PHOTOCATALYTIC EFFICIENCY OF ZnFe-MIXED METAL OXIDES IN CORRELATION WITH REACTION PARAMETERS

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Abstract

In the last decade, the interest for the photocatalytic phenomena has rapidly grown due to its great potential for the overall environmental decontamination. Photocatalysts based on ZnFe mixed oxides have been considered to be potentially photocatalyticly efficient in wastewater purification. This investigation is focused on the characterization of the synthesized and thermally treated photocatalysts, on their photocatalytic efficiency in the degradation process of organic dye pollutant Rhodamine B (RhB), as well as on the influence of process parameters on the photocatalytic efficiency. The results showed that the obtained mixed oxides are highly efficient in the RhB degradation. In addition, the pH effect of the reaction system on the photocatalytic activity was observed, which could be explained by the correlation with different textural and structural properties of the photocatalysts.

Introduction

The concern for the exponential increase of environmental pollution with no systematic solution has become overwhelming in the scientific community [1]. Organic dye pollutants from different industries regularly occur in wastewater and initiate vast hazardous environmental problems, considering their toxicity, unpleasant colouring and non-biodegradation [2]. Therefore, the search for the most effective removal method is still in progress and has become a challenging and motivating task with the aim to decrease or completely eliminate environmental problems regarding dye pollutants in wastewater. Zinc oxide (ZnO) has been considered to be a good candidate for the wastewater purification due to its wide band gap (3.2 eV) in the near-UV spectral region, strong oxidation ability, good photocatalytic property and low cost. It has been brought to the attention in scientific publications, that more efficient photodegradation is triggered by coupling of semiconductors with a wide band gap with another semiconductor with a narrow energy band [3]. Therefore, the motivation for this investigation was to develop a simple and inexpensive synthesis method for ZnFe-mixed metal oxides with the desired properties in order to enhance photocatalytic performance in photodegradation of organic dyes, as well as to investigate the influence of the process parameters on the photodegradation efficiency.

Experimental

Mixed metal oxides were synthesized by the coprecipitation method using $Zn(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ precursors that were added in the base solution (0.67 M Na_2CO_3 and 2.25 M NaOH) and vigorously stirred at constant temperature (40°C). The precipitates were aged and then washed with deionized water until pH 7 was reached. The products were dried for 24 h at 100°C (sample denoted as ZnFe-100) and thermally treated for 5 h at 300°C (denoted as ZnFe-300).

X-ray powder diffraction (XRD) analysis was used for the identification of the phase composition, conducted by Rigaku MiniFlex 600.

Photocatalytic tests were performed in an open cylindrical thermostated Pyrex reaction vessel using ULTRA VITALUX 300 W lamp, to simulate solar light irradiation. Before illumination, reaction mixtures (50 mg of catalysts and 100 ml of 10 μmol/l (RhB solution) were stirred in the dark for 30 min to ensure adsorption/desorption equilibrium. The reaction solutions were than submitted to light irradiation while stirred. Aliquots were analysed at the defined time intervals using UV-VIS spectrophotometer. The photocatalytic activity was estimated by RhB photodegradation, monitoring the decrease of the RhB concentration in time.

The effect of the initial pH of reaction solutions on the photodegradation efficiency of RhB was studied in the range of 2-12. Aqueous solutions of HCl and NaOH were applied for the adjustment of the initial pH and the photodegradation efficiency of ZnFe-300 sample was measured after 180 min of light irradiation.

Results and discussion

The results of the structural characterisation are presented in Figure 1 as XRD diffraction peaks of the ZnFe-photocatalysts (ZnFe-100 and ZnFe-300). The XRD diffraction patterns for the ZnFe-100 sample exhibited sharp intense diffraction peaks at 31.79°; 34.4°; 36.25°; 47.5°; 56.6°, 62.85° i 67.97° that correspond to (100), (002), (101), (102), (110), (103) i (112) crystalline lattice for the ZnO phase [4].

After thermal treatment at 300°C the formation of additional spinel phase $ZnFe_2O_4$ with the cubic structure was detected with diffraction peaks at 0.05°, 35.36°, 42.78°, 52.96°, 56.78° and 62.2° [5]. It can be concluded that the thermal treatment at higher temperature initiated the formation of the spinel phase that has been cited as the phase that enhances photocatalytic properties of the photocatalyst.

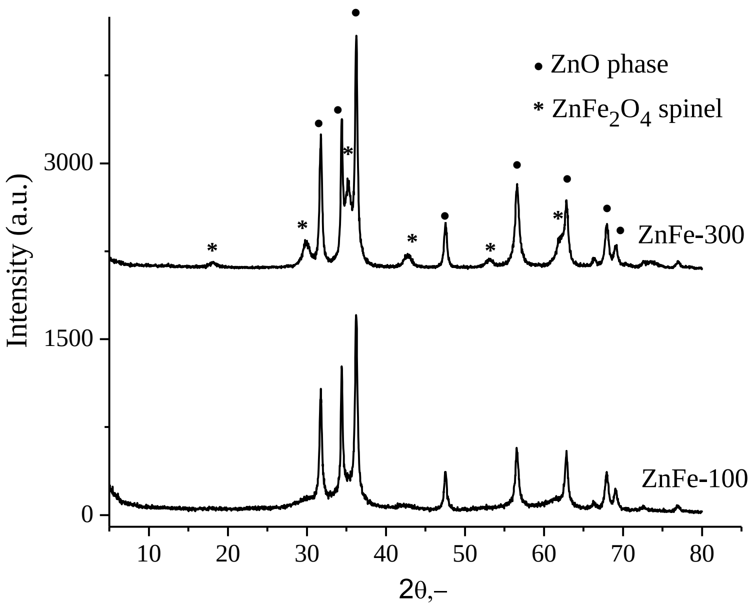

Figure 1. XRD diffraction peaks for sample: ZnFe-100 and ZnFe-300

The results of the RhB photodegradation, presented in Figure 2, show that the photocatalyst activated at higher temperature, ZnFe-300, exhibits higher photocatalytic efficiency (over 91% after 330min of UV irradiation) than photocatalyst treated at lower temperature, ZnFe-100 (around 50% after 330min f UV irradiation). The enhanced photodegradation could be assigned to the formation of the additional $ZnFe_2O_4$ spinel phase after thermal treatment.

