RESEARCH PAPER

Enhancing the Photocatalytic Activity of Nano Nd-TiO$_2$@SiO$_2$ by coupled systems

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ABSTRACT

Metal doped TiO$_2$ catalysts were synthesized by sol-gel method and their activities were determined for degradation of methyl orang as a pollutant. Nd-doped TiO$_2$ showed the maximum activity comparing with others. Colloidal SiO$_2$ was used as a support to increase the surface area and also the activity. Nano-TiO$_2$/SiO$_2$/Nd was synthesized by sol-gel method and it was characterized using XRD, XRF, SEM, TEM and BET methods. The major phase of synthesized catalyst was anatase and the crystal size estimated about 30 nm which was confirmed by TEM. BET analysis showed that deposition of catalyst on colloidal silica, enhanced the surface area significantly. It was found that the solution pH has great effect on kinetic and efficiency of the degradation process. At low pHs the degradation rate was faster comparing with alkaline solutions. Applying various fields to enhance the kinetic and efficiency of the photochemical process was studied. It was found that electric field (EP) has the most significant effect. Ultrasonic (UP) and magnetic (MP) fields were also effective in some cases. LC MS analysis showed that mineralization could be completed at the end of process.

INTRODUCTION

Increasing the organic pollutants in wastewaters by industries development is a challenging problem nowadays. Recent researches are focusing on finding efficient and low cost technology to decompose and remove the organic pollutants from wastes [1-3]. Among the new technologies, the Advanced Oxidation Process (AOPs), has been considered as an efficient way for the purpose. Photocatalytic oxidation, especially TiO$_2$/UV system is among the AOPs having great advantages such as low cost, milder condition, high activity, low toxicity for human, easy controllability, no-twain pollution and chemical stability, comparing to the others methods [4-6]. In this system UV irradiation on TiO$_2$ generate electron/hole pair which has strong redox properties. Since the process involves the generation of highly reactive hydroxyl radical (HO$^\bullet$), a wide range of organic pollutants can be treated. However, the poor quantum yield results from rapid electrons/holes recombination is a problem which restrict its widespread practical use [7]. Doping with some metal ions decreases the electrons/holes recombination and so increases the photocatalytic activity. By doping the electron-hole recombination produced by UV light irradiation reduces. Transition metals doping effect on photocatalytic activity was studied by many researchers [8-13]. Lanthanide ions also have been applied for doping of TiO$_2$. Lanthanides

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because of f-orbital configuration could form complex with lewis bases such as organic acids, amines alcohols and etc., so it can facilities the decomposition process [14, 15].

Despite the mentioned advantages for TiO_2, its use in nanoscal associated with some problems which leads to some difficulty in application. These problems are agglomeration, phase transformation, decrease in surface area by thermal treatment, and the difficult recovery of the nanocatalyst from aqueous media. To overcome the difficulties it can be deposited on low cost and thermally stable supports with high surface area, such as colloidal SiO_2. It also leads to increase the adsorption of organic materials on catalyst surface and having higher activity. Interaction between titanium dioxide and silica and different structure of titanate in surface from the bulk titania also leads to increasing the activity [16].

One of the most important parameters which affect the degradation process remarkably, is the solution pH. In alkaline solution, the repulsion between OH^- and the surface may prevent the radical production and so decreasing the degradation rate.

The point of zero charge (pzc) of TiO_2 is at pH 6.8, so in acidic solution, the catalyst surface is positively charged, because of the following equilibrium and it can affect the adsorption property of the surface toward the dye and so leads to increase its degradation [7].

$$TiOH + H^+ \Leftrightarrow TiOH_2^+$$
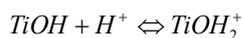
The pollutant protonation could also have significant effect in degradation process rate.

In this study the TiO_2 was deposited on SiO_2 surface to improve its properties as a photocatalyst. The photochemical process was also coupled with some field such as magnetic, ultrasonic and electric field to investigate their effect on improving the photocatalytic activity.

MATERIALS AND METHODS

Materials used in this study including titanium tetraisopropoxide (TTiP), nitric acid, absolute ethanol, methylorange and all metals nitrates were analytical grade and were purchased from Merck Company. HPC and colloidal silica solution (30%) was purchased from Aldrich Company. Double distilled water was used for preparation of all solutions.

