



Karaj branch

Degradation of Phthalocyanine by a Core-Shell TiO₂ Photocatalyst: Effect of Iron Dopping on Band Gap

Amir Hossein Haghighty¹, Shahram Moradi Dehaghi*, Kambiz Larijani²

Department of Chemistry, Islamic Azad University, Tehran North Branch, Tehran, Iran

(Received 14 May 2019; Final revised received 27 Aug. 2019)

Abstract

In this research, initially, the sol-gel method was employed to produce γ -alumina and TiO₂ catalysts with core-shell structure. Iron (III) was used as a dopant. The newly produced core-shells were Fe/TiO₂// Fe/ γ -Al₂O₃ (FTFA). Sulfonated cobalt phthalocyanine was used as a dye pollutant in Mercox process. By doping Fe in TiO₂ catalyst, the efficiency of photocatalytic activity in photodegradation of sulfonated cobalt phthalocyanine was increased. Photocatalytic activity of Fe/TiO₂// Fe/ γ -Al₂O₃ in UV irradiation was investigated and complete degradation of sulfonated cobalt phthalocyanine was confirmed via UV-Vis spectrophotometry and Total Organic Carbon analysis. Structure, morphology, and specification of new core-shell composites of FTFA were studied using several spectroscopic techniques. The efficiency of the FTFA catalyst is very good in alkaline media and close to the TiO₂ catalyst performance in acidic media. The complete destruction process was investigated with TOC and the synthesized catalyst degraded 5 ppm of solution polluted by SCP in a maximum of 30 min.

Keywords: Phthalocyanine, TiO₂, Core –Shell, Photodegradation.

* **Corresponding authors:** Shahram Moradi Dehaghi, Islamic Azad University, Faculty of Chemistry, Tehran North Branch, Tehran, Iran., Tel/Fax: 98-21-26705520. E-mail: shm_moradi@iau-tnb.ac.ir.

Introduction

Titanium dioxide catalyst is a powerful photocatalyst in the advanced oxidation process. The doped metal ions at the time of formation of the crystalline lattice of titanium dioxide, create structural defects in the anatase lattice. The doping process reduces the band gap between the valence and the conductive band and caused significant improvement in photocatalysts properties [1-13]. In a recent study, the use of organic dyes such as fluorescein and the organometallic dyes such as cobalt phthalocyanine caused a rapid increase in photocatalyst property of TiO₂ [14-25]. The mode of operation and the mechanism of the dyestuffs were studied by increasing the photocatalytic properties according to Sökmen et al. [26]. The excitement and rapid transference of electrons from the dye to the catalyst increased the speed of the photodegradation process speed. In the oil and gas industry, to remove pollutants from mercaptans, sulfonated cobalt phthalocyanine (SCP) is used. This process is called Merox [15, 17, 21, 24, 27-30]. However, dyes with these valuable properties, may highly contaminate industrial wastewater during production and after purification.

In this study, at first, the preparation of alumina nanoparticles was done by a sol-gel core-shell structure. Alumina nano particles into the sol-gel containing titanium tetra isopropoxy in the core by a layer of coated titanium dioxide. By embedding the metal ions of iron in the core and shell structure, the properties of photocatalysts were improved. The purpose of the study is to use the core-shell catalysts activated with iron (III) as a dopant to degrade cobalt phthalocyanine dye structure under ultraviolet irradiation. The second purpose is to use the activated montmorillonite clay to remove cobalt ions from the bleached effluent. Composite structures produced by different methods at each stage were characterized.

Experimental

Chemicals

Chemicals reagents including: Titanium tetra-isopropoxide (TTiP) 95%, Aluminum nitrate 9H₂O 99.5%, Iron(III)nitrate nonahydrate 99%, Ammonium Bicarbonate 99%, 1-Hexadecanaminium, N,N,N-tri methyl bromide 99%, Absolute Ethanol, Nitric Acid 65%, Ferric Cobalt 99%, Phthalic Anhydride, Cobalt(II) Chloride hexahydrate, Ammonium Molybdate 99%, Sulfuric acid 96%, Ammonia solution, Ethanol 96%, Hydroxypropyl Cellulose (HPC) 99% from Merck Co., (Germany) and Polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether (TRITON X100) were purchased from Sigma-Aldrich Co., (Germany). Calcium montmorillonite 94% was obtained from Saraian bentonite mine in Iran.

Instruments

X-Ray diffraction (XRD) pattern was measured via a “SEIFERT- 3003 PTS”, by Cu K α radiation at 40 kV and 30 mA. “Zeiss –Sigma VP-500 with Oxford Instrument” field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopes (EDAX), Fourier transform infrared (FT-IR) spectra (Thermo Nicolet spectrometer), and UV–Vis spectrophotometry (Cary-100-UV–Vis spectrophotometer, Varian) were used. The specific surface area was determined via Brunauer, Emmett, Teller (BET) porosity analyzer JW-BK122W (Beijing JWGB Sci. & Tech.Co., Ltd) according to a single-point technique ($p/p_0=0.2$).

Preparation of Nanocomposites

Aluminum nanoparticle, titanium dioxide, and their derivatives were prepared by sol-gel method.

Preparation of γ -Al₂O₃ (A)

0.0003 mole of 1-Hexadecanaminium, N,N,N-tri methyl bromide was added to 20 mL solution containing 0.06 mole of Al (NO₃)₃·9H₂O and homogenized via stirring. An aqueous solution of NH₄NO₃ (10%) was added drop wise to this solution while being stirred at room temperature, then this sol was aged for 24 h to form a gel. The gel was dried in an oven at 80°C for 5 h, and calcined at 300°C afterwards. Lastly, the solid resulted material was pulverized [5].

Preparation of the nanocatalyst, TiO₂ sample (T)

Nitric acid and TTiP were prepared alone in ethanol and thereafter, they were slowly mixed together. The mixture was stirred until the homogenized sol was formed. The solution was kept for 48 h at room temperature for the preparation of gel, next it was dried for 3 h at 120°C and calcined in a furnace at 500 °C for 5 h [5].

Preparation of γ -Al₂O₃//TiO₂ (TA)

The γ -alumina powder obtained from the above γ -Al₂O₃ procedures was added to the prepared sol of TTiP / nitric acid in ethanol and was homogenized for 1 h at 24,000 rpm. Then the mixture was kept and aged for 48 h at room temperature until the gel was produced; thereafter, it was dried for 4 h in an oven at 120°C and calcined for 5 h [5].

Preparation of Fe γ - Al₂O₃ (FA)

A 2.5 mL solution Fe(NO₃)₃· 9H₂O (0.001 molL⁻¹) was added to 50 mL of the sol precursor alumina and homogenized via stirring. An aqueous solution of NH₄NO₃ (10%) was added drop wise

to this solution while being stirred at room temperature. Then the sol was aged for 24 h to find a gel. The gel was dried in an oven at 120°C for 5 h, and calcined at 500°C afterwards. Lastly, the resulting solid material was pulverized.

Preparation of Fe/TiO₂/Fe/γ-Al₂O₃ (FTFA)

A 2.5 mL from the Fe (NO₃)₃ · 9H₂O (0.001 molL⁻¹) solution was added to 50 mL of TTiP sol which has been prepared according to the method described above and stirred for 30 min. The comminuted Fe /γ-Al₂O₃ powder was slowly added slowly to the Fe/TTiP sol and homogenized with a powerful homogenizer at 24000 rpm for 1h. It was dried for 4 h in an oven at 120°C and calcined for 5 h at 550°C.

Preparation of Sulfonated Cobalt Phthalocyanine (SCP)

Synthesis of SCP was performed according to Chaudhari with slight modifications [27].

18 g of phthalic anhydride, 17 g of urea, 1 g of ammonium molybdate and 7g of cobalt chloride hexahydrate were used during preparation. Firstly, the mixture was heated up using a burner while being vigorously stirred for 1 hour. Its physical appearance was blue dark solid. Then it was cooled and rinsed with 250 mL hot solution of hydrochloric acid 0.1M and was stirred and the product was filtered. Finally, it was dried for 4 h in an oven at 120°C.

Preparation of montmorillonite clay (MC)

MC was washed using distilled water and was separated from sand and SiO₂ using sieves (800 mesh). MC was completely dispersed in concentrated sulfuric acid solution by stirring vigorously for 72 h. Then, it was rinsed with diluted ammonia and deionized water for adjusting pH to 7. The suspension was centrifuged and the upper solution was decanted off, and the residue was calcined at 900°C for 2 h and at 400°C for 4 h. The sample was then pulverized and sieved to a very uniform powder.

Activation of the MC with TRITON X-100 (Activated Clay, AC)

MC was added to two solutions containing 4 and 8% w/w of polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether (TRITON X100) as nonionic surfactants, separately, and were vigorously stirred at 70°C for 24 h. TRITON X100 supported montmorillonite was prepared using a conventional ion exchange reaction of the montmorillonite and an aqueous solution of TRITON X100. To remove excess surfactant, the samples were washed with a solution of double distilled water and alcohol (ratio 1:1 v/v). The resulting solids were separated by centrifugation and were

washed using deionized water several times, and dried at 50°C for 3 days. To prepare a uniform absorbent, the sample was then sieved to 10 µm sieves. In total, 2 adsorbents were prepared.

Photocatalytic degradation monitoring

To study the activity of photocatalysts, degradation of SCP solution under ultraviolet radiation (two 8W, UVc Osram lamp) was investigated. Various parameters such as weight of catalyst, pH and concentration of the SCP solution were studied in order to confirm and evaluate the photocatalyst activity; then efficient conditions were obtained for each catalyst.

The effect of catalyst weight on the degradation of SCP

Initially, 50 mL of the solution containing a concentration of 5 ppm SCP with a pH~7 was prepared and the amounts of 0.02, 0.06, and 0.08 g of each prepared catalysts (T, TA, FTA and FTFA) were added to the reaction media, separately. At specific times, the concentration of the SCP was measured by the UV-Vis spectrophotometer and the most effective weight of the catalyst was selected at this level. According to the results, the most suitable weight for the catalyst is 0.06 g and the best concentration for the SCP, which can be considered in the acceptable time interval, is 5 ppm.

The effect of pH on photo catalytic activity

A 0.06 g of each catalyst was added to 50 mL of 5 ppm of SCP solution in five containers with the pH of 2, 4, 7, 9, and 12, separately. The change in the concentration of SCP versus time was determined via the UV-Vis spectrophotometer. In that way, each catalyst showed its own unique performance at various pH levels.

Adsorption of cobalt ion after photo degradation of SCP by MC and AC

In a study of cobalt adsorption, the ability of adsorption of the modified montmorillonites (MC, AC) was evaluated via measuring the adsorption of the cobalt solution. The decolorized solution of SCP was neutralized to pH 7 and concentrated bleached wastewater was used to achieve a concentration of cobalt ion solution of 5 ppm. Then, different amounts of MC and AC (0.4, 0.8, and 1.2g) were mixed with 25 mL of these solutions. The suspensions were ready at room temperature with continuous stirring at 150 rpm for 1-60 min. The cobalt concentration in the aqueous phase was determined by atomic absorption spectrophotometry. All samples were used for several times and washed by alkaline and acidic solutions and then adjusted to pH 7 by leaching, and dried at 50°C for 3 days this process was also applied for montmorillonite processed in acidic and alkaline

conditions. The method of determination of cobalt adsorption was followed to compare these sorbents. All experiments were carried out at least in triplicate at pH ~7 and 25° C. The results were the mean of three independent measurements.

Results and discussion

X-ray diffraction (XRD) analysis

The XRD results were carried out to identify the samples at room temperature. The results included phase analysis, crystallite size, and the major peaks were analyzed and presented in Table 1. The XRD patterns are shown in Figure 1. TiO₂ and the other nanophotocatalysts were prepared with high-quality and were clearly detected. Dominant phase in all photocatalyst has been approved as TiO₂anatase. [31].

In TA, FTA, and FTFA, γ -alumina and Fe metal ion are present as a dopant; the presence of these elements in the composite structure is clearly evident. Miller indices (hkl) lattice planes of the reflective orthogonal planes were compared to standard structure of TiO₂ and their derivatives, presented in Table 1. The sample sizes of the prepared crystals are calculated in accordance with Scherrer equation and presented in Table 1.

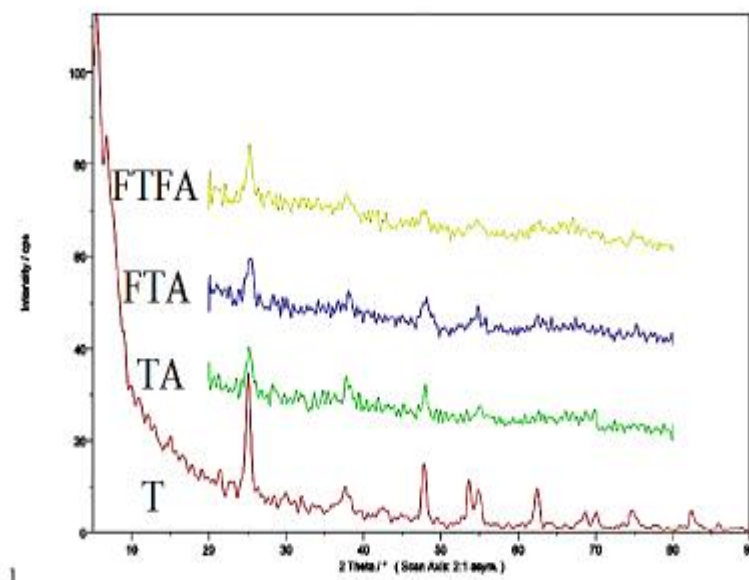


Figure 1. XRD patterns of the T, TA, FTA, and FTFA samples.

Table1. Shows the results obtained by instrumental techniques of T, TA, FTA and FTFA.

Analysis Results	T	TA	FTA	FTFA
Crystal phase	TiO₂ (anatase)	TiO₂ (anatase) + Al₂TiO₅	TiO₂ (anatase)+Fe₂Ti₃O₉	TiO₂ (anatase)+ Al_{0.11}Ti_{0.4}Fe_{0.9}
FE-SEM Average particle size (nm)	35	43	49	58
*XRD Major peaks (2θ°)	TiO₂: 25.81 (101)25.8	TiO₂: 25.42 (110) 25.43 Al₂TiO₅: 33.71 (203)33.7	TiO₂: 25.28 (101) 25.3 Fe₂Ti₃O₉: 54.32 (102) 54.33 Fe_{2.25}Ti_{0.75}O₄: 61.625 (404)61.6	TiO₂: 25.28 (101) 25.3 Al_{0.11}Ti_{0.4}Fe_{0.9}: 39.56 (111)39.6
Crystal size Sherrer equation (nm)	32.73	34.7	36.38	40
BET Specific surface area (m ² /g)	185	168	180	175
Band gap (E _g (eV)) λ (nm)	3.02 (410.59)	2.96 (418.91)	2.94 (421.28)	2.82 (440)
EDAX (W %)	O(25.76), Ti(74.24)	O(46.6), Ti(47.9) Al(5.5)	O(50.16) Al(33.9) Ti(14.69) Fe(1.05)	O(49.44) Al(2.25) Ti(47.54) Fe(0.79)

Energy-dispersive X-ray spectroscopy (EDAX)

Table 1 shows the quantitative analysis of Al, Ti, O, and Fe as elements on these composites.

These results are highly consistent with the results of X-ray diffraction which confirms the presence of the aluminum composite structure, and shows lamination of a layer of TiO₂ on the γ -alumina.

Dopping process of iron ions into the crystalline lattice of TiO₂ is confirmed.

Field Emission Scanning Electron Microscopy (FE-SEM)

Morphology and particle size of the synthesized nanophotocatalyst were determined with FE-SEM. The results are shown in Figure 2 and Table1. Particle size was increased through overlaying the thin layer of TiO₂ on the γ -alumina core without any change in the unique spherical form. Particle size by FE-SEM is obtained in Table1.

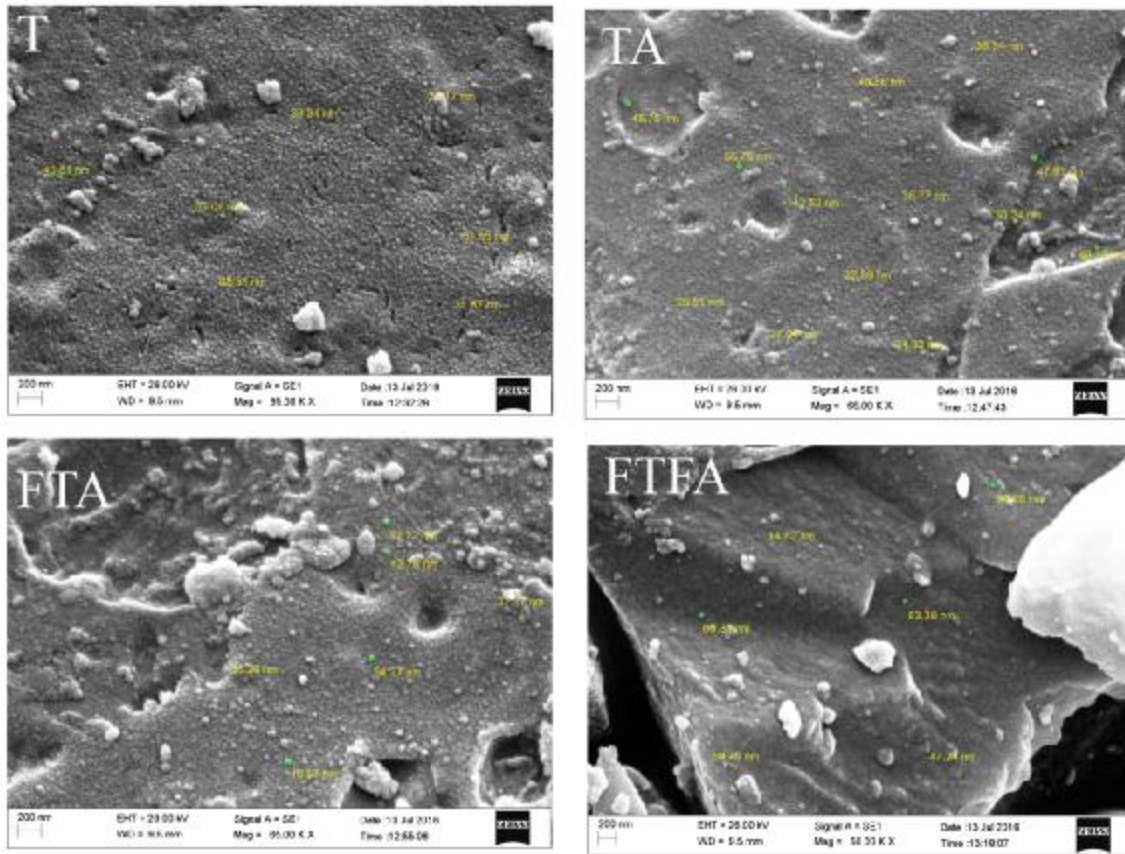


Figure 2. FE-SEM images of the T, TA, FTA, and FTFA samples.

FT-IR spectroscopy

FT-IR spectra of the photo catalysts (T, FTA, and FTFA) are shown in Figure 3. Bending and stretching vibrations associated with the connections in the composite are presented in Figure 3. The penetration of aluminum and iron in the TiO_2 lattice causes slight changes in the appearance of these spectra.

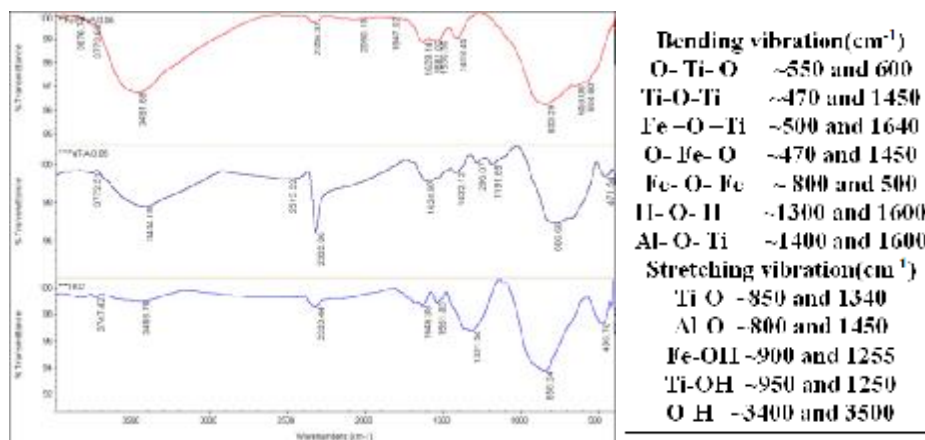


Figure 3. FT-IR spectra of the samples of T, FTA, and FTFA.

Photocatalytic degradation of nano composites

Photocatalytic degradation of the T, TA, FTA, and FTFA nano photocatalysts were carried out for degradation of SCP solution (10 ppm) under UV irradiation. The concentration of SCP solutions was measured at 673 nm by a UV-Vis spectrophotometer. The degradation times of all catalysts were investigated in five pH values (2, 4, 7, 9 and 12). The degradation of SCP was carried out in two-steps, decolorization process which was measured by using UV-Vis spectrophotometer and the complete degradation was determined by TOC analyzer (See Figure 4).

The weight of the catalyst was evaluated from 0.1 to 1g. The increase in the catalyst weight up to 0.4 g cause an increase in the degradation rates. Increasing the SCP concentration also prolongs the degradation time. In order to achieve optimal conditions, the amount of 0.4 g of catalyst and SCP with the concentration of 10 ppm, was chosen as the optimum conditions. Catalyst samples were added to 100 mL of SCP solutions in optimum condition, separately. Then, the processes of decolorization and degradation were investigated under UV irradiation. The results of the decolorization process and final degradation are presented in Figure 4.

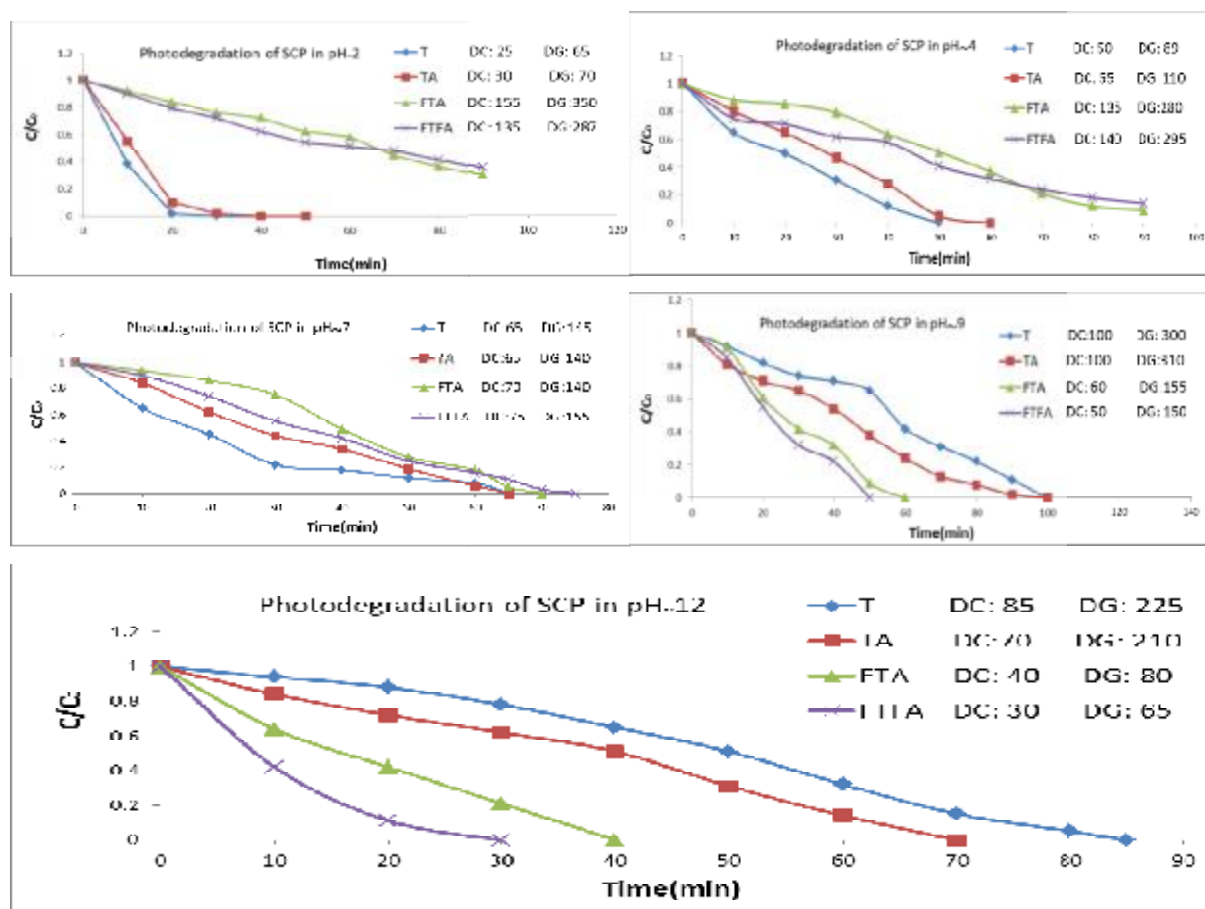


Figure 4. Represents the results obtained for the decolorization time (DC) by the UV-Vis spectrophotometer and degradation time (DG) by TOC analyzer for all photo catalysts.

The results of cobalt ions absorbed by MC and AC adsorbents are provided in Figure 5. The MC adsorbent performance was initially slow. Cobalt ion adsorption rate increased with increasing the adsorbent weight. Finally, after an hour of adsorption, 85% of cobalt ions were removed from the solution. Using 1.2 g of the AC adsorbent in 10 min, 90% of cobalt ions were absorbed. After 20 min, the remaining cobalt ions in the solution were less than 3%. The results show that the effect of non-ionic surfactants and stabilizers in accelerating the absorption of metal ions on the adsorbent is important. In this way, in addition to increasing the speed, the amount of the absorption capacity can be increased by 30% per gram of adsorbent.

