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Reference:

Ciocarlan Radu-George, Seftel Elena, Mertens Myrjam, Pui Aurel, Mazaj Matjaz, Novak Tusar Natasa, Cool Pegie, Seftel Elena.- Novel magnetic nanocomposites containing quaternary ferrites systems $Co_{0.5}Zn_{0.25}M_{0.25}Fe_2O_4$ (M= Ni, Cu, Mn, Mg) and TiO_2 -anatase phase as photocatalysts for wastewater remediation under solar light irradiation

Materials science and engineering: part B: solid state materials for advanced technology - ISSN 0921-5107 - 230(2018), p. 1-7

Full text (Publisher's DOI): <https://doi.org/10.1016/J.MSEB.2017.12.030>

To cite this reference: <https://hdl.handle.net/10067/1480840151162165141>

Novel magnetic nanocomposites containing quaternary ferrites systems $\text{Co}_{0.5}\text{Zn}_{0.25}\text{M}_{0.25}\text{Fe}_2\text{O}_4$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Mn}, \text{Mg}$) and TiO_2 -anatase phase as photocatalysts for wastewater remediation under solar light irradiation

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Abstract

In this study smart-removal magnetic nanocomposites are developed in an attempt to decrease the band gap energy of the catalyst and to enable separation of the catalyst from the wastewater after the process. Ferrite magnetic nanoparticles $\text{Co}_{0.5}\text{Zn}_{0.25}\text{M}_{0.25}\text{Fe}_2\text{O}_4$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Mn}, \text{Mg}$) (MNPs) are obtained by the co-precipitation method using carboxymethyl cellulose (CMC) as surfactant and NaOH as precipitation agent. Further, the magnetic nanocomposites $\text{Co}_{0.5}\text{Zn}_{0.25}\text{M}_{0.25}\text{Fe}_2\text{O}_4\text{-TiO}_2$ (anatase) (MNPs-TiO₂) are obtained by the TiO₂ deposition onto the MNPs using Pluronic P123 as template and tetra butyl titanate (TBOT) as titanium source. This type of photocatalyst can be used under solar light irradiation because of

the activation of TiO_2 with MNPs in visible light range and can be very easily recovered due to their strong magnetic properties. The MNPs- TiO_2 have proven to be very active for the degradation of different dyes, such as methyl orange and methylene blue, under solar light irradiation.

Keywords: ferrite magnetic nanoparticles, TiO_2 , solar light photocatalysis, dyes degradation, magnetic separation of the photocatalyst

1. Introduction

Nowadays water pollution is one of the most important social issues in many countries, mostly because of the presence of organic compounds in wastewaters after industrial use. The textile industry is well known for the use of considerable amounts of water for the big scale processes together with dyes[1, 2]. To overcome the water pollution problem, a suitable solution can be found in photocatalysis, by using solar light as photons source. This process occurs when the electrons (e^-) from the valence band (VB) of a semiconductor are excited by an energy that matches or exceeds the band gap energy of the semiconductor, leading to promoted electrons to the conduction band (CB). The pairs that are formed between conduction band electrons (e_{CB}^-) and valence band holes (h_{VB}^+) are mainly used further in the photocatalytic process, by forming radicals at the catalyst's surface able to degrade pollutant molecules. The drawback of the use of semiconductors (e.g. ZnO , TiO_2 , WO_3) comes from the high recombination rate between the pairs formed, resulting in the inactivation of the material. Another serious limitation is the difficulty of separation and reuse of the catalyst after the water treatment. High band gap energies required for the electrons to be promoted from the VB to the CB is also a disadvantage in using semiconductors, like TiO_2 which has a band gap energy around 3,2 eV (~ 387 nm)[3]. The necessity to activate TiO_2 in visible range

of light comes from the properties of the solar light, which has only 5% UV light. Over the years, many different approaches were used to make TiO_2 usable as catalyst under the solar light irradiation. For the visible light activation of TiO_2 many attempts were made, such as non-metal doping [4-6], transition metals doping [7-10] and noble-metal doping [11-13]. A part of these problems can be solved by combining TiO_2 with different mixed oxides, spinel type structures, which can induce unique properties to the nanocomposites[14].

