Photocatalytic Performance of a Novel Sr-Ce-TiO₂/HAp for Degradation of Methylene Blue Dye in the Presence of Visible Light

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Research Article

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Abstract

In this study, Sr-Ce-TiO₂/HAp as a novel and efficient nanocomposite was synthesized and characterized by Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), scanning electron microscopy (SEM), and surface area determination of porous using the Brunauer–Emmett–Teller (BET) method and degradation of methylene blue under visible radiation was investigated. Evaluations showed that doped with metal cations and the presence of hydroxyapatite reduced energy gap, increased surface area, increased adsorption and decreased electron-hole recombination. The results also showed that more than 92% of methylene blue was removed within 100 min. The pseudo-first order reaction synthetic was obtained.

Introduction

Due to the limited water resources and the need for optimal use of these resources, the importance of removing various pollutants from it is clear. Water pollution by toxins, heavy metals and dyes has become a serious problem due to its adverse effects on environmental systems and human health. Contamination of water with colored pollutants carries the risk of aquatic death and the risk of cancer for humans. There are more than one hundred thousand types of dyes that are used in industries such as paper, plastic, leather, textiles, *etc.* [1, 2]. Due to the environmental hazards and health effects of chemical toxins, heavy metals and dyes, various technologies such as membrane processes, activated sludge, chemical precipitation, ion exchange, adsorption, *etc.* have been developed to remove contaminants [3–5]. Among these methods, adsorption using photocatalysts is the most common method for removing contaminants [6]. Photocatalysts create electron-hole pairs by absorbing light. Electrons and holes produced on the photocatalytic surface form hydroxyl radicals. Eventually, these radicals lead to the oxidation of organic pollutants and their removal from the environment [7]. Because the photocatalytic reaction occurs at the surface of nanoparticles, its photocatalytic activity can be achieved by stabilizing the catalyst on substrates such as ceramic [8], polymer [9], graphene [10], magnetic nanoparticles [11] or contamination. With metal and non-metal [12], increase with improving surface properties [13].

Recently, in the photocatalytic research, heavy metals have received a great attention in organic synthesis [14–17]. Inorganic materials such as hydroxyapatite (HAp, Ca₁₀(PO₄)₆(OH)₂), having many important features as catalyst support in the organic reactions due to high reusability, easy preparation, high surface area, facile catalyst separation by a simple filtration and high loading capacity [18–20]. As well as, design and doped heavy metal ions on the surface of hydroxyapatite provide suitably heterogeneous systems. The TiO₂ exhibit a good role as catalyst in oxidation of organic compounds [21]. It is also, cheapness, low toxicity, chemical stability, and excellent chemical stability [22]. Despite its best potential, challenges for TiO₂ remain in practical applications. To reduce or eliminate these drawbacks, it must be immobilized on the surface support such as silica [23], zeolite [24], glass fibers [25], activated carbon [26], and hydroxyapatite [27] or doping of titanium oxide with noble metals [28].

Continuation of previous work for synthesis of nano hydroxyapatite composites [29], in this study, TiO_2 /hydroxyapatite nanocomposites co-doped with strontium and cerium were synthesized by co-precipitation method. Nanocomposites identified using XRD, SEM, EDX, and BET. The photocatalytic efficiency of this nanocomposite in the degradation of methylene blue dye was investigated. The prepared nanocomposite shows high photocatalytic activity in comparison with pure TiO_2 .

Experimental

General

The all solvents and reagents used in this work were obtained from Merck Company and used without further purification. Analytical thin layer chromatography was performed using Merck silica gel GF₂₅₄ plates. The crystal structure of the samples was determined using X-ray diffraction (XRD, X 'Pert Pro instrument as Panalytical Company). Using the data obtained from X-ray diffraction, the size of the existing crystals was calculated using the Scherer equation with respect to the full width at half maximum (FWHM). The surface morphology of the synthesized compounds was studied using the emission field of the scanning electron microscope (FESEM, ZEISS Company, SIGMA VP model).

Preparation of hydroxyapatite

Hydroxyapatite was synthesized using co-precipitation method [30]. 2.36 gr of calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) was mixed with 20 mL distilled water. Then, $(\text{NH}_4)_2\text{HPO}_4$ solution (2.8285 gr in 50 mL distilled water) was slowly added dropwise at rate 1 mL/min to the calcium solution, the liquid mixture was stirred with 300 rpm and done the variation of stirring time of 30 min while heated at temperature of 70°C. The pH of the mixture was controlled above 9 by adding ammonium hydroxide 3 M (NH_4OH (25 %)). The mixture was stirred by magnetic stirrer for 50 min and heated at temperature of 70°C. The solution was filtered to obtain the precipitate of HAp. The precipitate of HAp was dried at temperature of 80°C for 2 h. Finally, HAp was calcined at temperature of 750°C for 3 h using the furnace to obtain the pure hydroxyapatite.

Preparation of TiO_2

To the sol-gel synthesized TiO_2 , titanium tetraetoxide ($\text{Ti}(\text{OEt})_4$, 3.75 mmol) was dissolved in absolute ethanol (100 mL) and distilled water was added to the solution in terms of a molar ratio of ethanole: water (1:4). Nitric acid (HNO_3) was used to adjust the pH and for restrain the hydrolysis process of the solution. The obtained solutions were stirring on a magnetic stirrer for 15 h at room temperature. In order to obtain nanoparticles, the gels were dried under 50 °C for 1.5 h to evaporate water and organic material. Then calcinated at 400°C for 2 h to carry out to obtain desired TiO_2 nanocrystalline.

Synthesis of TiO_2 /HAp nanocomposites

TiO₂/HAp nanocomposite was prepared by co-precipitation method [31]. First, the pH of 50 mL of calcium nitrate solution (0.075 mol / L) and 50 ml of ammonium phosphate (0.045 mol / L) were adjusted separately by ammonia solution to 11–12. 0.2 g of nanoparticles of TiO₂ were added to calcium nitrate solution and stirred at room temperature for 20 minutes. Ammonium phosphate was then added dropwise to form a precipitate and mixed for one hour to form a TiO₂/HAp nanocomposite. Then, the reaction mixture was centrifuged and washed to remove excess ammonium ions. The resulting precipitate was dried at 60°C. Finally, calcination was performed at an oven temperature of 750 ° C for 3 h.

Synthesis of Sr-Ce-TiO₂

Titanium tetraetoxide (3.75 mmol, 0.85 g), cerium acetate (1.89 mmol, 0.60 g) and strontium nitrate (1.89 mmol, 0.40 g) dissolved in 100 mL of ethanol and stirred for 30 minutes. The resulting white precipitate was separated by centrifugation and dried at 100°C for 8 h. It was then calcined at 600°C for 4 h.

Synthesis of Sr-Ce- TiO₂/HAp nanocomposites

The pH of 50 mL of calcium nitrate solution (0.075 mol/L) and 50 mL of ammonium phosphate (0.045 mol/L) was adjusted separately by ammonia solution to 11–12. Sr-Ce- TiO₂ (0.2 g) was added to the calcium nitrate solution and stirred at ambient temperature for 20 minutes. Ammonium phosphate was then added dropwise to form a precipitate and mixed for one hour to form the Sr-Ce- TiO₂/HAp nanocomposite. Then, the reaction mixture was centrifuged and washed to remove excess ammonium ions. Finally, the precipitate was dried at 60°C and calcined for 3 hours at 750°C.

Photocatalytic Experiments

In order to investigate the photocatalytic activity, 0.02 g of catalyst was added to 100 ml of solution of methylene blue dye (10 ppm). The mixture of methylene blue and catalyst was first stirred in the dark conditions, for 20 minutes and then exposed to a Xe arc 300 W Oriel with maximum radiation was used as source of the visible light for 100 minutes. At specified intervals, 3 ml of the sample was taken and after separating the suspended particles, its absorption spectrum was taken at the maximum methylene blue absorption wavelength at 660 nm. Finally, the amount of photocatalytic activity of the prepared samples was calculated and compared. The percentage of destruction yield is calculated using Equation (1) [32].

$$R \% = [(C_0 - C)/C_0] \times 100 \quad (1)$$

C₀ is the initial concentration of the solution and C is concentration at certain times.

Results And Discussion

The photocatalytic activity of Sr-Ce-TiO₂/HAp nanocomposite was investigated for degradation of methylene blue under visible radiation. The synthesized Sr-Ce-TiO₂/HAp nanocomposite was fully characterized using XRD, SEM, EDX, and BET.

X-ray diffraction results of HAp, TiO₂, TiO₂/HAp and Sr-Ce-TiO₂/HAp samples are shown in Fig. 1.

The XRD pattern of hydroxyapatite (Fig. 1a) shows that the diffraction peaks of the crystal planes (210), (211), (112), (212), (222), (213), (321) and (004) conform to the hexagonal structure and are compatible with the standard card (JCPDS-9-0432) [37]. XRD pattern of TiO₂ nanoparticles (Fig. 1b) indicates crystal planes (101), (004), (200), (105), (211), (204), and (116) according to standard card number JCPDS card. #84-1286 [38]. No impurity-related diffraction peaks were observed in the TiO₂ X-ray pattern, indicating that nanoparticles of pure oxide formed. Figure 1c shows the XRD pattern of the TiO₂/HAp sample, which in addition to the peaks of TiO₂ shows new peaks, which is related to the presence of hydroxyapatite and indicates the composition of the sample. In the XRD pattern of the Sr-Ce-TiO₂/HAp nanocomposite (Fig. 1d), the peaks of the TiO₂ and HAp structures are found. XRD of the co-doped catalyst also showed that the peak positions of the obtained structure are shifted slightly towards the left as compared with that of pure TiO₂.

The morphology of Sr-Ce-TiO₂/HAp nanocomposite was investigated by scanning electron microscopy images (SEM). SEM technique shows high magnification images of the sample surface. Figure 2a shows HAp with spherical shaped particles with clumped distributions. Figure 2b shows TiO₂ with a spherical structure and size of ~ 30 nm. The TiO₂/HAp have about 40 nm (Fig. 2c). As shown in Fig. 2d, the TiO₂/HAp co-doped with Se and Sr are made up of nanometer-sized with the diameters in the range 70 nm.

In EDX analysis, it will be possible to identify the constituent elements of the sample semi-quantitatively. Figure 3 shows the EDX spectra of the a) HAp, b) TiO₂, c) TiO₂/HAp and d) Sr-Ce-TiO₂/HAp. The presence of Ca, P and O is well shown in the EDX spectrum of the HAp (Fig. 3a). The EDX spectra of the TiO₂ show the presence of O and Ti (Fig. 3b). The presence of Ca, P, Ti and O in the TiO₂/HAp sample is shown in Fig. 3c. In addition to Ca, P, Ti and O the presence of cerium and strontium in the EDX spectrum of the Sr-Ce-TiO₂/HAp nanocomposite is shown at Fig. 3d.

BET analysis (Brunauer-Emmet-Teller) is one of the most important methods for determining the amount of porosity, which is based on measuring the adsorption/desorption isotherm of nitrogen gas which adsorbed to form a single layer of nitrogen on the adsorbent. The results are shown in Table 1. In the synthesized samples, the specific levels of TiO₂ and Sr-Ce-TiO₂/HAp increased from 67.02 m²/g to 110.34 m²/g, respectively. The pore volumes of TiO₂ and Sr-Ce-TiO₂/HAp decreased from 0.29 cm³/g to 0.10 cm³/g, respectively.

Table 1
Results obtained from the BET method

Sample	BET surface area (m ² /g)	pore volume (cm ³ /g)
HAp	87.95	20.19
TiO ₂	67.02	0.29
TiO ₂ /HAp	80.24	0.19
Sr-Ce- TiO ₂ / HAp	110.34	0.10

Photocatalytic behavior of HAp, TiO₂, TiO₂/ HAp and Sr-Ce- TiO₂/ HAp

The photodegradation capabilities of the HAp, TiO₂, TiO₂/ HAp and Sr-Ce- TiO₂/ HAp uses the solutions of methylene blue dye in water, were examined under visible light irradiation at room temperature. Figure 4 shows the photodegradation process by UV–Vis spectroscopy using decrease in the bands at 660 nm for methylene blue dye. The results are as follows:

Hap < TiO₂ < TiO₂/ HAp < Sr-Ce- TiO₂/ HAp

Under dark conditions, the photocatalytic degradations have been performed using the HAp, TiO₂, TiO₂/ HAp and Sr-Ce- TiO₂/ HAp. For the methylene blue dye, 3 mL of reaction solution containing photocatalyst in neutral pH value was taken and then centrifuged for separation of photocatalyst particles from the solution and consequently was analyzed by UV–Vis spectroscopy. In fact, no photocatalytic degradation was observed under dark conditions.

The photodegradation rate chart versus time (100 min) of all the samples for methylene blue is depicted respectively in Fig. 5.

According to results of photodegradation of methylene blue dye, Sr-Ce-TiO₂/Hap exhibits the efficient photodegradation compared with the other samples (Hap, TiO₂, TiO₂/ Hap, and pure TiO₂) and presented an applicable strategy to increase the photocatalytic activities (Table 2).

Table 2
photodegradation results of methylene blue dye

Entry	Photocatalyst	Time (min)	Dye conversion (%)
1	Hap	100	26
2	TiO ₂	100	39
3	TiO ₂ /Hap	100	64
4	Sr-Ce-TiO ₂ /Hap	100	92

The highest photodegradation percentage was obtained for Sr-Ce-TiO₂/Hap under visible light irradiation. In the present investigation, the concentrations of methylene blue is considered to be 20 mg/L at pH = 7. It can be observed that the photodegradation percentage of the pure TiO₂ are respectively obtained to be 39% for methylene blue dyes after 100 min of light exposure. However, the photodegradation ability of the Sr-Ce-TiO₂/Hap is respectively equal to 92% (Fig. 6).

In the Fig. 6 the chart of $-\ln C/C_0$ versus time were drawn for methylene blue dyes. According to Langmuir-Hinshelwood (Eq. 2) the chart can be fitted into the pseudo-first order rate equation.

$$-\ln(C_t/C_0) = k_{app}t \quad (2)$$

in which C₀ is the initial concentration, C_t is the concentration at the certain times (t) and k_{app} is the calculated apparent rate constant [36]. Additionally, the kinetic constant (k) and linear regression coefficient (R²) values are calculated and summarized in Table 3. The rate constants of methylene blue dye for the HAp, TiO₂, TiO₂/ HAp and Sr-Ce- TiO₂/ HAp were 0.0457, 0.0911, 0.2374 and 0.5486, respectively. Therefore, Sr-Ce- TiO₂/ HAp nanocomposite, which has a higher constant velocity value than other prepared samples, also has a higher photocatalytic efficiency.

Table 3
k and R² values for the samples Hap, TiO₂, TiO₂/ Hap, and Sr-Ce- TiO₂/Hap for photodegradation of methylene blue dye under visible light

Degradation of Rhodamine B	Kinetic constant (k, min ⁻¹)	R ²
Hap	0.0457	0.9540
TiO ₂	0.0911	0.9571
TiO ₂ /Hap	0.2374	0.9904
Sr-Ce-TiO ₂ /Hap	0.5486	0.9987

Stability and reusability of Sr-Ce-TiO₂/Hap

Then check the stability and reusability of the Sr-Ce-TiO₂/Hap photocatalyst, 7 consecutive cycles were tested. At the end of each run, the photocatalyst was recovered by a simple filtration and immediately washed with water, acetone and ethanol. Afterwards, after drying it was exposed by visible light for 30 min before the next run (Fig. 8). After 7 consecutive runs, methylene blue dye was adsorbed on the surface of Sr-Ce-TiO₂/Hap photocatalyst.

UV – vis diffuse reflectance spectral analysis (DRS)

The optical response of the prepared nanocomposites was investigated with a UV–vis diffuse reflectance spectral analysis (DRS). Figure 9 (a-d) shows the DRS spectra of the nanocomposites a) HAp, b) TiO₂, c) TiO₂/ HAp, and d) Sr-Ce- TiO₂/ HAp, respectively. The presence of fluctuations in these spectra indicates the crystalline levels of TiO₂. In the UV-Vis spectrum of pure hydroxyapatite, no absorption peak is seen in the range of 200 to 800 nm [33]. In this figure, there is a peak in the range of 325 nm, which is related to the TiO₂ wavelength [34]. All the corresponding bands are "red shift" compared with pure TiO₂ nanoparticles. This increase in adsorption can be attributed to electron excitation from HOMO to LUMO hydroxyapatite, which will improve the photocatalytic activity of Sr-Ce- TiO₂/ HAp nanocomposite. On the other hand, it can be shown that the doping of cerium and strontium on TiO₂/HAp improves the photocatalytic activity of TiO₂-hydroxyapatite nanoparticles by reducing the energy gap and increasing the surface [35].

