

Article

Synthesis of Monodisperse Magnetic Fe₃O₄ Microspheres and Their Photocatalytic Degradation of Xylenol Orange

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Abstract: To further enhance the safety and energy efficiency of the Fe₃O₄ preparation experiment, we proposed a strategy for synthesizing monodisperse Fe₃O₄ microspheres through a one-step solvothermal process. In this environmentally friendly synthesis method, stable FeCl₃·6H₂O was utilized as the sole raw material, while ethylene glycol, characterized by its high boiling point and favorable safety profile, served as the solvent. Additionally, inexpensive and readily available urea was selected to function either as a mineralizer or surfactant. Through this one-step solvothermal reaction, the target product of Fe₃O₄ could be obtained without subsequent calcination under reducing or inert atmospheres, thereby enhancing experimental safety and promoting energy conservation. By controlling the amount of urea added, it became feasible to produce monodisperse magnetic Fe₃O₄ microspheres characterized by complete crystallinity and high yield. Utilizing the as-synthesized Fe₃O₄ as a catalyst, we investigated its photocatalytic activity against xylenol orange organic dyes along with its regeneration characteristics. When 40 mmol of urea was incorporated into the reaction mixture, the resulting Fe₃O₄ sample exhibited optimal photocatalytic performance; a 20 mg/L xylenol orange solution became colorless and transparent after just 1.5 h of UV light irradiation. Furthermore, during five consecutive regeneration cycles, its catalytic activity could be restored to its initial level. Importantly, Fe₃O₄ demonstrated excellent magnetic sensitivity properties that facilitated rapid targeted separation under an external magnetic field, providing convenience for recovery and collection purposes.

Keywords: Fe₃O₄; magnetism; monodisperse; solvothermal; photocatalysis; dye



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1. Introduction

Magnetic microspheres represent a significant area of research within the field of nanoscience and technology [1–5]. Due to their remarkable magnetic responsiveness, biocompatibility, and chemical stability [6,7], these microspheres exhibit extensive application potential across various domains including medicine [8], pharmaceuticals [9], catalytic chemistry [10], and separation and purification processes [11], as well as wastewater treatment [12]. Magnetic microspheres can be primarily categorized into two types: organic magnetic microspheres and inorganic magnetic microspheres. Organic magnetic microspheres are polymer composites that consist of metal–organic complexes [13,14]. In

contrast, there exists a diverse range of inorganic magnetic microspheres such as CrO_2 [15], NiFe_2O_4 [16], CoFe_2O_4 [17], elemental metals (including Fe, Co, Ni) [18,19], Fe_4N [20], and iron oxides (notably Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$) [21,22]. Among these materials, Fe_3O_4 magnetic microspheres are the most widely utilized [23–25]. Currently, the preparation methods for Fe_3O_4 magnetic microspheres predominantly include five approaches: chemical coprecipitation, sol–gel synthesis, microemulsion techniques, hydrothermal/solvothermal methods, and high-temperature thermal decomposition [26,27].

The chemical coprecipitation method is one of the most widely employed techniques for synthesizing Fe_3O_4 magnetic microspheres. In this process, iron ions (Fe^{3+}) and ferrous ions (Fe^{2+}) are mixed in a molar ratio of 2:1, and NH_4OH or NaOH is then introduced as a precipitating agent. The Fe^{3+} and Fe^{2+} ions precipitate in the form of hydrated oxides or hydroxides, ultimately yielding Fe_3O_4 magnetic microspheres [28]. However, this method has certain drawbacks; specifically, it requires strict adherence to the $\text{Fe}^{3+}:\text{Fe}^{2+}$ molar ratio, as Fe^{2+} ions are prone to oxidation. Additionally, the use of NH_4OH [29] or NaOH [30] solution with higher concentrations is necessary as a precipitating agent. The sol–gel method represents an alternative approach for the preparation of Fe_3O_4 magnetic microspheres. Initially, Fe^{3+} and Fe^{2+} ions are mixed in a specific ratio, followed by the addition of a controlled amount of acid to adjust the pH of the solution to an appropriate level. Subsequently, the solution undergoes hydrolysis, condensation, nucleation, growth, and other processes. Finally, heat treatment is applied to remove excess acid and water, resulting in the formation of Fe_3O_4 magnetic microspheres [31]. A significant drawback of this method is its cumbersome operational process; each step requires precise control to ensure successful outcomes [32]. The microemulsion method typically employs $\text{C}_{18}\text{H}_{29}\text{NaO}_3\text{S}$ as the surfactant, toluene as the oil phase, and aqueous solutions of Fe^{3+} and Fe^{2+} , along with NaOH , as the water phase to create a W/O emulsion [33]. However, this method has certain drawbacks; specifically, it involves a more complex preparation process that necessitates the use of various organic substances and requires precise control over multiple parameters [34].

It is worth noting that the chemical coprecipitation method, sol–gel method and microemulsion method primarily facilitate the preparation of Fe_3O_4 at room temperature or below $100\text{ }^\circ\text{C}$. Consequently, the crystallinity of the resulting Fe_3O_4 product tends to be relatively low. As a result, hydrothermal/solvothermal processes have been proposed as alternative approaches. The hydrothermal/solvothermal method utilizes water or an organic solvent as the reaction medium [35]. A notable disadvantage of this method is its requirement for specialized reaction equipment, commonly referred to as a hydrothermal autoclave reactor.

From the aforementioned methods of preparing Fe_3O_4 , namely chemical coprecipitation, sol–gel, and microemulsion, it is evident that the iron source employed consists of a mixture of Fe^{2+} and Fe^{3+} ions, which must be present in a specific ratio. To simplify the types of iron sources utilized, researchers have begun to investigate methods for synthesizing Fe_3O_4 using a single iron source. However, most approaches initially yield the nonmagnetic $\alpha\text{-Fe}_2\text{O}_3$ [36–38], which is subsequently reduced to Fe_3O_4 through high-temperature roasting (typically around $500\text{ }^\circ\text{C}$ [39–41]) in an atmosphere of hydrogen [42] or nitrogen [43] gas. Additionally, high-temperature thermal decomposition techniques have been developed. These involve mixing organic precursors of iron, such as $\text{C}_{54}\text{H}_{99}\text{FeO}_6$ [44], $\text{Fe}(\text{CO})_5$ [45], $\text{Fe}(\text{C}_5\text{H}_5)_2$ [46], and $\text{Fe}(\text{acac})_3$ [47], with surfactants (e.g., 1,2-hexadecanediol [48]) in organic solvents with elevated boiling points (such as oleic acid [49] and oleamine [50]). By employing heating reflux under these conditions, Fe_3O_4 magnetic microspheres can be obtained. A notable drawback of this method is that the organic iron sources exhibit certain

toxicity; furthermore, their use entails significant amounts of organic materials and results in harmful emissions detrimental to both human health and the environment.

