5 g of Ilmenite powders were treated with 250 mL of the respectively concentration of HCl in v/v% (15, 20, 25, 30 and 35%). The samples were denoted as H-X, where X represents the HCl concentration, i.e. H-15 indicates the Ilmenite has been pre-treated with 15% HCl. The bottle was immersed in a silicon oil bath under mechanical stirring (450 rpm) at 100 °C for 24 h to minimize the distortion-induced surface and lattice defects in Ilmenite during HCl treatment process. Since dissolution of Ilmenite via chemical process is a surface phenomenon, physical contact of the diluted HCl acid with iron element required more time to dissolve and release the ion. Then, the suspension was centrifuged, washed and dried at 70 °C for 12 h [28]. The photo-catalytic activity performance of the synthesized samples was evaluated by using 5 mg/L of RB5 dye at pH 3 to identify an optimum acid concentration (HCl) used to produce pre-treated Ilmenite with the highest photo-degradation efficiency. The photo-catalytic measurement of pre-treated Ilmenite was conducted in batch photo-catalytic reaction system. In a typical experiment, 1.0 g/L of pre-treated Ilmenite powder was dispersed into 50 mL of RB 5 dye (5 mg/L). The pH of the RB 5 solution was adjusted to pH 3 by using 1 M of nitric acid (HNO_3). The schematically diagram of the photo-reactor was shown in Fig. 1. The reaction was set for 30 min in the dark and then followed by 30 min of 150 W xenon (1 sun) light irradiation. The suspension was then filtered and measured by a UV–Vis spectrophotometer to determine the remaining concentration of RB 5 at 597 nm.

The kinetic rate of photo-catalytic activity of raw and pre-treated Ilmenite was determined using Eq. (1); k' denote as the pseudo-first order rate constant, C_0 is the initial concentration of RB 5 and C is the concentration at time "t".

$$\ln\left[\frac{C}{C_0}\right] = k't \qquad (1)$$

The crystal structures of the samples were analysed by using a Raman spectrometer (Renishaw in Via) with an Argon ion laser at 514.5 nm as the excitation source. The phase structure of the raw and pre-treated Ilmenite was recorded by a Bruker axs D8 advanced diffractometer (Cu Kα radiation: λ = 0.15406 nm) operated at 40 kV and 30 mA with step size of 0.02° s^{-1} in the 2θ scanning range of 20–70°. FESEM analysis was used to observe the morphology of the raw and pre-treated Ilmenite. The chemical composition of the samples was determined via EDX. Both analyses were conducted using a JEOL JSM 7600F field emission scanning electron microscope. The chemical and oxidation states of the raw and pre-treated Ilmenite were executed on a PHI Quantera II scanning X-ray microprobe using an Al cathode (hν = 1486.8 eV) with 100 μm spot size and 280 eV pass energy. The textural properties of the samples were determined from nitrogen adsorption isotherms taken at 77 K (Micromeritics ASAP 2020). The zeta potential of the raw and pre-treated Ilmenite was measured by Malvern Zetasizer Nano Seires ZS. The band gap energies of the samples were examined using a diffuse reflectance UV–Vis Spectrophotometer (Shimadzu UV-2700) and barium sulphate was used as the reference.

3. Results and discussion

3.1. EDX analysis

The influence of HCl concentration during single step of chloride process on the pre-treated Ilmenite with reduction of Fe content is discussed. Table 1 shows the EDX of the pre-treated Ilmenite at different HCl concentrations at 110 °C. As determined through EDX, the increment of HCl concentration imposed a significant effect on Fe removal from the raw Ilmenite, as nearly 0.77% of Fe content remained or 99.2% of Fe has been removed when pre-treated with 35% HCl. On the other hand, the remaining Fe content within Ilmenite showed the highest at% when pre-treated with 15%

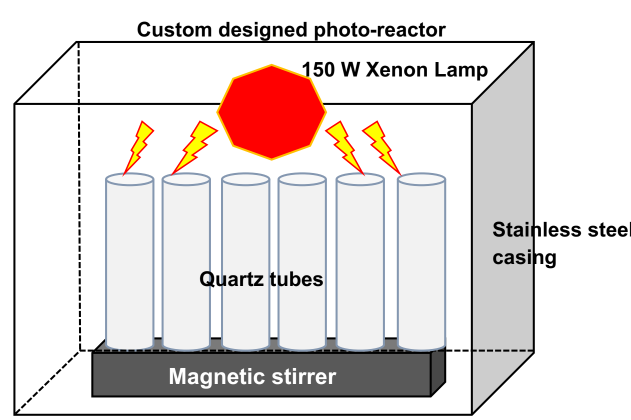

Fig. 1. Schematic diagram of the custom-designed photo-reactor set up for photo-degradation of RB 5 dye solution under 150 W xenon lamp (1 sun).

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