Spinel structures are representative for a group of mixed oxides, having the general formula AB_2O_4 , where A is a divalent cation (e.g. Fe^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+}) and B is a trivalent cation (e.g. Al^{3+} , Fe^{3+} , Cr^{3+})[15, 16]. Ferrites represent a special case of the spinel structure in which B sites are occupied with Fe^{3+} cations resulting in a ferromagnetic compound. Spinel ferrites (MFe_2O_4) nanoparticles have been used in many and different applications [17-21], including advanced oxidation processes (AOPs), due to their narrow band gap energy (~ 2 eV) [22]. The advantage of using MFe_2O_4 in AOPs is the facility to vary the properties of the catalyst by using a metal with strong magnetic properties in its structure, such as iron. In this way, the catalyst is very easy to recover from the treated wastewaters [23]. Moreover, ferrites can be obtained using a broad variety of metals in their spinel-type structure, in order to gain the contribution of more cations to the final properties of the catalyst [24]. He et al. reported the photodegradation of methylene blue dye using as catalyst $\text{Zn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ [25], considering the strong magnetic influence of Co-ferrite phase and narrow band gap energy of Zn-ferrite phase [22].

Having good photoabsorptive properties in the visible region of the solar spectrum, the MFe_2O_4 nanoparticles may represent an interesting and advantageous type of materials for the activation of TiO_2 -anatase in the wavelength region above 400 nm. Therefore, magnetic nanocomposite systems denoted $\text{MFe}_2\text{O}_4\text{-TiO}_2$ may be obtained and used in wastewater treatment for the removal of various organic pollutants[26]. Magnetic-photocatalysts like

CoFe₂O₄-TiO₂ [27-32] and Fe₃O₄-TiO₂ [32-40], were previously reported as very efficient catalysts in dyes photodegradation as well as easy to recover at the end of the process.

Herein, we report the synthesis, characterization and the evaluation of photocatalytic performances of a new smart-removal catalyst Co_{0.5}Zn_{0.25}M_{0.25}Fe₂O₄-TiO₂ (anatase) (MNPs-TiO₂, M: Ni, Cu, Mn and Mg) for the methyl orange and methylene blue dyes removal using solar light irradiation. To achieve convenient properties for the nanocomposites we used a Co-Zn-M (M: Ni, Cu, Mn and Mg) combination to have the strong magnetic properties of Co-ferrite (majority) and a low band gap energy characteristic for Zn-ferrite. In addition we added another metal in the system to vary the properties as follows: Ni²⁺, Cu²⁺ for good catalytic properties, Mn²⁺ to have small MNPs for a good dispersion and Mg²⁺ for the high purity spinel structure [28, 32, 41-43]. The magnetic nanoparticles were obtained by a three step procedure, which involved the co-precipitation of the MNPs, followed by the controlled hydrolysis of the Ti-precursor onto the MNPs and a thermal treatment for the crystallization of the TiO₂-anatase structure.

2. Experimental

2.1. Chemicals

CoCl₂•6H₂O (Min. 98%, VWR BDH Prolabo), ZnCl₂ (Min. 98%, Sigma-Aldrich), FeCl₃•6H₂O (Min. 98%, VWR BDH Prolabo), NiCl₂•6H₂O (Min. 98%, Sigma-Aldrich), CuCl₂•2H₂O (99%, Sigma-Aldrich), MnCl₂•4H₂O (99%, Sigma-Aldrich), MgCl₂•6H₂O (99%, ACS reagent), Titanium (IV) butoxide (TBOT) (99%, ACS reagent), Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)-block (Pluronic P123) (Sigma-Aldrich), Carboxymethyl cellulose (CMC) (Sigma-Aldrich), Absolute Ethanol (EtOH), Sodium hydroxide (NaOH) (Min. 98,5%, ACS reagent) were used as received, without any additional purification.

