

Improvement in the Photocatalytic Activity of Nanostructured Manganese Ferrite - Type of Materials by Mechanochemical Activation

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Abstract : The synthesized nanosized manganese ferrite-type of samples have been tested as photocatalysts in the reaction of oxidative degradation of model contaminant Reactive Black 5 (RB5) dye in aqueous solutions under UV irradiation. As it is known this azo dye is applied in the textile-coloring industry and it is discharged into the waterways causing pollution. The co-precipitation procedure has been used for the synthesis of manganese ferrite-type of materials: Sample 1 - $Mn_{0.25}Fe_{2.75}O_4$, Sample 2 - $Mn_{0.5}Fe_{2.5}O_4$ and Sample 3 - $MnFe_2O_4$ from 0.03M aqueous solutions of $MnCl_2 \cdot 4H_2O$, $FeCl_2 \cdot 4H_2O$ and/or $FeCl_3 \cdot 6H_2O$ and 0.3M NaOH in appropriate amounts. The mechanochemical activation of co-precipitated ferrite-type of samples has been performed in argon (Samples 1 and 2) or in air atmosphere (Sample 3) for 2 hours at a milling speed of 500 rpm. The mechano-chemical treatment has been carried out in a high energy planetary ball mill type PM 100, Retsch, Germany. The mass ratio between balls and powder was 30:1. As a result mechanochemically activated Sample 4 - $Mn_{0.25}Fe_{2.75}O_4$, Sample 5 - $Mn_{0.5}Fe_{2.5}O_4$ and Sample 6 - $MnFe_2O_4$ have been obtained. The synthesized manganese ferrite-type photocatalysts have been characterized by X-ray diffraction method and Moessbauer spectroscopy. The registered X-ray diffraction patterns and Moessbauer spectra of co-precipitated ferrite-type of materials show the presence of manganese ferrite and additional akaganeite phase. The presence of manganese ferrite and small amounts of iron phases is established in the mechanochemically treated samples. The calculated average crystallite size of manganese ferrites varies within the range 7 - 13 nm. This result is confirmed by Moessbauer study. The registered spectra show superparamagnetic behavior of the prepared materials at room temperature. The photocatalytic investigations have been made using polychromatic UV-A light lamp (Sylvania BLB, 18 W) illumination with wavelength maximum at 365 nm. The intensity of light irradiation upon the manganese ferrite-type photocatalysts was 0.66 mW.cm⁻². The photocatalytic reaction of oxidative degradation of RB5 dye was carried out in a semi-batch slurry photocatalytic reactor with 0.15 g of ferrite-type powder, 150 ml of 20 ppm dye aqueous solution under magnetic stirring at rate 400 rpm and continuously feeding air flow. The samples achieved adsorption-desorption equilibrium in the dark period for 30 min and then the UV-light was turned on. After regular time intervals aliquot parts from the suspension were taken out and centrifuged to separate the powder from solution. The residual concentrations of dye were established by a UV-Vis absorbance single beam spectrophotometer CamSpec M501 (UK) measuring in the wavelength region from 190 to 800 nm. The photocatalytic measurements determined that the apparent pseudo-first-order rate constants calculated by linear slopes approximating to first order kinetic equation, increase in following order: Sample 3 ($1.1 \times 10^{-3} \text{ min}^{-1}$) < Sample 1 ($2.2 \times 10^{-3} \text{ min}^{-1}$) < Sample 2 ($3.3 \times 10^{-3} \text{ min}^{-1}$) < Sample 4 ($3.8 \times 10^{-3} \text{ min}^{-1}$) < Sample 6 ($11 \times 10^{-3} \text{ min}^{-1}$) < Sample 5 ($15.2 \times 10^{-3} \text{ min}^{-1}$). The mechanochemically activated manganese ferrite-type of photocatalyst samples show significantly higher degree of oxidative degradation of RB5 dye after 120 minutes of UV light illumination in comparison with co-precipitated ferrite-type samples: Sample 5 (92%) > Sample 6 (91%) > Sample 4 (63%) > Sample 2 (53%) > Sample 1 (42%) > Sample 3 (15%). Summarizing the obtained results we conclude that the mechanochemical activation leads to a significant enhancement of the degree of oxidative degradation of the RB5 dye and photocatalytic activity of tested manganese ferrite-type of catalyst samples under our experimental conditions. The mechanochemically activated $Mn_{0.5}Fe_{2.5}O_4$ ferrite-type of material displays the highest photocatalytic activity ($15.2 \times 10^{-3} \text{ min}^{-1}$) and degree of oxidative degradation of the RB5 dye (92%) compared to the other synthesized samples. Especially a significant improvement in the degree of oxidative degradation of RB5 dye (91%) has been determined for mechanochemically treated $MnFe_2O_4$ ferrite-type of sample with the highest extent of substitution of iron ions by manganese ions than in the case of the co-precipitated $MnFe_2O_4$ sample (15%). The mechanochemically activated manganese ferrite-type of samples show good photocatalytic properties in the reaction of oxidative degradation of RB5 azo dye in aqueous solutions and it could find potential application for dye removal from wastewaters originating from textile industry.

Keywords : nanostructured manganese ferrite-type materials, photocatalytic activity, Reactive Black 5, water treatment

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