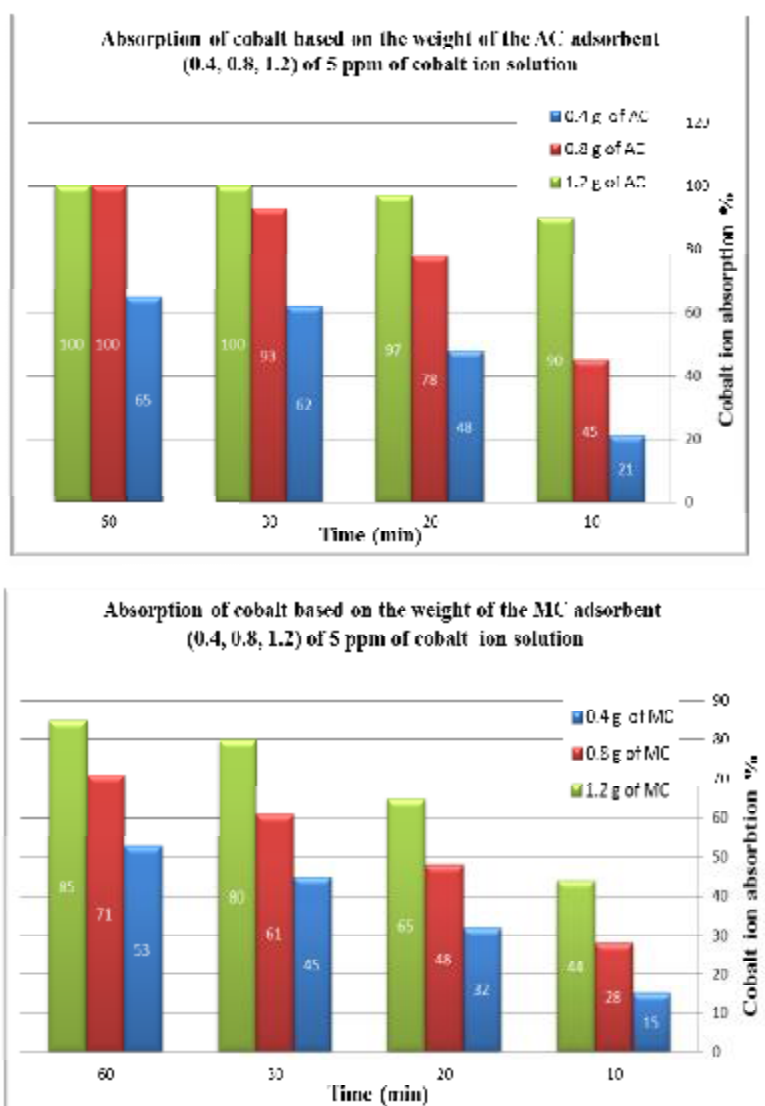


Figure 5. Adsorption percentage of cobalt ions on three weights of MC and AC adsorbent.

Conclusion

In the present research, we first produced strong catalysts for various media conditions. One of the weak points of the TiO_2 as a catalyst is its reduced activity in alkaline media, in which, its surface is inactivated by the hydroxide ion. Our results showed that using iron as dopant increased the strength and stability of TiO_2 in the alkaline media. Considering high resistance of the γ -alumina and its very strong bonding with TiO_2 , it was used as the central core in this study. The presence of the central core reduces the used catalyst mass per surface area after deposition of TiO_2 on the core. This keeps wasting a lot of catalysts in the center of the nanoparticle.

Catalytic degradation of SCP was performed on the industrial wastewater samples of a factory owning alkaline pH. In the next step, the introduction of iron as dopant decreased the band gap of the photocatalyst. According to the results, the efficiency of catalyst in alkaline conditions was higher than TiO_2 to degradation the wastewater as it degraded and decolorized the samples in the shortest time.

Based on the studies done by Sökmen, the nonbonding electrons in a chromatic structure such as cobalt phthalocyanine can be easily transferred to the π^* orbital. During the degradation process, this electron can be transferred to the conductive band of the photocatalyst. These electrons can increase the photocatalytic rate in the catalytic degradation processes. The reduction in the band gap reduced the difference between catalyst energy and electron excitation energy of the chromophore. In this study, the mentioned reduction increased photocatalytic activity. In fact, the aid of SCP to the catalyst resulted in its own degradation. Based on the results, the efficiency of the FTFA catalyst is very good in alkaline media and close to the TiO_2 catalyst performance in acidic media. The final issue after degradation the dye was the presence of the remaining cobalt ions in solution. In this regard, by modifying the montmorillonite with the help of non-ionic surfactants, we increased the removal efficiency of cobalt ion.

References

- [1] M. Nozari, S. Moradi Dehaghi, *Fresen. Environ. Bull.*, 24, 3505 (2015).
- [2] T. Bigdeli, S. Moradi Dehaghi, *J. Emerging Science*, 2, 157 (2018).
- [3] S. Moradi Dehaghi, H. Ghasemi Mobtaker, S. Javad Ahmadi, P. Aberoomand Azar, *Fresen. Environ. Bull.*, 21,1(2012).
- [4] N. Nasralla M. Yeganeh, Y. Astuti, S. Piticharoenphun, N. Shahtahmasebi, A. Kompany, M. Karimipour, B.G. Mendis, N.R.J. Poolton, L. Šiller, *Sci. Iran*, 20, 1018 (2013).
- [5] A.H. Haghigaty, S. Moradi Dehaghi, *Orient. J. Chem.*, 34, 1046 (2018).