2.2. Synthesis of $\text{Co}_{0.5}\text{Zn}_{0.25}\text{M}_{0.25}\text{Fe}_2\text{O}_4$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Mn}, \text{Mg}$) nanoparticles (MNPs)

Magnetic nanoparticles, ferrites type $\text{Co}_{0.5}\text{Zn}_{0.25}\text{M}_{0.25}\text{Fe}_2\text{O}_4$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Mn}, \text{Mg}$) were obtained according to a previously reported co-precipitation method [43]. First, a mixed solution containing appropriate amounts of metallic salts, e.g. 0.2 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2 M ZnCl_2 , 0.2 M $\text{MCl}_2 \cdot x\text{H}_2\text{O}$ and 0.4 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added to a 40 mL of surfactant solution containing 1wt% CMC and kept in contact for 1h at 80°C. The CMC surfactant having HO^- and COO^- surface functional groups was used in order to inhibit the particles size growth and to achieve a good particle size distribution. After 1h stirring at 80°C, the precipitation agent, afterwards, a 3M NaOH solution was added drop-wise and the pH was maintained constant between 11-12. The obtained black precipitate was magnetically separated after 1h and washed several times with distilled water and ethanol, until there were no more Cl^- ions in the solution (test with AgNO_3). The precipitate was calcined in air at 500°C for 6 hours in order to remove the organics and to crystallize the spinel structure.

2.3. Synthesis of MNPs- TiO_2 system

Appropriate amounts of $\text{Co}_{0.5}\text{Zn}_{0.25}\text{M}_{0.25}\text{Fe}_2\text{O}_4$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Mn}, \text{Mg}$) were suspended into water/ethanol mixture containing P123 and sonicated for 1.5h followed by additional vigorous stirring for another 1h. Afterwards, TBOT was added drop-wise and the obtained mixture was kept under stirring for 3h at 60°C. The weight ratio between $\text{H}_2\text{O}:\text{EtOH}:\text{P123}:\text{TBOT}:\text{MNPs}$ was 1:31.6:0.6:1.2:0.02. The greyish final product was separated from the suspension, washed with distilled water and ethanol, dried in air at 70°C and calcined at 400°C for 6h in order to remove the P123 template and crystallize the TiO_2 -anatase. The three steps synthetic approach is schematically illustrated in figure 1:

Figure 1. Schematic representation of the three steps procedure for the synthesis of MNPs-TiO₂ nanocomposites.

A pure anatase TiO₂ reference sample was prepared by using the same above described procedure.

2.4. Characterization

Structural characteristics, crystallinity, purity information, chemical composition and micro textural characteristics of the catalysts were investigated by X-ray Diffraction (XRD), UV–vis diffuse reflectance spectroscopy (UV-DR), Transmission Electron Microscopy (TEM), N₂ sorption measurements.

The structural analysis of the annealed samples was performed by powder X-ray Diffraction (XRD) using an X-ray diffractometer (PANalytical X'Pert PRO MPD) equipped with CuK α radiation ($\lambda = 0.15406$ nm); measurements were done in the 2θ range from 20° to 80° using a bracket sample holder with a scanning speed of $0.04^\circ/4$ s in continuous mode. The average crystallite size was estimated using the Scherrer equation [37]. Raman spectra were obtained on a Micro-Raman Horiba (Xplora Plus Microscope) equipped with a 532 nm laser, in the range $50\text{--}1000\text{ cm}^{-1}$ raman shift.

The morphology, particle size and chemical composition of the fine annealed powders were characterized by Transmission Electron Microscopy, TEM (type JEOL JEM 2100). UV–vis absorption spectra were recorded on a Nicolet Evolution 500 UV–vis spectrometer for the

liquids; for solid state measurements of powders, UV-vis- DR spectra were recorded by using a diffuse reflectance DR accessory and using KBr standard as white reference.

