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Enhanced magnetic separation and photocatalytic activity of nitrogen doped titania photocatalyst supported on strontium ferrite

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Introduction

The advanced oxidation technologies (AOPs), are state-of-art technology for treating wastewater. Among the advanced oxidation processes heterogeneous photocatalysis is one of the prominent systems to degrade various types of organic pollutants in water and wastewater [1–4]. There has been an enormous amount of research and development in this area due to its effectiveness in degrading and mineralising the recalcitrant organic compounds [5]. The extensive occurrence of phenols in wastewater and associated environmental hazards has increased concern over the public health [5,6]. These toxic organic compounds in wastewater effluent are reported to be a massive impediment to the widespread acceptance of water recycling [5,7]. Furthermore, it has major challenge to achieve the effective removal of persistent organic pollutants from wastewater effluent to minimise the risk of pollution problems from such toxic chemicals and make it able to reuse [5]. Conventional methods such as adsorption by activated carbon and ion exchange resins finally generate wastes during the treatment, thus require additional treatment methods and costs as well [5].

Hence, heterogenous photocatalytic oxidation process employing titanium dioxide (TiO_2) has emerged as a promising new alternative process for the degradation of these persistent organic pollutants [8,9].

Heterogeneous photocatalysis using TiO_2 semiconductors was initially discovered by Fujishima and Honda in 1972 on the photoinduced splitting of water [10]. The process gradually breaks down the contaminant molecule, thus no residue of the original material remains and therefore no sludge requiring disposal to landfill is produced [8,9]. TiO_2 is known as the best heterogeneous photocatalyst due to its cost-effective, strong photo oxidative activity, non toxic, chemical stability, resistant against photo and chemical corrosion [11]. Moreover, it exists in three different structural

forms, which are anatase, rutile, and brookite. Among them anatase TiO_2 has higher photocatalytic reactivity compared to the rest [12]. In general the TiO_2 named viz., Degussa P_{25} was highly employed for commercial purposes. In addition it was also studied for the suitability of photocatalytic treatment of wastewater. Such commercialized TiO_2 (Degussa P_{25}) semiconductor photocatalyst has wide band gap energy (3.20 eV) and hence successfully used as an efficient photocatalyst [13–17]. Unfortunately, it cannot take up the visible light from sunlight due its wide band gap. It can only utilize ultraviolet (UV) radiation (_ < 400 nm) for photo excitation [17]. However the sunlight contains only 5–6% of UV radiation in its electromagnetic spectrum. Therefore an external UV source is needed to maximize the photocatalytic activity of such TiO_2 photocatalyst [17]. It becomes a major limitation since it cannot be a sustainable green catalyst for treating the organics in wastewater.

Hence several attempts have been employed to improve the efficiency of TiO_2 photocatalyst in utilizing solar light or precisely daylight as irradiation source. One such modification is made by doping the photocatalyst with transition metal ions, ion implantation, hydrogen plasma reduction of TiO_2, organic dye sensitization, and hydroxide or surface coordination. Doping of the catalyst with metals ion such as Fe, Sb, Co, etc., can extend the absorption spectrum to visible light region (400–800 nm), where the sunlight can be utilized effectively [17,18]. This type of doping was studied comprehensively by few researchers [17,19–21]. Some of their findings are as follows: Sikong et al. [22] in their work prepared Fe-doped TiO_2/SnO_2 by sol–gel method and photoactivity was investigated for Escherichia coli killing. The E. coli were completely diminished within 90 min under UV radiation and almost 100% inactivated under visible light exposure [22]. Nahar et al. [23] in their study observed that Fe doping increases the UV and visible light performance [23]. Nonmetal ion [24–33] doping such as nitrogen alternatively, narrowed the band gap by the mixture of N 2_p states with O 2_p on the top of valence band at substitutional lattice sites in the form of nitride (Ti–N) or oxynitride (Ti–O–N) [33].

In recent years, magnetic based TiO_2 photocatalyst synthesis has evolved as a mean to resolve the difficulty of separation of TiO_2 photocatalyst from the treated water, by applying an external magnetic field [34]. Till date few reports has been reported of which most findings focused on soft ferromagnetic materials, which is magnetite (Fe_3O_4) that can oxidized to maghemite (_-Fe_2O_3), which is also ferromagnetic if the particles are heated over 150–170 ◦C [35–39]. Unfortunately, the nanosized core magnetic materials are easily oxidized and transform rapidly when the heat treatment temperature is over 400 ◦C [34,40]. Therefore,

it is inherently difficult to produce titania-coated particles with high visible light photoactivity without losses of magnetic property.

Hence the major objective of the present work is to develop ferromagnetic property improved TiO_2 photocalayst by supporting it on strontium ferrite ($SrFe_{12}O_{19}$) for enriched recovery and reuse. The objective also focused on visible light absorption by Nitrogen doping onto TiO_2 for utilizing sunlight radiation for excitation. The photocatalytic activity was investigated by degrading a biorecalcitrant and toxic pesticide pollutant viz., 2,4-dichlorophenol (2,4-DCP) under bright and diffused sunlight irradiation.