Considering the potential environmental and human health risks associated with opening the system during the preparation of Fe_3O_4 , utilizing a hydrothermal autoclave reactor as the reaction vessel in the hydrothermal solvothermal method is a prudent choice [51]. This reactor features an inner lining made from polytetrafluoroethylene (commonly referred to as “plastic king”), which exhibits excellent resistance to both acids and alkalis, ensuring durability and reusability. Most importantly, the hydrothermal reactor creates a closed environment for chemical reactions. At specific reaction temperatures (generally between 100 and 200 °C), volatilization of the solvent occurs, generating significant pressure within this sealed system (up to 6 MPa). The combined effects of elevated temperature and pressure facilitate the nucleation, growth, and crystallization processes of Fe_3O_4 . Furthermore, this enclosed setting effectively mitigates the release of toxic gases into the atmosphere while minimizing physical hazards to both the environment and operators involved in these procedures. Currently, Teflon-lined stainless-steel autoclaves of varying capacities are employed for the synthesis of Fe_3O_4 microspheres, including 40 mL at 180 °C [52], 50 mL at 200 °C [53], 100 mL at 200 °C [54], and 200 mL at 200 °C [55].

The selection of solvent is crucial in hydrothermal/solvothermal processes, with several factors to be considered: solubility, compatibility, solvent reduction capacity, potential for co-crystallization, thermal stability, and safety, as well as cost and availability. At present, ethylene glycol is widely utilized as a solvent in the solvothermal process for the preparation of metal oxides such as ZnO [56], CeO_2 [57], Fe_3O_4 [58], and SrTiO_3 [59]. Ethylene glycol demonstrates solubility in a range of solvents, including water, methyl ether, and ethanol. Its good solubility and chemical stability contribute to its high compatibility and fluidity in the synthesis of other chemicals. Although ethylene glycol possesses some level of toxicity, it is relatively low; furthermore, due to its high boiling point (197.4 °C), it does not readily produce vapor that can be inhaled into the body or lead to poisoning. Additionally, ethylene glycol is comparatively inexpensive and easily accessible; it can be recycled after use and remains usable following treatment while also offering favorable environmental protection characteristics alongside economic benefits. Given these considerations, ethylene glycol emerges as an excellent candidate for such applications [60,61].

As for the selection of a precipitating or mineralizing agent, drawing inspiration from the urea-assisted synthesis of CeO_2 [62–64], it is reasonable to suggest that a comparable approach for the synthesis of Fe_3O_4 could represent a viable method. Urea is one of the simplest organic compounds; it is odorless, water-soluble, and exhibits minimal toxicity. When dissolved in water, urea does not exhibit acidic or alkaline properties. Furthermore, ethylene glycol can effectively dissolve urea, allowing for their combination. In practical applications, ethylene glycol is frequently utilized as an anti-crystallization agent added to automotive urea to prevent crystallization or solidification at low temperatures. Consequently, during the solvothermal synthesis process of Fe_3O_4 , urea is anticipated to serve as a more favorable alternative to ammonia and other strong alkali substances traditionally used as precipitating or mineralizing agents.

Based on this, we aim to propose a safe, effective, and environmentally friendly synthesis process for the preparation of monodisperse magnetic Fe_3O_4 microspheres. Monodisperse Fe_3O_4 microspheres were synthesized through a straightforward one-step solvothermal method utilizing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as the sole iron source, ethylene glycol as the exclusive solvent, and mild urea as both the precipitant and mineralizer. The catalytic degradation effect of Fe_3O_4 on organic dye (XO) was investigated with Fe_3O_4 serving as the catalyst. The synthesis strategy proposed in this study offers advantages not only in the synthesis method but also in the selection of raw materials. First and foremost, the

process requires only a single step of solvothermal treatment to obtain the target product, making it straightforward to operate. Additionally, there is no release of toxic or harmful gases during the chemical reaction, which underscores its environmentally friendly characteristics. Secondly, the chosen trivalent ferric salt ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) exhibits chemical stability, while the selected solvent (ethylene glycol) is non-flammable and non-explosive, ensuring high safety standards. Furthermore, the precipitating agent or mineralizing agent (urea) employed is typically non-corrosive. Consequently, this approach is anticipated to serve as an alternative method for preparing monodisperse Fe_3O_4 and other related materials.

2. Results and Discussion

XRD was utilized to determine the phase composition, crystallographic structure, grain size, and crystallinity of the samples. Figure 1 presents the XRD patterns of samples synthesized via a solvothermal method at 200 °C for 48 h with varying urea dosages of 5, 10, 20, 40, 60, and 80 mmol. It was noteworthy that a control experiment was conducted in the absence of urea; however, no precipitated material was obtained. As illustrated in Figure 1, the diffraction peaks for all samples exhibited a strong correlation with those of standard cubic Fe_3O_4 (magnetite), characterized by Fd-3m(227) (JCPDS no. 99-0073) [65]. The corresponding crystallographic planes included (111), (220), (311), (222), (400), (422), (511), (440), and (533) for magnetite. Each diffraction peak from the samples aligned precisely with its standard Fe_3O_4 counterpart; furthermore, these peaks were sharp and devoid of any impurity phases such as Fe_2O_3 . This indicated that the as-obtained Fe_3O_4 powders were pure and single-phase with well-formed crystals.

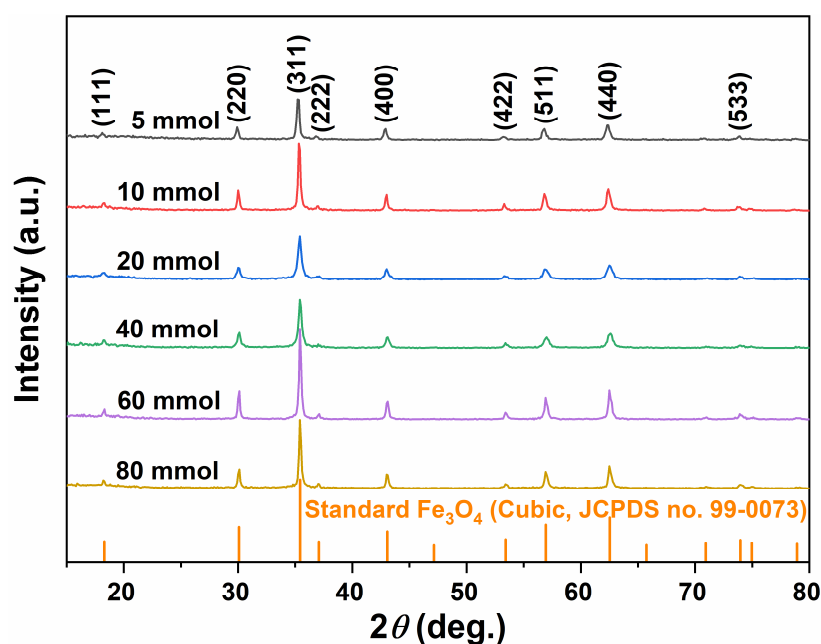


Figure 1. XRD patterns of samples synthesized by the solvothermal method with varying urea dosages of 5, 10, 20, 40, 60, and 80 mmol. Note: The control experiment was conducted in the absence of urea, and no precipitated material was obtained.

During the material preparation process, yield served as a critical economic indicator that reflected both the effectiveness and efficiency of the production process. In this work, the yield (η , %) was calculated using the following equation: η (%) = $[(m_A/m_T) \times 100\%]$, where m_A represents the actual output quality of Fe_3O_4 and m_T denotes the theoretical amount of Fe_3O_4 that should be produced from 5 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. Figure 2 illustrates the yield of Fe_3O_4 samples synthesized solvothermally at 200 °C for 48 h with varying urea dosages of 5,

10, 20, 40, 60, and 80 mmol. As observed, when the urea dosage was set at 5 mmol, the yield of the Fe_3O_4 sample was approximately only 27.8%. However, upon increasing the urea dosage to 10 mmol, there was a significant rise in yield to about 85.8%. Further increments in urea dosage resulted in yields exceeding 87.0%. The highest yield of 94.2% occurred when the urea content reached an impressive level of 80 mmol. Based on experimental observations indicating that no precipitate could be obtained without adding urea, it could be inferred that urea acted at least as a precipitating agent during the solvothermal synthesis of Fe_3O_4 by facilitating its crystallization and growth. When more than 10 mmol of urea was introduced into the system, over 85% of Fe^{3+} ions present in ethylene glycol were successfully converted into high-quality crystalline Fe_3O_4 . Additionally, this experiment employed trivalent Fe^{3+} ions as an iron source without incorporating any additional reducing agents beyond those provided by solvent (ethylene glycol) and precipitating agent (urea). This suggested that both ethylene glycol and urea might function effectively as reducing agents within this context. Previous studies have reported that both ethylene glycol [66,67] and urea [68,69] demonstrate certain reducibility, allowing them to function as reducing agents in various chemical reactions.

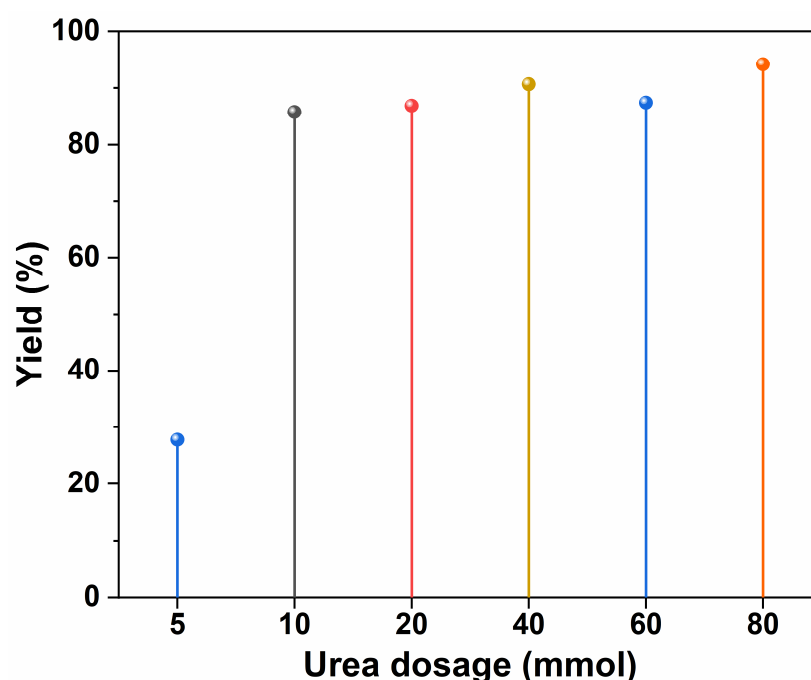


Figure 2. Yield of Fe_3O_4 samples synthesized with varying urea dosages of 5, 10, 20, 40, 60, and 80 mmol.

In the XRD patterns presented in Figure 2, varying degrees of broadening phenomena were observed, accompanied by differences in the intensity of the diffraction peaks. These signals indicated variations in both grain size and crystallinity of the synthesized Fe_3O_4 . Consequently, the mean grain sizes and crystallinities of Fe_3O_4 produced with different urea dosages, specifically 5, 10, 20, 40, 60, and 80 mmol, were estimated using the Scherrer formula and peak responsibility method-based XRD data, respectively, and the results are illustrated in Figure 3a,b. The grain sizes of Fe_3O_4 synthesized with varying urea dosages of 5, 10, 20, 40, 60, and 80 mmol were measured at 25.6, 29.6, 20.9, 21.6, 34.7, and 32.5 nm, respectively (Figure 3a). The grain size of Fe_3O_4 may be influenced by several factors, including the challenges associated with nucleation, the nucleation rate, and the growth rate of Fe_3O_4 during the solvothermal reaction. Additionally, it was possible that under specific temperature and pressure conditions, Fe_3O_4 crystals formed within the solvothermal system had undergone a subtle dissolution–recrystallization process. These

phenomena are likely attributed to the introduction of urea and the resultant changes in pressure and pH levels due to the varying amounts of urea added. However, the crystallinity exhibited less variation within a range of 71% to 78% (Figure 3b). The impact of urea addition on the crystallinity of Fe_3O_4 products was minimal. This was primarily due to the fact that the crystallinity of Fe_3O_4 crystals was predominantly influenced by the reaction temperature. In this experiment, the solvothermal reaction was conducted at 200 °C. Although urea generates CO_2 and NH_3 during the solvothermal reaction process, leading to an increase in pressure within the closed reaction system, this elevated pressure had a negligible effect on the crystallization of Fe_3O_4 in the liquid phase. This observation suggests that the addition of urea may influence the formation and growth of Fe_3O_4 crystal nuclei.

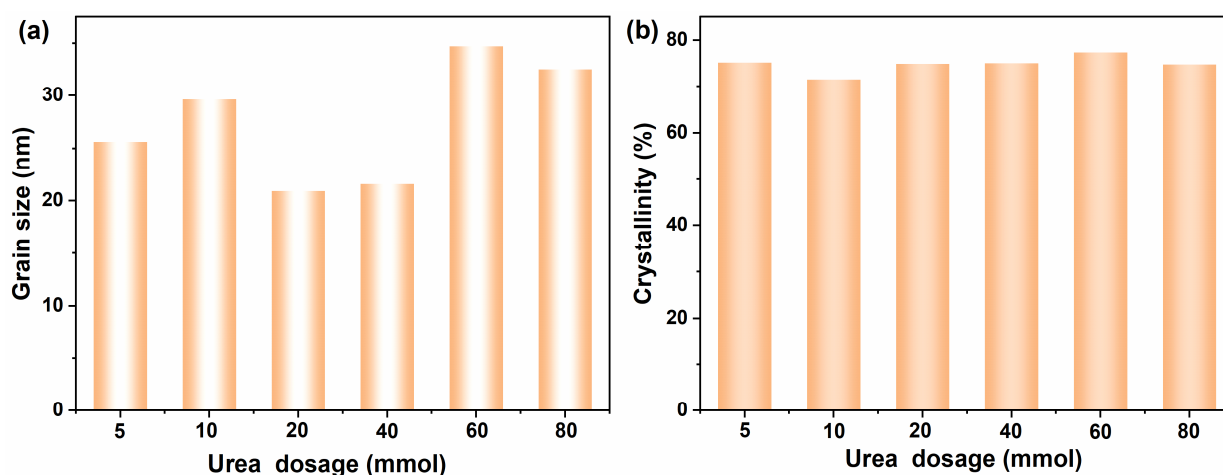


Figure 3. (a) Grain sizes and (b) crystallinities of Fe_3O_4 synthesized with varying urea dosages of 5, 10, 20, 40, 60, and 80 mmol.

The impact of varying urea addition levels on the microstructure of Fe_3O_4 particles was examined using SEM, as depicted in Figure 4. Furthermore, an image analysis technique employing ImageJ software (1.8.0) was introduced to assess the particle size distribution of Fe_3O_4 particles, as illustrated in Figure 5. As illustrated in Figure 4a,b, when the amount of urea added was 5 mmol, the Fe_3O_4 particles exhibited a spherical and uniform morphology, with sizes predominantly ranging from 1.0 μm to 1.2 μm (Figure 5a). However, the surfaces of these spherical particles were uneven, and there was significant agglomeration among them (Figure 4b). Upon increasing the urea addition to 10 mmol (Figure 4c,d), the resulting Fe_3O_4 particles remained mostly spherical but displayed smoother surfaces; however, their size decreased significantly, now primarily distributed within the range of 0.3 μm to 0.5 μm (Figure 5b). Additionally, some incomplete spherical particles were observed, and substantial agglomerations persisted. When the urea dosage was increased to 20 mmol (Figure 4e,f) and 40 mmol (Figure 4g,h), the spherical Fe_3O_4 particles remained intact, exhibiting a smooth surface with size distributions ranging from 0.6 μm to 0.9 μm (Figure 5c) and from 0.55 μm to 0.75 μm (Figure 5d), respectively. Upon increasing the urea addition to 60 mmol (Figure 4i,j), the resulting Fe_3O_4 particles retained their spherical shape, with sizes varying between 0.34 μm and 0.65 μm (Figure 5e); however, numerous holes appeared on their surfaces. When the urea dosage was further raised to 80 mmol (Figure 4k,l), the resultant spherical Fe_3O_4 particles exhibited significant agglomeration similar to that observed in Figure 4a–d, accompanied by a reduction in size predominantly within the range of 0.3 μm to 0.45 μm (Figure 5f). In conjunction with grain size analysis presented in Figure 3a, it was evident that the grain sizes of Fe_3O_4 produced under different amounts of urea addition fell within a range of approximately 20–35 nm. Conversely, particle

size measurements obtained through SEM analysis depicted in Figure 4 and particle size distribution assessments illustrated in Figure 5 primarily indicate dimensions ranging from approximately 0.3 to 0.9 μm . The resulting spherical Fe_3O_4 particles were characterized as polycrystalline structures composed of numerous nanocrystals.

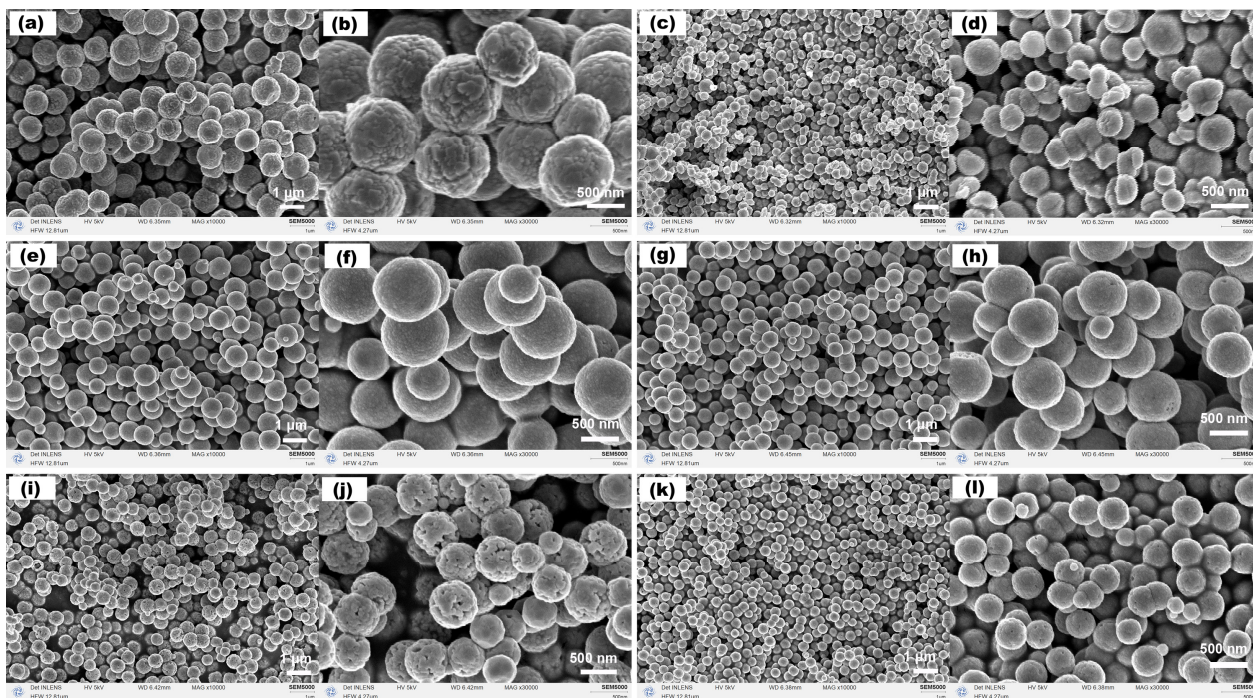


Figure 4. SEM images of Fe_3O_4 samples synthesized by the solvothermal method with varying urea dosages: (a,b) 5, (c,d) 10, (e,f) 20, (g,h) 40, (i,j) 60, and (k,l) 80 mmol.

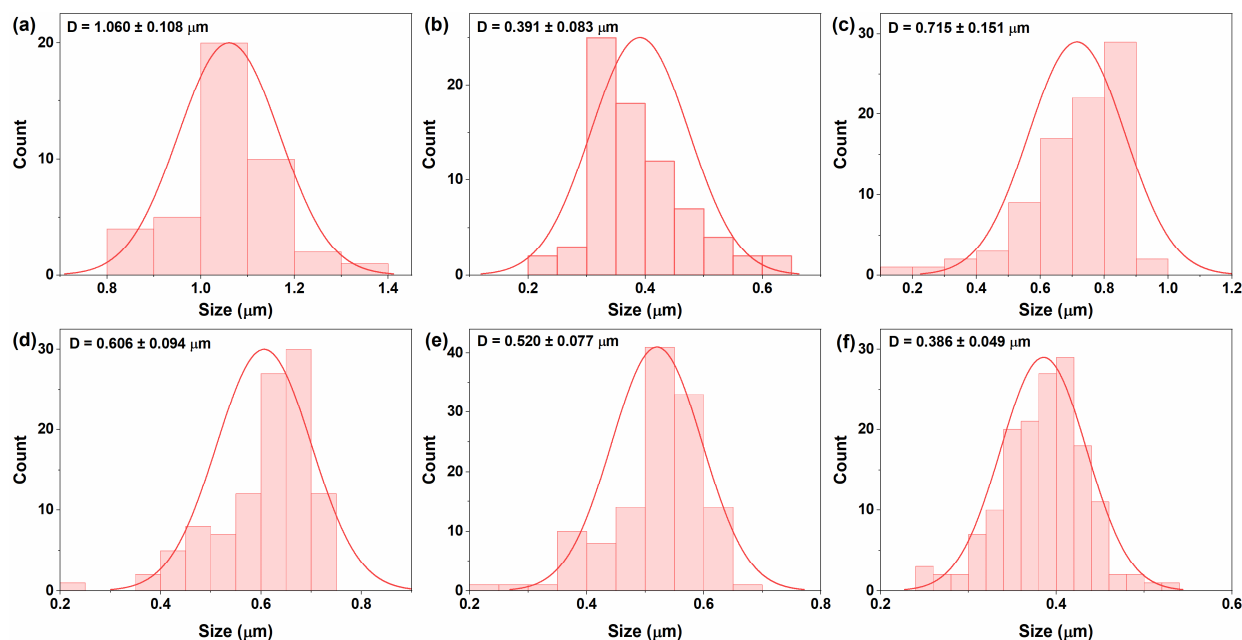


Figure 5. Particle size distribution manually traced on the SEM images using imageJ software: Fe_3O_4 particles synthesized by the solvothermal method with varying urea dosages of (a) 5, (b) 10, (c) 20, (d) 40, (e) 60, and (f) 80 mmol.

According to the analysis presented in Figures 1–5, it could be observed that both the dispersion and particle size distribution of Fe_3O_4 products could be effectively regulated by

varying the amount of urea added. The dispersion, grain size, crystallinity, and particle size of Fe_3O_4 samples all played significant roles in influencing the photocatalytic degradation of XO dye. Consequently, the photocatalytic activity of Fe_3O_4 was a result of the combined effects of multiple factors.

In order to assess the magnetic sensitivity of Fe_3O_4 samples, we investigated their magnetic response behavior in water under the influence of an external magnetic field. Figure 6a illustrates the dispersion state of Fe_3O_4 samples in water without the application of a magnetic field. The Fe_3O_4 samples synthesized with urea contents of 5, 20, and 60 mmol exhibited rapid sedimentation in water. In contrast, other samples, specifically those prepared with urea contents of 10, 40, and 80 mmol, also demonstrated sedimentation; however, a greater number of particles remained suspended in the solution. This phenomenon could be attributed to particle size variations among the Fe_3O_4 samples, as supported by Figure 5. Larger particle sizes resulted in more pronounced deposition while smaller particles were more likely to remain suspended. The suspension of Fe_3O_4 particles facilitated contact between the Fe_3O_4 catalyst and XO molecules, thereby enhancing photocatalytic activity. Figure 6b illustrates the magnetic separation of all Fe_3O_4 samples in water under the influence of an external magnetic field. The volume of the vial was 30 mL, with a distance of 50 mm between the magnet and each sample vial, and the magnet was held in place for a duration of 5 min. As observed in Figure 6b, the black Fe_3O_4 particles were attracted to the side nearest to the magnet, forming a linear arrangement that diverged outward. The solution remained colorless and transparent, indicating that the obtained Fe_3O_4 exhibited strong magnetic sensitivity characteristics. This property was crucial for its recovery and reuse following catalytic processes, as it effectively shortened both separation time and processed duration while minimizing catalyst loss during recovery. The magnetic hysteresis loop of the as-synthesized Fe_3O_4 particles, produced with a urea dosage of 40 mmol, was measured using a VSM at room temperature in the applied magnetic field ranging from -15 to 15 kOe. As illustrated, the hysteresis loop traversing the origin of coordinate axes (the red dot in Figure 6c) exhibited minimal hysteresis behavior. Consequently, these Fe_3O_4 particles could be classified as soft-magnetic materials exhibiting superparamagnetism [53]. The saturation magnetization (M_s) was 90.0 emu/g, comparable to or even exceeding values reported in other studies [10,54].

Before the photocatalytic reaction, we investigated the adsorption performance of Fe_3O_4 samples on XO dye under dark conditions. As illustrated in Figure 7a, it was evident that the adsorption efficiency of all Fe_3O_4 samples for 20 mg/L XO dye at 12 h was less than 7% . This suggested that Fe_3O_4 exhibited a weak adsorption capacity towards XO, and the predominant mechanism appeared to be physical adsorption, primarily driven by electrostatic interactions. Figure 7b illustrates the photocatalytic degradation rates of XO in the presence of Fe_3O_4 synthesized with varying urea dosages of 5, 10, 20, 40, 60, and 80 mmol. As observed, XO molecules were progressively degraded in aqueous solution as the duration of UV radiation was extended. For the Fe_3O_4 produced with a urea addition of 5 mmol, nearly complete degradation (XO solution became colorless and transparent) was achieved after 2.5 h of ultraviolet exposure. When the amount of urea added was equal to or greater than 10 mmol, all resulting Fe_3O_4 samples exhibited a rapid degradation effect on XO; specifically, the degradation reached nearly complete levels within just 1.5 h of photocatalysis. Furthermore, extending the ultraviolet radiation time by an additional 2 h resulted in no detectable signals from XO molecules. Notably, among all tested Fe_3O_4 catalysts, the Fe_3O_4 sample derived from a urea dosage of 40 mmol demonstrated slightly superior photocatalytic activity. In subsequent studies, this particular Fe_3O_4 sample would be selected as the catalyst for investigating its recycling and regeneration characteristics. To maximize the removal of any potentially adsorbed XO molecules on the surface

of the Fe_3O_4 catalyst, a longer period, specifically 2 h of UV radiation, was chosen for this purpose.

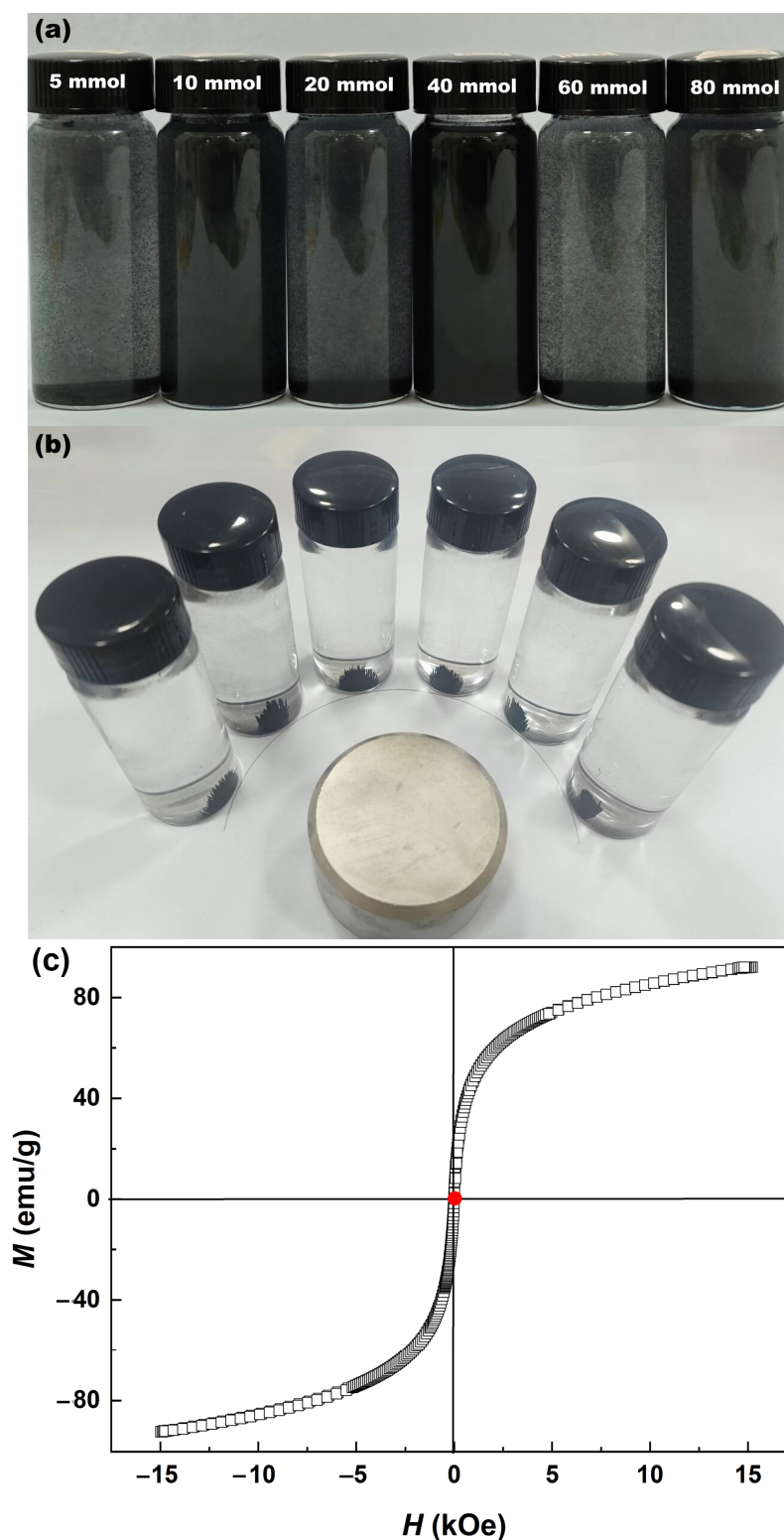


Figure 6. Pictures of progressive separation of Fe_3O_4 synthesized with varying urea dosages of 5, 10, 20, 40, 60, and 80 mmol from the suspension: (a) without magnetic field presence and (b) upon application of a Nd-Fe-B magnet for 5 min ($[\text{Fe}_3\text{O}_4] = 100$ mg, $[\text{H}_2\text{O}] = 30$ mL; the vials were 27.5 mm in diameter and 72.5 mm in height; the magnet was 50 mm away from the vials). (c) Room-temperature magnetic hysteresis loop of Fe_3O_4 synthesized with the urea dosage of 40 mmol.

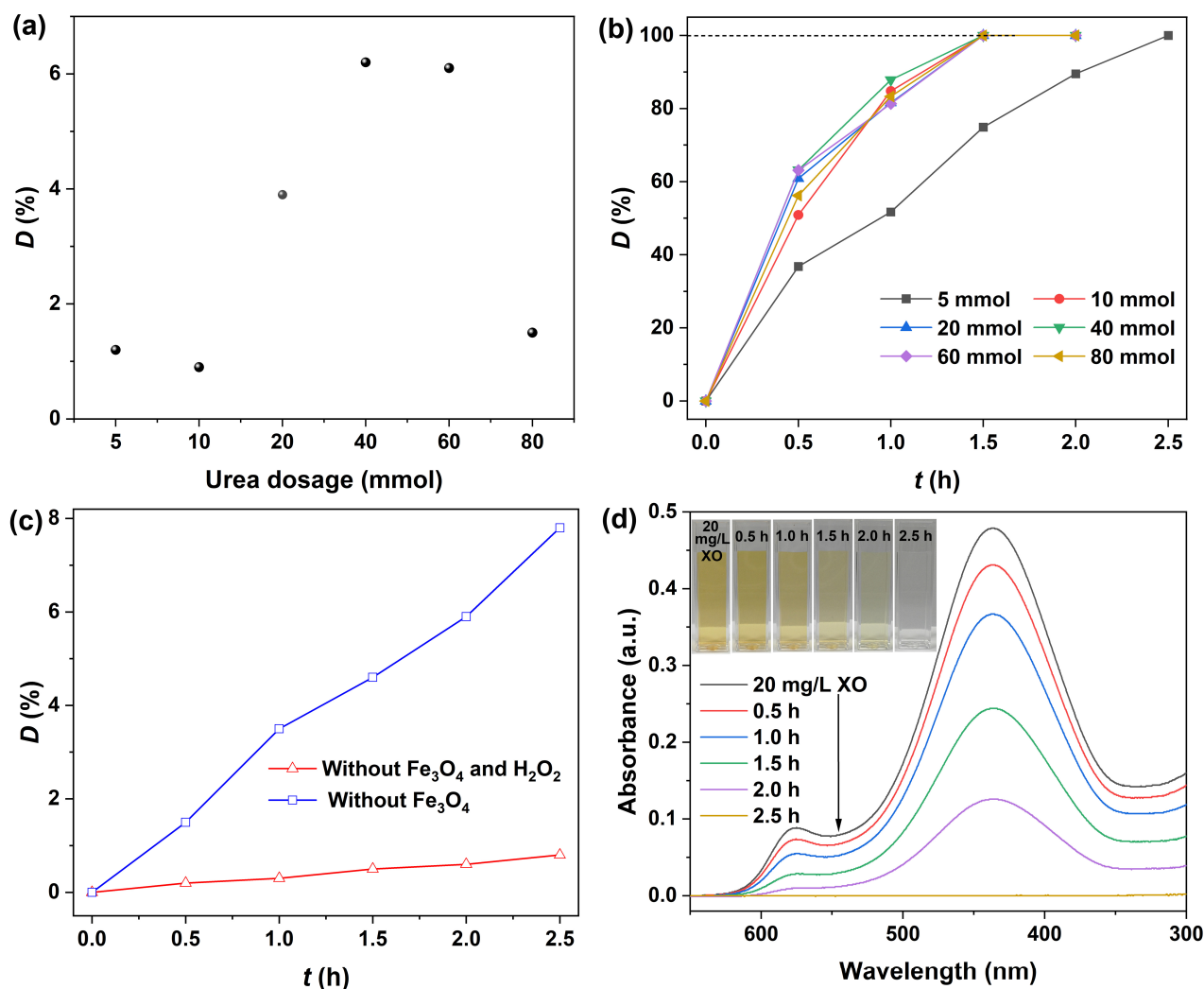


Figure 7. (a) Adsorption of XO in the dark over a period of 12 h and (b) photocatalytic degradation in the presence of Fe_3O_4 synthesized with varying urea dosages of 5, 10, 20, 40, 60, and 80 mmol; (c) photocatalytic degradation of XO solution without Fe_3O_4 and without both Fe_3O_4 and H_2O_2 ; (d) UV-Vis spectra along with photographs depicting the initial concentration of 20 mg/L XO solution and the degraded XO solution in the presence of Fe_3O_4 synthesized with a urea dosage of 5 mmol under UV radiation for durations of 0.5, 1.0, 1.5, 2.0, and 2.5 h. ($[\text{Fe}_3\text{O}_4] = 100 \text{ mg}$; $[\text{XO}] = 20 \text{ mg/L}$; $V = 100 \text{ mL}$; $[30\% \text{H}_2\text{O}_2] = 1 \text{ mL}$; room temperature; without pH pre-adjustment).

For comparative analysis, we conducted two control experiments on photocatalytic degradation: one without Fe_3O_4 and another devoid of both Fe_3O_4 and H_2O_2 . As illustrated in Figure 7c, the degradation rate of the XO solution under UV light was less than 2% when neither Fe_3O_4 nor H_2O_2 was present, rendering it almost negligible. In the absence of Fe_3O_4 , H_2O_2 exhibited a limited degradation effect on the XO solution, achieving an efficiency of less than 8%. These results underscored the essential role that the Fe_3O_4 catalyst played in facilitating the photocatalytic degradation of XO. Figure 7d presents the UV-Vis spectra of a 20 mg/L XO solution and the degraded XO solution in the presence of Fe_3O_4 , synthesized with a urea dosage of 5 mmol, under UV radiation for durations of 0.5, 1.0, 1.5, 2.0, and 2.5 h. As the duration of ultraviolet radiation increased, the absorption peaks in the UV-Vis spectra at 437 nm and 577 nm gradually diminished, resulting in a lighter coloration of the XO solution (Figure 7d inset). After conducting the photocatalytic reaction for 2.5 h, the UV-Vis spectrum approached a straight line, and the XO solution became colorless and transparent.

Catalyst regeneration not only enhanced the utilization and production efficiency of catalysts but also mitigated catalyst consumption and environmental pollution, thereby conserving resources. Furthermore, catalyst regeneration offered economic advantages by reducing production costs for enterprises. Figure 8 illustrates the regeneration cycle test of Fe_3O_4 samples with an addition of 40 mmol urea, where the UV radiation duration in each cycle was maintained at 2 h. As depicted in Figure 8, Fe_3O_4 retained nearly complete degradation for a 20 mg/L XO solution after five catalytic cycles. However, there was a noticeable decline in catalytic activity during subsequent cyclic degradations, with degradation rates recorded at 99.0%, 97.6%, and 95.8% for the sixth, seventh, and eighth cycles, respectively. It was evident that following the regeneration process of the Fe_3O_4 catalyst, its catalytic activity could be restored to its initial level within five cycles before experiencing a slight reduction thereafter.

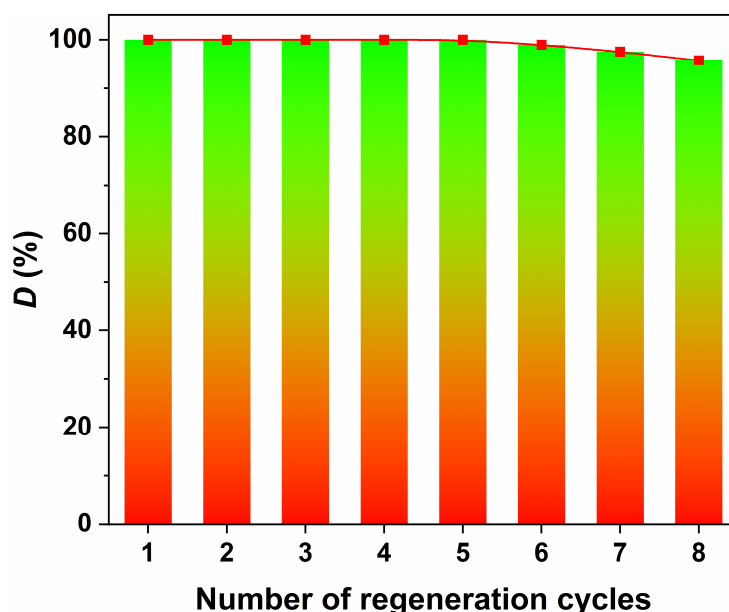
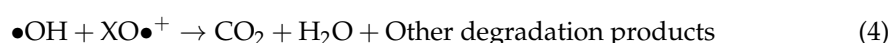
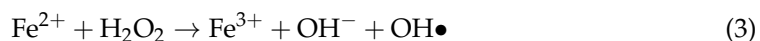
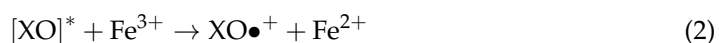


Figure 8. Regeneration cycles of Fe_3O_4 synthesized with the urea dosage of 40 mmol for the degradation of XO dye at room temperature.