Porosity and surface area measurements were performed on a Quantachrome Quadrasorb SI (Quantachrome Instruments, Odelzhauzen, Germany) automated gas adsorption system using nitrogen as the absorbate at liquid nitrogen temperature (-196°C). All the samples were outgassed in an AS-6 degasser under vacuum for 16 h at 200°C before adsorption measurements. The surface area was calculated using the BET method in the range of relative pressure 0.05–0.35.

2.5. Photocatalytic tests

The photocatalytic performances of the obtained MNPs-TiO₂ nanocomposites were evaluated for the photodegradation of methyl orange (MO) and methylene blue (MB) dyes. The solid/liquid ratio was kept constant at 1g/L and the dyes concentration, both MO and MB, was 4×10^{-5} M and the solutions were prepared in milli-Q water. In a typical experiment, the catalyst was suspended in the dye solution and stirred in dark for approximately half hour in order to establish the adsorption–desorption equilibrium between the dyes and the catalyst surface. Afterwards, the catalyst/dye suspensions were irradiated with solar light using an Unnasol US 800 solar simulator, 180 W, equipped with an UV and a visible block filters. The reactions were carried out in 200 mL reactor with water cycling jacket to avoid the evaporation and to keep the system at a constant volume and temperature. The photodegradation process was monitored by combining the UV-vis (photo-bleaching) and Total Organic Carbon TOC (photo-mineralization) measurements. UV-vis spectra were measured between 200-900 nm using a quartz cuvette and the maximum absorption was observed at $\lambda = 464$ nm for MO and $\lambda = 664$ nm for MB, respectively. TOC analysis was performed on a Shimadzu TOC-V_{CPH} (Shimadzu, Kyoto, Japan) analyzer equipped with a NDIR detector and using a high precision syringe (Hamilton 1725 gastight) for sample

injection. The TOC values were obtained by measuring the TC (total carbon) and the IC (inorganic carbon) and subtracting the IC concentration from the TC concentration.

3. Result and discussion

3.1. Structural and textural characterization of MNPs-TiO₂

Powder XRD patterns for MNPs-TiO₂ and TiO₂ are presented in figure 2. The patterns indicate that, for the pure titania as well as for the nanocomposite samples, the thermal treatment at 400°C leads to the crystallization of titania phase having anatase structure as indicated by the appearance of the characteristic reflection planes (101), (004), (200), (105) and (204) centered at 25.4°, 37.9°, 48.1°, 54.1° and 62.8°. No traces of rutile or brookite phases were detected in all samples. The reflections characteristic for the MNPs may be observed at 30.26°, 36.6°, 43.2° and 57.1° associated with the (220), (311), (400) and (440) diffraction planes, confirming the formation of the spinel structure of the CoFe₂O₄ ferrite component in the system. The diffraction peaks associated to the MNPs have lower intensity and this observation may be correlated with the small concentration in the final nanocomposites.

Figure 2. The XRD patterns for the pure TiO₂ and MNPs-TiO₂ nanocomposites.

The average crystallite size of the titania can be calculated using the Scherrer equation (results are given in table 1). From this table it can be observed that smaller TiO₂ nanoparticles are formed when ferrites are not introduced during the synthesis, meaning that the crystallinity of TiO₂-anatase is better in the presence of MNPs. Furthermore, the average crystallite sizes are in good agreement with the TEM analysis results of the materials.

$$\text{Crystallite size, } D = \frac{K \times \lambda}{\beta \times \cos \theta}$$

Where D is the average grain size, K is a shape factor, with the value of 0.89, λ is the X-ray wavelength, β is full width at half maximum and θ represents the Bragg angle [44].

Table 1. Band gap energy, TiO₂ average crystallite size and surface area for MNPs-TiO₂ and TiO₂.