2. Materials and methods

2.1. Synthesis of N-doped TiO_2

All chemicals were of analytical grade and obtained from Sigma Aldrich, Malaysia. Milli-Q water (>18.2 M _ cm) was used for all experiments. The N-doped TiO_2 was synthesized by the following technique: an aqueous $Ti_2(SO_4)_3$ was prepared by 20 wt.% of $Ti_2(SO_4)_3$ and 80 wt.% of distilled water. Subsequently, 300 mL of $Ti_2(SO_4)_3$ solution and 1.2 L of Milli-Q water were added into 2 L beaker, then the ready solution was hydrolyzed in magnetic stirring apparatus by the addition of 30% NH_3 aqueous solution until the pH of the mixture reached 7. The hydrolysis product, which is in the form of white suspended semi-solid was rinsed with Milli-Q water until the concentration of the sulphate, SO_4^{2-} in the rinsing water reached 0.5 mg/L. The concentration of SO_4^{2-} was determined using the standard methods for the examination of water and wastewater. Finally, dried and calcined at 500 ◦C for an hour.

2.2. Synthesis of SiO_2-coated $SrFe_{12}O_{19}$ nanoparticles

$(NaPO_3)_6$ aqueous solution (5%) was prepared using 5 g $(NaPO_3)_6$ and 95 g of Milli-Q water. It was then added into 150 mL $SrFe_{12}O_{19}$ dispersion. As to get the mixed dispersion with 16 wt.% $(NaPO_3)_6$ for $SrFe_{12}O_{19}$, 3.62 g of $SrFe_{12}O_{19}$ was added into Milli-Q water and made up to 150 mL dispersion. It is followed by the addition of 33 mL of $Na_2O{\cdot}3SiO_2$ solution (10%) into the dispersion to get 200 wt.% $SiO_2/SrFe_{12}O_{19}$ dispersion. The dispersion was sonicated for 15 min in ultrasonic water bath and followed by heating to 90 ◦C on a magnetic stirrer provided with heater. The pH value of the dispersion was adjusted to ca. 10.0 by titrating H_2SO_4 solution (5%) under vigorous stirring. Further stirring was carried out at 90 ◦C to obtain a viscous dispersion. A thin SiO_2 layer was deposited on the $SrFe_{12}O_{19}$ nanoparticles. The SiO_2-coated $SrFe_{12}O_{19}$ nanoparticles were washed by centrifugation and redispersed for quite a lot of times with Milli-Q water to prevent them from agglomerating.

2.3. Synthesis of N-doped TiO_2 supported on $SrFe_{12}O_{19}$ photocatalyst

About 6 mL of SiO_2-coated $SrFe_{12}O_{19}$ dispersion (0.15 g) and 1.0 g of N-doped TiO_2 were mixed. Then a small portion of water was added to alter the mixture to be a paste. The mixture was sonicated for 15 min to well mix the substances, then dried, grinded, and calcined for 30 min at 400 ◦C. Hence, the magnetically separable N-doped TiO_2 supported on $SrFe_{12}O_{19}$ photocatalyst was obtained.

2.4. Characterization of synthesized photocatalyst

The X-ray diffraction (XRD) analysis was performed with Bruker D8 Advance diffractometer using Cu K_ (_ = 1.5406A˚) radiation, to explore the crystal structure and crystallinity of the photocatalyst. The average crystallite size was obtained using the Scherrer's equation (D = k_/˘ cos _). A transmission electron microscope (TEM) (Philips CM-12) was performed by dispersing the samples in ethanol and were dispersed using an ultrasonicator (Starsonic, 35) for 15 min and fixed on carbon-coated copper grid to obtain the structure of the prepared photocatalysts at the nanoscale. The inorganic composition of the prepared photocatalysts were analyzed by energy dispersive X-ray spectroscopy (EDS) of Zeiss Auriga® FESEM. Brunauer–Emmett–Teller (BET) surface measurements using nitrogen as adsorption molecule was carried out with Quantachrome 6B Autosorb Automated Gas Sorption System. The degassing of sample was carried out for 5 h at 150 ◦C. The pore-size distribution curve was obtained from the analysis of the desorption portion of the isotherm using the BJH (Barrett–Joyner–Halenda) method. X-ray photoelectron spectrum (XPS) was obtained from Axis Ultra DLD instrument of KRATOS using monochromatic Al K_ radiation (225 W, 15 mA, 15 kV). The magnetization with applied magnetic field was measured by vibrating sample magnetometer (VSM, Lakeshore 7410) at room temperature. It reveals the magnetic properties like coercivity, saturation magnetization and remanence of the synthesized material. The absorption spectra of the prepared catalysts was analyzed with visible spectrophotometer (Merck, Spectroquant Pharo 100) over a wavelength ranging between 350 and 800 nm. The prepared catalysts were dispersed with distilled water in a quartz cell (10 mm path length), and their spectral was examined. The band gap energy was calculated as per the literature report [41] using the following equation: