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Magnesium Ferrite (MgFe_2O_4) Nanoparticles for Photocatalytic Antibiotics Degradation

<https://doi.org/10.1515/zpch-2019-1430>

Received March 29, 2019; accepted September 18, 2019

Abstract: Removal of drug residuals in waste water by easy-separable catalysts is of fundamental interest for clean water provision by photocatalytic water remediation. Here, we present our studies to use the ferrimagnetic earth-abundant absorber MgFe_2O_4 , prepared by microwave-assisted synthesis, for the photocatalytic removal of methylene blue and tetracycline from model solutions under dark and sunlight conditions. The surface of MgFe_2O_4 has a strong influence on the tetracycline removal, while more than 75% tetracycline degradation can already be achieved in 2 h with unmodified MgFe_2O_4 . Using surface-modified MgFe_2O_4 nanoparticles, the adsorption of tetracycline is even more pronounced, however goes in line with release of the surface capping agent.

Keywords: antibiotics degradation; ferrites; photocatalysis; wastewater treatment.

1 Introduction

Heterogeneous photocatalysis is a promising method to use solar energy for the generation of solar fuels (hydrogen, products of CO_2 -reduction), but also for the remediation of wastewater to produce clean water [1, 2]. Very interesting is this approach for the remediation of industrial wastewaters, which can contain relatively large amounts of residual solvent molecules [3].

Especially due to more often occurring resistances, residual antibiotics are emerging pollutants in wastewaters important to be degraded [4, 5]. The amount of antibiotics in groundwater is increasing for many years in many regions, also due to high concentrations in manufacture effluents [6]. Here, advanced oxidation processes (AOP) like photocatalytic degradation of antibiotics like tetracycline

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[7–9], ciprofloxacin [10–12] or levofloxacin [13, 14] utilizing solar light could be a possible solution.

Recently we reported on the photocatalytic and photoelectrochemical activity of different ternary ferrite materials, including MgFe_2O_4 [15], ZnFe_2O_4 [16], CaFe_2O_4 [17] and LiFe_5O_8 [18] as promising absorber materials. All those oxides exhibit band gaps far in the visible light range (1.9–2.4 eV), are non-toxic, stable in aqueous media above pH 4, and consist only of earth-abundant elements [19]. The latter would render an industrial utilization and low cost production feasible. Moreover, due to their ferrimagnetism, they could be easily separated after wastewater treatment with a magnet.

We could also show that MgFe_2O_4 (MFO) can be used to degrade the model dye rhodamine B using solar light, and that surface modification can have a profound effect on the degradation activity [15]. While the band gap of MFO is around 2 eV, the valence band position is above the one-electron oxidation potential of water to hydroxyl radicals ($E^0 = 2.8 \text{ V}$) [20]. Thus, a direct hole oxidation of the dye is supposed.

Here, we present our investigation on the photocatalytic degradation of tetracycline, a common antibiotic, using MFO nanoparticles under simulated sunlight irradiation. MFO can degrade tetracycline and methylene blue in sunlight quite efficiently, and tailored surface modification leads to a high surface adsorption of the compound for the degradation process.

2 Experimental

2.1 Syntheses

MFO nanoparticles were prepared according to Kirchberg et al. [15], including stripping and stabilization with betaine hydrochloride (BETA) or citrate (CIT). The as-prepared MFO nanoparticles after microwave-assisted synthesis need no calcination step afterwards.

2.2 Characterization

Photocatalytic degradation experiments were performed using 0.5 mg/mL nanoparticles mixed with an ultrasonic bath with a cooling spiral, connected to a thermostat, to keep the temperature of the dispersion constant at 25 °C. Typical concentrations were 10^{-5} mol/L for methylene blue test reaction and 10^{-4} mol/L for tetracycline (Scheme 1).

Irradiation was performed using a 150 W sun simulator from Newport (Sol1A).

Scheme 1: Chemical structures of methylene blue (left) and tetracycline (right).

For separation of nanoparticles for the absorption measurements, non-stabilized nanoparticles were separated with a magnet, while stabilized nanoparticles were precipitated using sodium sulfate (betaine-stabilized) or sodium hydroxide (citrate stabilization).

Absorption spectra were measured on a PerkinElmer Lambda750 UV/Vis/NIR spectrometer. TOC measurements were performed on a DIMATOC 2010 K1. TG analysis was performed on a Netsch STA409PC thermobalance.