Sample	^a Band gap energy (eV)	^b D _{TiO₂} (nm)	^c S _{BET} (m ² /g)
Co _{0.5} Zn _{0.25} Ni _{0.25} Fe ₂ O ₄ -TiO ₂	3.24	13	36
Co _{0.5} Zn _{0.25} Cu _{0.25} Fe ₂ O ₄ -TiO ₂	3.27	12	53
Co _{0.5} Zn _{0.25} Mn _{0.25} Fe ₂ O ₄ -TiO ₂	3.29	13	52
Co _{0.5} Zn _{0.25} Mg _{0.25} Fe ₂ O ₄ -TiO ₂	3.3	13	45
TiO ₂	3.28	9	38

^a Band gap energy was determined from the UV-DR spectra

^b Average crystallite size of TiO₂ nanoparticles calculated with the Scherrer's equation

^c BET surface area

Raman spectroscopy confirmed the presence of anatase having the characteristic bands corresponding to E_{1g}, B_{1g} and A_{1g} modes as shown in figure 3 [45].

Figure 3. Raman spectra for the pure TiO₂ and MNPs-TiO₂ nanocomposites.

All samples have very similar textural features as can be observed in figure 4a, with more or less spherical aggregates with the size up to 500 nm. Even though the relatively large thickness of the aggregates makes observations of the bulk particles difficult, typical features can still be observed on the edges of the aggregates. Some individual crystallites clearly show a different contrast than the matrix, which implies that they are composed of heavier elements than the rest of the matrix (crystallites highlighted in figure 4a by dotted circles). More detailed HR-TEM observations at Gauss-focus conditions are shown in figure 4b. The micrograph confirms the presence of two types of nanoparticles. Crystallites with the darker contrast, with irregular shape and an estimated size of 10 nm, show the crystal planes which correspond to the CoFe_2O_4 ferrite-type phase in the system. A closer investigation on the HR-TEM image obtained for the $\text{Co}_{0.5}\text{Zn}_{0.25}\text{Ni}_{0.25}\text{Fe}_2\text{O}_4\text{-TiO}_2$ sample indicates the presence of two types of crystallites which can be well correlated to the XRD observations. First, brighter anatase nanoparticles oriented along the [011] crystal plane corresponding to the basal distance of $3.5\text{\AA}$ and, secondly, darker nanoparticles with the basal spacing of $3.0\text{\AA}$ and $4.8\text{\AA}$ attributed to the [111] and [022] crystal planes are detected within the $\text{Co}_{0.5}\text{Zn}_{0.25}\text{Ni}_{0.25}\text{Fe}_2\text{O}_4$ phase, respectively.

Figure 4. TEM micrographs of the composites: a - $\text{Co}_{0.5}\text{Zn}_{0.25}\text{Ni}_{0.25}\text{Fe}_2\text{O}_4\text{-TiO}_2$, where MnPs crystallites are highlighted by dotted circles; and HR-TEM images of: b -

$\text{Co}_{0.5}\text{Zn}_{0.25}\text{Ni}_{0.25}\text{Fe}_2\text{O}_4\text{-TiO}_2$; c - $\text{Co}_{0.5}\text{Zn}_{0.25}\text{Cu}_{0.25}\text{Fe}_2\text{O}_4\text{-TiO}_2$.

The photoresponsive properties of the nanocomposites were recorded in order to provide important information about the band gap energies of the nanocomposite catalyst materials. The UV-vis DR spectra together with the graphs obtained when calculating the values of band gap energies (E_g) are presented in figure 5.

Literature reports indicate that pure anatase TiO_2 exhibits an absorption band in the range of 250-350 nm [46, 47] which is also observed for the as-prepared TiO_2 nanoparticles (figure 5-green curve). The wavelength of the absorption edge was determined by extrapolating the sharply rising and horizontal portion of the UV-vis curve and defining the edge as the wavelength of the intersection [48]. The calculated band gap energy of 3.28 eV

($E_g = 378$ nm) is in good agreement with the literature reports for anatase nanoparticles [37, 47]. No absorption has been observed above 400 nm indicating that in this form, the anatase nanoparticles are not active in the visible light region. For this purpose, the magnetic nanocomposites combining the anatase TiO_2 and the MNPs were developed. As a result, the UV-vis DR profiles show major changes in the region above 400 nm indicating the visible light activation of the nanocomposites.

As such, the MNPs- TiO_2 nanocomposites absorb the light in both UV and visible regions. Figure 5b shows the relation between $h\nu$ and $(\alpha h\nu)^2$ obtained from UV-DR spectra for each composite material. The band gap energies (table 1) were obtained from the intercept of the linear fitting of a specific domain with X-axis at $(\alpha h\nu)^2 = 0$, as shown in figure 5b and corresponding to the titania phase with values between 3.2 and 3.3 eV for all the samples [48]. Furthermore, a wide absorption in the 400 to 800 nm region is observed, which can be correlated to the presence of Co^{2+} , Fe^{3+} , Zn^{2+} and alternatively Ni^{2+} , Cu^{2+} , Mn^{2+} , Mg^{2+} cations in the spinel-type structure [28, 32, 41-43]. The choice of combining specific cations, e.g. Co^{2+} and Zn^{2+} as constant cations and varying the Ni^{2+} , Cu^{2+} , Mn^{2+} , Mg^{2+} in different combinations, in the form of spinel-type structures relies on the following features: i) Co^{2+} cations may introduce strong magnetic properties which represent an advantage for the recovery of the catalyst after use; ii) Zn^{2+} is known for its good catalytic properties in the oxide state; iii) Ni^{2+} is having good catalytic properties and is reported to manifest a synergistic effect with Co^{2+} ; iv) Cu^{2+} is well-known as having good catalytic properties; v) Mn^{2+} containing spinel structures contribute to the formation of small nanoparticles and therefore, enhancing the good dispersion in the final nanocomposites and vi) Mg^{2+} can be found in both sites of the spinel structure, leading to a high purity system without any segregation of other oxide species [43, 49, 50].

Figure 5. a. UV-vis-DR absorption spectra and b. band gap calculation results for TiO₂ and MNPs-TiO₂.

Figure 6. N₂-sorption isotherms for MNPs-TiO₂.

N₂ adsorption/desorption isotherms are shown in figure 6 and include typical hysteresis loops. The isotherms present similarities with IV type and H3 classification, according to IUPAC [51]. Surface areas for the composites are between 36 and 53 m²/g and 38 m²/g for TiO₂ (table 1), in good agreement with non-porous metal oxides structures.

3.2. Photocatalytic degradation of methyl orange (MO) and methylene blue (MB)

Figure 7. Methyl orange (a) and methylene blue (b) chemical dye structures.

The photocatalytic tests were performed at a solid/liquid ratio of 1g/L. As a benchmark a pure TiO_2 sample was used, obtained in the same condition but without introducing MNPs in the synthesis to observe the effect of MNPs on the composites. Considering the mechanism of heterogeneous catalysis, the adsorption process is a very important step in the total degradation process and for this reason we selected two dyes with different charge in the aqueous solution, e.g. methyl orange-negatively charged (anionic) and methylene blue-positively charged (cationic). The catalyst surface charge influences directly the adsorption process of the dyes. This process was studied from the equilibrium time and after 30 min without irradiation. A stronger interaction was observed between the catalyst's surface and methylene blue (cationic) which suggests a negatively charged surface for the composites, in good agreement with previous reports on isoelectric point of TiO_2 synthesized in neutral pH [29, 50].

Plots of C/C_0 (%) vs. irradiation time for methyl orange (MO) are presented in figure 8. The stability of the methyl orange solution under solar light irradiation was studied in the absence of catalyst over 6h, resulting in a degradation of 2.5%. Photocatalytic degradation of MO is different for each composite. The best result was obtained with $\text{Co}_{0.5}\text{Zn}_{0.25}\text{Ni}_{0.25}\text{Fe}_2\text{O}_4\text{-TiO}_2$, having a 95% degradation according to UV-vis spectroscopy and ~80% by TOC measurements in 6h of irradiation as shown in figure 7 and figure 9. For pure TiO_2 , we

observed a degradation of 87% followed by UV-vis analysis, having the same time of irradiation.

Figure 8. Degradation study of MO under the solar light irradiation using UV-vis spectroscopy.