Conclusion

In this work, the characterization and synthesis of the efficient novel recoverable Sr-Ce-TiO₂/HAp nanocomposite as photocatalyst for the degradation of methylene blue dye in the presence of visible light is investigated. Sr-Ce-TiO₂/HAp nanocomposite were analyzed by various spectroscopic methods including XRD, SEM, EDX, and BET. Furthermore, Sr-Ce-TiO₂/HAp nanocomposite can be simply and reused for 7 times without considerable loss of photocatalytic activity. The recyclability, simple separation, and easy recovery of this catalyst with the high activity make the protocol highly advantageous over conventional procedures for the degradation of methylene blue dye in the presence of visible light. The results showed that with Sr-Ce- TiO₂/ HAp nanocomposite, more than 92% of methylene blue was removed within 100 min after the start of the reaction. Also, in kinetic studies, it was found that photocatalytic degradation follows the kinetics of the pseudo-first-order equation.

References

1. (a) Wang J., Fan X. M., Wu D. Z., Dai J., Liu H., Liu H. R., Zhou Z. W. *Appl. Surf. Sci.*, 258: 1797–1805 (2011). (b) Abdussalam-Mohammed W., Qasem Ali A., Errayes O.A., *Chem. Methodol.*, 4:408–423 (2020). (c) Bader N., Hasan H., EL-Denali A *Chem. Methodol.*, 2:56–63 (2018).
2. Sun C., Fu Y., Wang Q., Xing L., Liu B., Xue X. *RSC Adv.*, 6: 87446–87453(2016).
3. Chong M. N., Jin B., Chow C. W., Saint C *Water Res.*, 44: 2997–3027 (2010).
4. Huang J. J., Hu H. Y., Tang F., Li Y., Lu S. Q., Lu Y, *Water Res.*, 45:2775–2781(2011).
5. Haaken D., Schmalz V., Dittmar T., Worch E. *J. Water Supply Res. Technol.*, 62: 442–451(2013).
6. Derakhshan-Nejad A., Cheraghi M., Rangkooy H., Jalillzadeh Yengejeh R *Chem. Methodol.*, 5:50–58 (2021).
7. Abbasi M. A., Ibupoto Z. H., Khan A., Nur O., Willander M. *Mater. Lett.*, 108: 149–152 (2013).
8. Bai X., Wang L., Zong R., Lv Y., Sun Y., Zhu Y., *Langmuir*. 29: 3097–3105 (2013).