The mechanism of the XO degradation process utilizing an Fe_3O_4 catalyst as a Fenton-like agent is illustrated in Equations (1)–(4). In this photo-Fenton system, XO molecules are excited by UV radiation to reach the appropriate triplet state ($[\text{XO}]^*$), as shown in Equation (1). The electron from the excited dye is captured by Fe^{3+} on the surface of Fe_3O_4 , resulting in the reduction of Fe^{3+} , which subsequently leads to the oxidation of the dye ($\text{XO}\bullet^+$), as depicted in Equation (2). The catalytic decomposition mechanism of H_2O_2 in the presence of Fe^{2+} can be described according to the classical Haber–Weiss mechanism [70], generating active species such as hydroxyl radicals ($\text{OH}\bullet$), as represented in Equation (3). Consequently, Fenton reactions are initiated, leading to the degradation of XO dye accordingly. The end products of this process include CO_2 , H_2O , and other less toxic minerals such as nitrates and sulfates (Equation (4)) [71,72].



3. Materials and Methods

3.1. Starting Materials

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), urea (99.999%) and xylenol orange (XO, indicator grade) were procured from Aladdin Co., Ltd. (Shanghai, China), while ethylene glycol (AR) and hydrogen peroxide (H_2O_2 , 30%) were sourced from Chengdu Kelong Chemical Co., Ltd. (Chengdu, China). All reagents were utilized directly without any further treatment, and purified water was employed in all experimental procedures.

3.2. Synthesis of Monodisperse Magnetic Fe_3O_4

Magnetic Fe_3O_4 catalysts were synthesized using a solvothermal method without subsequent calcination, employing only $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and ethylene glycol as raw materials. Typically, 5 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 60 mL of ethylene glycol under magnetic stirring. The desired amounts of urea (5, 10, 20, 40, 60, and 80 mmol) were then added with continuous stirring for 1 h. Subsequently, the resulting mixed solution was sealed in a Teflon-lined stainless-steel autoclave and heated at 200 °C for 48 h. After the solvothermal reaction, the system was allowed to cool naturally to room temperature. The obtained black precipitates were collected and washed with ethanol and purified water. Finally, a series of Fe_3O_4 powders were acquired by drying in a vacuum at 60 °C for 24 h.

For comparison purposes, the control experiment was performed following the same procedure as controls but without the addition of urea. As a result, no precipitated material was obtained.

3.3. Characterization

The compositional phases of the samples were analyzed through a DX-2700 X-Ray Diffraction (XRD, Dandong Haoyuan Instrument Co., Ltd., Dandong, China) using graphite-monochromatized Cu K α radiation with 30 kV tube voltages and 25 mA current. The measurement method employed was step measurement, with a step angle of 0.04°/s. The sampling duration was set at 1 s, and the scanning range extended from 10° to 80°. The morphological characteristics of the samples were elucidated using an SEM5000 Scanning Electron Microscope (SEM, CIQTEK Co., Ltd., Hefei, China) at a 5 kV voltage. The magnetic properties of samples were examined by a Lakeshore 7307 vibrating sample magnetometer (VSM, Novi, MI, USA). The absorbance spectra of XO dye solutions were recorded employing a U-3900 Ultraviolet–Visible spectrophotometer (Uv-Vis, Hitachi Ltd., Tokyo, Japan).

3.4. Degradation of XO Dye

The photocatalytic degradation of XO under UV light illumination using as-obtained Fe_3O_4 catalysts was evaluated. Briefly, 100 mg of Fe_3O_4 powders was dispersed into 50 mL of an aqueous solution containing XO at a concentration of 20 mg/L through ultrasound treatment for 5 min. Subsequently, 1 mL of a 30% H_2O_2 aqueous solution was added and mixed thoroughly. The resulting suspension was then transferred to a culture dish with a diameter of 120 mm and illuminated by simulated UV light generated from a medical ultraviolet lamp (220 V, 300 W, 254 nm).

During each sampling, the UV light was turned off, and a magnet was positioned beneath the culture dish to facilitate sampling and immediate absorbance testing. The absorbance of the liquid supernatant at the maximum absorption wavelength of 437 nm was measured using an Uv–Vis spectrophotometer. Subsequently, the supernatant was carefully reintroduced into the catalytic system and gently stirred to ensure uniform dispersion of Fe_3O_4 particles. Finally, the UV light was activated to resume the photocatalytic reaction. The degradation rate (D , %) was calculated using the following equation: $D(\%) = [(A_0 - A_t)/A_0] \times 100\%$, where A_0 represents the absorbance of the initial XO solu-

tion at a concentration of 10 mg/L and A_t denotes the absorbance of the XO supernatant at a given time t .

3.5. Regeneration of Fe_3O_4 Catalyst

After the first degradation under UV illumination and magnetic separation, Fe_3O_4 particles were mixed with 50 mL of 20 mg/L XO aqueous solution. This mixture was subjected to ultrasound treatment for 5 min. Subsequently, 1 mL of a 30% H_2O_2 aqueous solution was added and thoroughly mixed into the suspension. The resulting mixture was then transferred to a culture dish and exposed to simulated UV light for 2 h. Each subsequent regeneration experiment adhered to the same procedure as described above.

4. Conclusions

In the absence of subsequent roasting processes in reduction or inert atmospheres, a sample one-step solvothermal method was successfully employed to synthesize well-defined and monodisperse Fe_3O_4 microspheres. This environmentally friendly synthesis process utilized only three types of raw materials: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (iron source), ethylene glycol (solvent), and urea (mineralizer or surfactant). The advantages of this approach included stability, safety, availability, and low cost. When the amount of urea added exceeded 5 mmol, pure cubic Fe_3O_4 polycrystalline structures were obtained, with crystallinities ranging from 71% to 78%. Furthermore, when the addition of urea surpassed 10 mmol, the yield of as-synthesized Fe_3O_4 exceeded 85.0%. In contrast, at an addition level of 5 mmol urea, the yield dropped significantly to only 27.8%. Regarding morphology, Fe_3O_4 samples synthesized with urea additions of 20 and 40 mmol exhibited particularly rounded spherical shapes with narrow particle size distributions primarily ranging from 0.6 μm to 0.9 μm and from 0.55 μm to 0.75 μm , respectively. All as-obtained Fe_3O_4 microspheres demonstrated excellent photocatalytic degradation activity towards XO dye; a 20 mg/L XO solution became colorless and transparent under UV radiation in just 1.5 h, except for the sample derived from a urea addition of 5 mmol which required approximately twice that time (about 2.5 h) to achieve similar results. The cyclic regeneration performance was further explored using the Fe_3O_4 sample produced with a urea addition of 40 mmol as a catalyst; its catalytic activity could be restored to initial levels within five cycles before experiencing slight declines thereafter. Notably, during the eighth cycle period, it still maintained an impressive XO degradation rate of 95.8%. The strategy proposed in this work for synthesizing monodisperse Fe_3O_4 microspheres via a one-step method is characterized by low energy consumption while adhering to high safety standards and achieving elevated yields.

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