Photodegradation curves of methylene blue (MB) are presented in figure 9. Comparing to MO, the time necessary to degrade MB is significantly less. At the same time, methylene blue (MB) is less stable under the solar light irradiation with a 15% degradation in 80 minutes. The best degradation profiles were found for Co_{0.5}Zn_{0.25}Ni_{0.25}Fe₂O₄-TiO₂ and Co_{0.5}Zn_{0.25}Mn_{0.25}Fe₂O₄-TiO₂ with a degradation of 99% by UV-vis in 80 minutes of irradiation with solar light. TOC measurements showed a 75% degradation in 360 minutes of irradiation with solar light for Co_{0.5}Zn_{0.25}Ni_{0.25}Fe₂O₄-TiO₂ catalyst (figure 10).

Figure 9. Degradation study of MB under the solar light irradiation using UV-vis spectroscopy.

Figure 10. Degradation study of MO and MB under the solar light irradiation using TOC measurements.

As already mentioned, an important advantage of the MNPs-TiO₂ composite systems is the easy recovering of the catalyst after use, as it is visualized in figure 11. The left bottle represents the pure TiO₂ suspension in MO solution and the right bottle Co_{0.5}Zn_{0.25}Ni_{0.25}Fe₂O₄-TiO₂ in MO solution, at different times. Already after 1 hour, a better separation can be observed for the magnetic catalyst instead of for the pure TiO₂ obtained in the same condition. After 24h the separation is complete and the separation is much more efficient for MNPs-TiO₂.

Figure 11. Visual magnetic separation of $\text{Co}_{0.5}\text{Zn}_{0.25}\text{Ni}_{0.25}\text{Fe}_2\text{O}_4\text{-TiO}_2$ in aqueous solution of methyl orange.

4. Conclusion

Novel nanocomposites have been prepared in a three step procedure by coupling ferrites with TiO_2 , resulting in magnetic nanoparticles (MNPs). In a first step, MNPs of the type $\text{Co}_{0.5}\text{Zn}_{0.25}\text{M}_{0.25}\text{Fe}_2\text{O}_4$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Mn}, \text{Mg}$) were prepared by a co-precipitation method using the appropriate metal salts. In a second step the ferrites were suspended into water/ethanol mixture containing surfactant P123 and adding a Ti-source. The final anatase TiO_2 -MNP nanocomposite structures were obtained after drying and calcination at 400°C for 6h in order to remove the P123 templates and crystallize the TiO_2 -anatase.

The obtained photocatalysts were used to degrade methyl orange (MO) and methylene blue (MB) under solar light irradiation. The possibility of using various combinations of cations in the spinel structure like Co-Zn-M ($\text{M}: \text{Ni}, \text{Cu}, \text{Mn}$ and Mg) may be regarded as a facile solution to overcome limitations often encountered in photocatalytic reactions. Cations

like Co^{2+} exhibit strong magnetic properties in ferrites systems, allowing the possibility to separate and then reuse the photocatalysts; Zn^{2+} is known for its low band gap energy and good catalytic properties in the oxide state. The UV-vis DR spectra confirm the visible light activation of the nanocomposites. Furthermore, a better crystallinity of the titania phase has been observed in the presence of MNPs. Photocatalytic results showed that around 80% and 75% of MO respectively MB dyes could be effectively mineralized under the solar light irradiation in the presence of $\text{Co}_{0.5}\text{Zn}_{0.25}\text{Ni}_{0.25}\text{Fe}_2\text{O}_4\text{-TiO}_2$, correlated to the good catalytic properties of Ni^{2+} and synergistic effect in combination with Co^{2+} . This type of magnetic-nanocomposites have great potential for further use in the field of photocatalysis, due to the possibility of fine tuning the materials properties.

Acknowledgments

This work was supported by the FWO-Flanders (project nr. G038215N).

Elena M. Seftel greatly acknowledges the Fund for Scientific Research – Flanders (FWO – Vlaanderen) for financial support. The authors gratefully acknowledge the financial support of the Slovenian Research Agency (ARRS) through the Programme P1-0021 and bilateral FWO-ARRS Project N1-0028.

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