9. Von Wenckstern, H., Schmidt H., Brandt M., Lajn A., Pickenhain R., Lorenz M., Grundmann M., Hofmann D.M., Polity A., Meyer B.K. Saal H *Prog. Solid. State Chem*, 37: 153–172 (2009).
10. Pourtaheri A., Nezamzadeh-Ejhieh A. *Spectrochim. Acta A*, 137: 338–344 (2015).
11. Lv H., Ji G., Yang Z., Liu Y., Zhang X., Liu W., Zhang H. *J. Colloid Interface Sci.*, 450: 381–387 (2015).
12. Chang X., Li Z., Zhai X., Sun S., Gu D., Dong L., Yin Y., Zhu Y., *Materials & Design*, 98:324–332 (2016).
13. Zhang L., Wang W., Sun S., Sun Y., Gao E., Zhang Z., *Appl. Catal. B*, 148:164–169 (2014).
14. Sajjadifar, S., Arzehgar, Z., Khoshpoori, S., *J. Inorg. Organomet. Polym.* 28, 837 (2018).
15. Tamboli, Q.Y., Pathange, S.M., *Chem. Methodol.*, 2, 73 (2018).
16. Soleiman-Beigi, M., Arzehgar, Z., *Monatsh Chem.*, 147, 1759 (2016).
17. Sajjadifar, S., Rezayati, S., Arzehgar, Z., Abbaspour, S., Torabi Jafroudi, M., *J. Chin. Chem. Soc.*, 65, 960 (2018).
18. Stanić, V., Dimitrijević, S., Antić-Stanković, J., Mitrić, M., Jokić, B., Plećaš, I.B., Raičević, S., *Appl. Surf. Sci.*, 256, 6083 (2010).
19. de Vasconcelos, B.R., Minh, D.P., Sharrock, P., Nzihou, A., *Catal. Today*, 310, 107 (2018).
20. Mori, K., Hara, T., Mizugaki, T., Ebitani, K., Kaneda, K., *J. Am. Chem. Soc.*, 126, 10657 (2004).
21. Nishikawa H., Kato S., Ando T., *J. Mol. Catal. A Chem.*, 236, 145 (2005).
22. You X.F., Chen F., Zhang J.L., Anpo M., *Catal. Lett.*, 102, 247 (2005).
23. Anderson, C., Bard, A.J., *J. Phys. Chem. B*, 101, 2611 (1997).
24. Zhang, G., Song, A., Duan, Y., Zheng, S., *Microporous Mesoporous Mater.*, 255, 61 (2018).
25. Hofstadler, K., Bauer, R., Novalic, S., Heisler, G., *Environ. Sci. Technol.*, 28, 670 (1994).
26. Wang, W., Silva, C.G., Faria, J.L., *Appl. Catal. B*, 70, 470 (2007).
27. Hu, M., Yao, Z., Liu, X., Ma, L., He, Z., Wang, X., *J. Taiwan Inst. Chem. Eng.*, 85, 91 (2018).
28. Pathak, T.K., Kroon, R.E., Craciun, V., Popa, M., Chifiriuc, M.C., Swart, H.C., *Heliyon*, 5, e01333 (2019).
29. Heshmatpour, F., Lashteneshae, S.H. and Samadipour, M., *J. Inorg. Organomet. Polym. Mater*, 28, 2063 (2018).
30. Sari, M., Yusuf, Y., *Int. J. Nanoelectron. Mater*, 11, 357 (2018).
31. Shatnawi, M., Alsmadi, A.M., Bsoul, I., Salameh, B., Mathai, M., Alnawashi, G., Alzoubi, G.M., Al-Dweri, F., Bawa'aneh, M.S., *Results Phys.*, 6, 1064 (2016).
32. Stanić, V., Dimitrijević, S., Antić-Stanković, J., Mitrić, M., Jokić, B., Plećaš, I.B., Raičević, S., *Appl. Surf. Sci.*, 256, 6083 (2010).
33. Yang J.H, Zheng J.H, Zhai H.J, Yang L.L, Zhang Y.J, Lang J.H, Gao M., *J. Alloys Compd.*, 475:741–744 (2009).
34. S. Dalai, S. Pakrashi, R.S. Kumar, N. Chandrasekaran, A. Mukherjee, A comparative cytotoxicity study of TiO₂ nanoparticles under light and dark conditions at low exposure concentrations. *Toxicology Research* 1(2), 116–130 (2012)
35. Nikpour P, Slimi kenari H., Rabiee S. M., *Iran. Polym. Technol. Rese. Dev.*, 3:5–17 (2018).

36. D.P. Das, N. Biswal, S. Martha, K.M. Parida, Solar-light induced photodegradation of organic pollutants over CdS-pillared zirconium–titanium phosphate (ZTP). *J. Mol. Catal. A: Chem.* **349**(1–2), 36–41 (2011)
37. El-Sherbiny, S., Morsy, F., Samir, M. and Fouad, O.A., *Appl. Nanosci.*, 4, 305 (2014).
38. Li, B., Wang, X., Yan, M. and Li, L., *Mater. Chem.Phys.*, 78, 184 (2003).

Figures

Figure 1

X-ray pattern for compounds a) HAp, b) TiO₂, c) TiO₂/ HAp and d) Sr-Ce- TiO₂/ HAp

Figure 2

SEM for compounds a) HAp, b) TiO₂, c) TiO₂/ HAp and d) Sr-Ce- TiO₂/ HAp

Figure 3

EDX for compounds a) HAp, b) TiO₂, c) TiO₂/ HAp and d) Sr-Ce- TiO₂/ HAp

Figure 4

UV-Vis absorption spectrum of all the samples toward methylene blue dye in 100 min

Figure 5

Photocatalytic activities of all the samples toward methylene blue dye in 100 min of exposure (1×10^{-4} mmol of photocatalyst, light intensity 300 w, pHf = 7, temperature 30–35 °C, concentration of methylene blue dye in water solution 20 mg/dm³)

Figure 6

Comparison of the maximum degradation by different photocatalysts

Figure 7

Comparison of the linear kinetic curves for degradation by different photocatalysts

Figure 8

Figure 9

UV-vis diffuse reflectance spectra (DRS) of all the samples