3 Results and discussion

Unstabilized MgFe_2O_4 (MFO) nanoparticles were used to evaluate the photocatalytic degradation of methylene blue (MB). Recently, Bahnemann et al. used ZnFe_2O_4 for MB degradation [21].

Before irradiation, the dispersions of MFO in MB solution were stirred under dark condition to establish the adsorption-desorption equilibrium. The absorption spectra before and after this period are shown in Figure 1a, indicating hardly any difference. The absorption spectra after equilibration are always used as the starting point for the kinetic evaluation.

Starting the irradiation, the absorption spectra change indicating an ongoing bleaching of MB in sunlight. For comparison, a 2 h irradiation of a photocatalyst-free dye solution shows only minor but measurable differences, indicating a degradation under sunlight of about 5% (Figure 1b). Therefore, the kinetic analysis has to be evaluated with care.

In the presence of MFO, the degradation after 2 h is 39% (Figure 1c), indicating a photocatalytically-induced enhancement in MB bleaching, with a rate constant of 0.239 h^{-1} assuming first order kinetic at such low concentrations. Bahnemann et al. recently addressed the mechanism of MB bleaching to a sensitization effect on ZnFe_2O_4 with MB, which we believe to be also viable for MFO due to its very similar band positions with ZnFe_2O_4 . Moreover, these authors

Fig. 1: MB degradation with unstabilized MFO nanoparticles: (a) UV-vis spectra of the ongoing reaction; (b) degradation of MB in sunlight without photocatalysts; (c) concentration over time of the degradation of MB with MFO, 39% after 2 h; (d) kinetic analysis, $k = 0.239 \text{ h}^{-1} \pm 0.038 \text{ h}^{-1}$.

confirmed that no hydroxyl radicals were generated by photo-excitation of ZFO in aqueous suspension [21], which we suppose is viable for MFO, too.

MFO nanoparticles after the microwave synthesis can exhibit residual precursors on the surface, as indicated earlier. Surface functionalization however can have a profound effect on the degradation activity of MFO [15]. After treating the MFO nanoparticles with Meerwein salt to strip any ligands from the surface, the activity for MB degradation is reduced to 29% after 2 h (Figure 2), indicating that the surface after microwave-assisted sol-gel synthesis at 275 °C might be more attracting to MB molecules for degradation.

When the surface of MFO was modified for stabilization with betaine hydrochloride (BETA) according to our earlier work, no traceable MB degradation could be observed, most probably due to electrostatic repulsion of the stabilized surface and MB. Stabilized MFO nanoparticles can be easily precipitated with small addition of NaOH for separation and absorption measurement.

Fig. 2: MB degradation with stripped MFO nanoparticles: (a) concentration over time of the degradation of MB with stripped MFO, 29% after 2 h; (b) kinetic analysis, $k = 0.173 \text{ h}^{-1} \pm 0.018 \text{ h}^{-1}$.

Figure 3 shows the absorption spectrum of tetracycline solution. As can be seen, this antibiotic compound exhibits no observable decomposition under sunlight illumination (Figure 3a). However, it strongly interacts with the unstabilized MFO surface, as indicated by the strong changes in the absorption spectrum after equilibration in the dark (Figure 3b). Starting sunlight illumination, 76% degradation after 2 h and 95% degradation after 5 h was observed, with a rate constant of 0.517 h^{-1} , which is much higher than the MB degradation with MFO.

When MFO was stabilized for reaction in aqueous media with BETA, the changes in the absorption spectra are even more drastic, as shown in Figure 4. After 30 min of stirring in the dark, 90% of tetracycline is removed from solution. The following degradation under light irradiation has been followed, too.

In order to understand the effect of adsorption and degradation of tetracycline on MFO, we measured thermogravimetry (TG), infrared spectroscopy (IR), and total organic carbon (TOC) to evaluate the degree of mineralization.

TG measurements of unstabilized MFO nanoparticles before and after tetracycline addition & stirring in the dark show an increased mass loss in the region between 200 and 380°C , up from 11.3 wt.-% to 13.5 wt.-% (Figure 5), indicating the increase of compounds on the MFO surface. According to the measured absorption spectra (Figure 3b), this goes in line with tetracycline adsorption.

Moreover, TOC analysis for every respective absorption spectrum in Figure 3b shows reduced amounts of organic carbon in solution after dark adsorption before irradiation, going in line with the changes in intensity of the absorption spectra for tetracycline removal by adsorption.