- [6] S. Moradi, P. Aberoomand-Azar, S. Raeis-Farshid, S. Abedini-Khorrami, M. H. Givianrad, *J. Saudi. Chem. Soc.*, 20, 373 (2016).
- [7] N.D. Abazović, L. Mirengi, I.A. Janković, N. Bibić, D.V. Šojić, B.F. Abramović, and M.I. Čomor, *Nanoscale Res Lett.*, 4, 518 (2009).
- [8] M. Reza Toosi, M. HasanPiravi, J. Sajadi, M. J. Bayani, H. Manghabati, *Int. J. Chem. React. Eng.*, 11, 561 (2013).
- [9] A. Vargas, J.A. Montoya, C. Maldonado, I. Hernandez-Perez, D.R. Acosta, J. Morales, *Microporous Mesoporous Mat.*, 74, 1 (2004).
- [10] V. Vetrivel, K. Rajendran, V. Kalaiselvi, *Int J. Chemtech Res.*, 7, 1090 (2015).
- [11] R. Awwad Shawabkeh, O. A. Khashman, O. A. Khashman, G. I. Bisharat, *Int J. Chem.*, 2, 10 (2010).
- [12] H. Yao, Y. Zhao, *J. Phys. Chem. Biophys.*, 6, 1 (2016).
- [13] P. Borker & A. V. Salker, *Indian J. Chem. Technol.*, 13, 341 (2006).
- [14] A. B. Sorokin, *Chemical Reviews*, 113, 8152 (2013).
- [15] B. Basu, S. Satapathy & A. K. Bhatnagar, *Cat. Rev.*, 35, 571 (2012).
- [16] D. W. Dixon, A. F. Gill, B. R. Sook, *J. Porphyr. Phthalocyanines*, 8, 1300 (2004).
- [17] F. Oprea, E.-F. Mirela, M. Nicolae, O. Pântea, The Sixth Jordan International Chemical Engineering Conference, 12-14, Amman, Jordan (2010).
- [18] S. Chin Lee, H. O. Lintang & L. Yulianti, *J. Exp. Nanosci.*, 9, 78 (2014).
- [19] E. M. El-Nemma, N. M. Badawi, S. S.M. Hassan, *Talanta*, 78, 723 (2009).
- [20] W. Shu Lian, F. Yan Fen, Y. Yong, L. Jun Zi, D. An Ping, Z. Xiao Rong & H. Ying Ping, *Chin. Sci. Bull.*, 56, 969, (2011).
- [21] A. Vashurin, I. Kuzmin, M. Razumov, S. Pukhovskaya, O. Golubchikov, A. Voronina, G. Shaposhnikov, O. Koifman, *J. Porphyr. Phthalocyanines*, 19, 1159 (2015).
- [22] L. Lei, H. Wang, Y. Zhang, X. Li, J. Mu, G. Wang, Z. Jiang, S. Zhang, *Macromolecular Research*, 18, 331 (2010).
- [23] A. Ebrahimian Pirbazari, *J. Chem. Eng. Process Technol.*, 8, 333 (2017).
- [24] G. Das, B. Sain, S. Kumar, M.O. Garg, G. Murali Dhar, *Catalysis Today*, 141, 152 (2009).
- [25] S.-H. Wu, J.-L. Wu, S.-Y. Jia, Q.-W. Chang, H.-T. Rena, Y. Liu, *Appl. Surf. Sci.*, 287, 389 (2013).
- [26] M. Sökmen, M. K. Kesir, S. Y. Alomar, *American J. Nanosciences*, 3, 63 (2017).
- [27] P. K. Chaudhari, Removal of Mercaptance from Diesel, International Conference on Future Environment and Energy IPCBEE vol.28 © IACSIT Press, Singapore (2012).
- [28] J. Li, X. Li, Y. Liu, J. Zhang, *Chinese J. Chemical Eng.*, 25, 171 (2017).
- [29] A. S. Afshar, H. Harrafi, S.M. Javad G. Zahedi, *Int. J. Chem. Molecular Nuclear, Materials and*

Metallurgical Eng., 6, 563 (2012).

[30] P. M. Rawson, C.-A. Stansfield, R. L. Webster, D. Evans, *Fuel*, 139, 652 (2015).

[31] A. EbrahimianPirbazari, *Procedia Materials Science*, 11, 622 (2015).