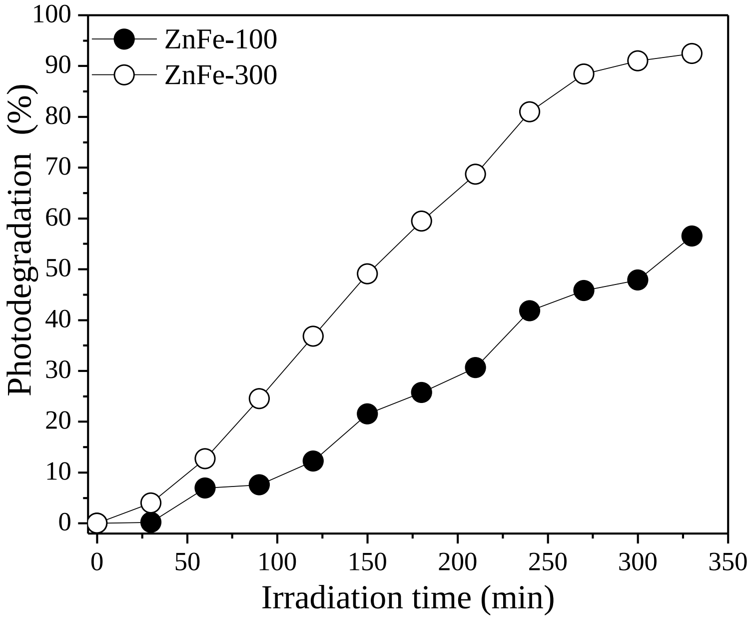

Figure 2. The photodegradation of RhB as a function of light irradiation time

In order to determine the influence of the pH on the photocatalytic effieciency, numerous photodegardation reactions were conducted using better performing photocatalyst (ZnFe-300) at different pH values, measuring the photodegradation efficiency at the same time intervals (Figure 3). The optimal pH resulting in the most efficient photodegradation for ZnFe-300 photocatalyst was observed at pH 6. The photodegradation efficiency increased with the increase of the pH values up to pH 6 and than gradually decreased in the alkaline pH region.

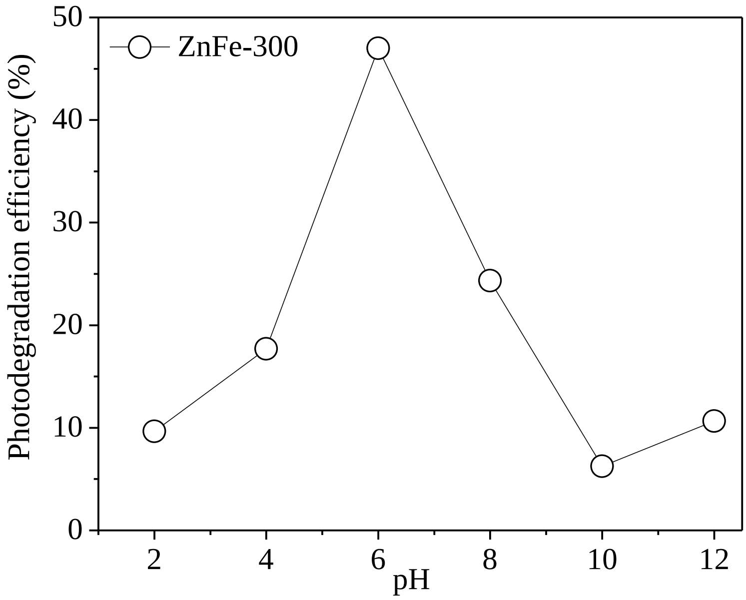

Figure 3. Influence of the pH values on the photocatalytic efficiency of ZnFe-300

Conclusion

In this investigation, ZnFe-mixed oxides were successfully synthesized and thermally treated at 100 and 300°C. The XRD and photocatalytic results confirmed that the ZnFe-300 catalyst, composed of wurzite ZnO and spinel structured $ZnFe_2O_4$ phases, had better crystallinity and enhanced photocatalytic efficiency in the RhB photodegradation compared to ZnFe-100 photocatalyst. The results proved that the $ZnFe_2O_4$ spinel phase conclusively affects the photocatalytic efficiency probably due to the synergic coupling effect of ZnO and $ZnFe_2O_4$. Additionally, the ZnFe-300 photocatalyst exhibited significant loss of activity in the acidic (pH from 2 to 6) and alkaline solutions (pH higher than 7) suggesting that the optimal pH for RhB photodegradation using ZnFe mixed oxides, is around pH 6. This research enabled a better insight into the influence of photocatalyst thermal activation on physico-chemical properties of ZnFe-mixed oxide based photocatalysts in correlation with their photocatalytic performance at various pH reaction conditions.

Acknowledgements

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