Fig. 3: (a) irradiation of tetracycline solution without MFO; (b) UV-vis spectra of tetracycline degradation with unstabilized MFO nanoparticles; (c) concentration over time for the degradation of tetracycline with MFO nanoparticles, 76% after 2 h; (d) kinetic analysis, $k = 0.517 \text{ h}^{-1} \pm 0.044 \text{ h}^{-1}$.

However, during irradiation the TOC increases slowly with time (Figure 5b). These results might arise from an ongoing degradation of tetracycline. Since the TOC values do not reach the values before dark adsorption, however continuously increase, we assume only a small degree of mineralization, which has to be confirmed by more measurements in the future.

In contrast, with BETA-stabilized MFO nanoparticles after tetracycline dark adsorption, a reduced mass loss in TG measurements between 200 and 380 °C is surprisingly observed (Figure 6a). IR spectra before and after dark tetracycline adsorption however show interesting results, indicating intense signals for typical tetracycline bands as marked after dark adsorption (Figure 6c), including the C=O vibration at 1718 cm^{-1} . In TOC measurements, an increase in TOC is observed even after dark adsorption (Figure 6b), followed by an ongoing increase in the TOC with irradiation in accordance with the unstabilized MFO nanoparticles (compare Figure 5b).

Fig. 4: tetracycline absorption and degradation of tetracycline with betaine-stabilized MFO: (a) UV-vis spectra of the ongoing reaction; (b) enlarged UV-vis spectra after tetracycline adsorption onto BETA-stabilized MFO.

Fig. 5: (a) TG curves of unstabilized MFO nanoparticles before and after tetracycline adsorption; (b) TOC results measured during illumination-induced tetracycline degradation with unstabilized MFO (compare Figure 3).

The TOC after dark adsorption indicates that carbon-containing organics are released into the liquid in the dark, while tetracycline is adsorbed on MFO according to IR, and the overall mass is reduced. These results indicate an entropic effect of ligand exchange of the initial BETA capping with tetracycline, resulting in several BETA molecules being removed for one tetracycline adsorption. This leads to a release of more organic carbon to the solution from BETA molecules than adsorption of carbon (from tetracycline) onto MFO, resulting in an increase in TOC before irradiation. The entropic effect manifests also in the stronger reduced absorption bands of tetracycline in Figure 4 for BETA-stabilized MFO compared to the dark adsorption on unfunctionalized MFO.

Fig. 6: (a) Thermogravimetric analyses of BETA-stabilized MFO nanoparticles, before and after adsorption of tetracycline; (b) TOC results of the solution according to irradiation-induced degradation in Figure 4; (c) IR spectra of BETA-stabilized MFO nanoparticles before and after tetracycline adsorption.

Quantitative analysis of the ligand exchange and the degree of mineralization have to be conducted in much more detail in the future. Nevertheless, as reported for rhodamine B degradation, the surface of MFO can have a strong influence on the mechanism of pollutant removal from waste waters.

4 Conclusion

Magnesium ferrite nanoparticles have been used to treat model solutions of the antibiotic drug tetracycline for photocatalytic degradation. It turns out that tetracycline can be easily adsorbed on unstabilized magnesium ferrite nanoparticles, acting already as promising adsorbent for antibiotics removal from waste waters. Subsequently, the drug is further degraded upon solar light irradiation. Using surface-modified magnesium ferrite nanoparticles, the adsorption of tetracycline

is even more pronounced, however goes in line with release of the surface capping agent. This mechanism and further products of the degradation process have to be investigated in more detail in the future to prove to viability of this adsorption-degradation process for wastewater treatment.

Acknowledgements: We thank Dr. Christian Suchomski (Institute of Physical Chemistry, Justus-Liebig University Giessen) for his support in the beginning of this project, and Prof. Dr. Bernd M. Smarsly for his continuing support. We want to thank Dr. Astrid Spielmeyer and Prof. Dr. Gerd Hamscher for letting us use their TOC instrument (both Justus-Liebig University Giessen). We would like to thank the Center of Materials Research (LaMa) at Justus-Liebig-University Giessen for the support of this project. R.M. and K.K. gratefully acknowledge funding by the German Research Foundation DFG under the priority program SPP 1613, Funder Id: <http://dx.doi.org/10.13039/501100001659>, project MA 5392/5-1.

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