Photocatalyst preparation

The catalysts were synthesized by sol-gel method. The process was as following: an appropriate amount of titanium tetraisopropoxide (TTiP) was dissolved in 100 ml of ethanol under stirring to form solution A. Hydroxypropyl cellulose (HPC) was added as stabilizer. Solution B was prepared by adding 0.18 ml of nitric acid into 10 ml ethanol (and the appropriate amount of colloidal silica in case of $TiO_2/SiO_2/M$). Metal nitrate were dissolved in ethanol to prepare the solution C. $M^{n+}/$ Ti (IV) molar ratio was 1:1000. Solution B was added drop by drop to solution A under vigorous stirring to make a clear sol. Solution C was added to previous solution under stirring. The reaction system was dispersed for 30 minutes by a homogenizer at ~20000 rpm. Then the prepared sol was placed in ultrasonic bath for 30 minutes, aged at room temperature (25–30°C) for 48 hour (to form gel) and dried at 70°C for about 24 hour to remove the water and organic solvents. Finally the obtained powder was calcined in an electric furnace at 500 °C for 4 hour [18].

Characterization of photocatalysts

X-ray diffraction method was used to detect the phases of the prepared catalysts. It was done using a STOE STADI MP X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm). The average particle size was estimated by Sherrer equation. TEM image was obtained by a Philips EM 208 S
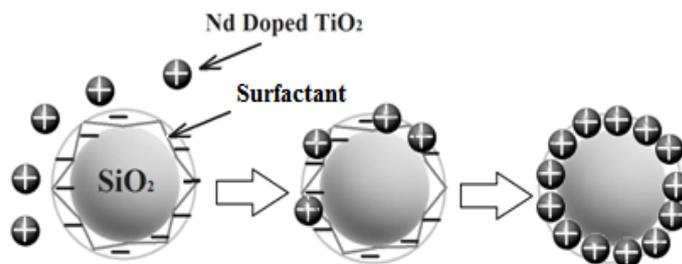
Fig. 1. Deposition of TiO_2 on SiO_2 colloides

electron microscopy instrument. SEM image of samples was prepared on a KYKY EM3200 device. Chemical compositions were determined via XRF method using an Oxford ED 2000 equipment. The surface area of the samples was determined by BET method using a Quantachrome Nova 2200 nitrogen adsorption apparatus. Methylorange concentration of solutions were determined using a Cary UV–Vis spectrometer at the maximum absorption wavelength (λ = 465 nm). To detect the intermediate species and confirm the complete decomposition of methylorange at the end of degradation, LC-MS analysis was applied. It was done by an Agilent MSD1100 system.

Photocatalytic degradation process

Methylorange solution (5 ppm) was used as a model pollutant to determine the photocatalytic activity of prepared catalysts. The catalyst to solution weight ratio was 1:10000. The solution was stirred by a magnet stirrer for 1 hour in darkness to determine the adsorption of dye by catalyst. The solution was irradiated by a 15 W UV lamp which was placed in a quartz pipe in the middle of reactor. It was turned on after 1 hour stirring the solution. Sampling (about 10 ml) was done every 15 min. The samples were filtered, centrifuged and their concentration was determined by UV-Visible spectrometry.

To study the pH effect, four solutions of methylorang with pH of 2, 4, 7 and 9 were prepared and irradiated by UV lamp. The initial pH adjustment was done by nitric acid and ammonia solutions.

Magnetic, ultrasonic and electric field effects were studied by coupling the mentioned field with photochemical process. A power supply (30 V), and two steel electrodes with dimension of 10×20 cm were used in EP process. MP system was studied using two magnets (1.5 T) with dimension of 10×5×4 cm which were placed beside the reactor. An ultrasonic bath (Ultrawave Limited, Cardif CF2UK), was placed beside the reactor in UP coupling system.

RESULTS AND DISCUSSION

Characterization of the catalysts

Phase analysis of the samples were done by X-Ray Diffraction. Fig. 2 shows the XRD pattern of two samples (TiO₂ and TiO₂@SiO₂). In both cases the major part of the catalysts are anatase; the rutile exist as a minor phase. Crystallite size of the

samples were estimated by the Scherrer equation [17]. It was about 45 nm for TiO₂ and 27 nm for TiO₂/SiO₂. Peak broadening is observed in TiO₂/SiO₂ pattern which confirms the smaller particles comparing TiO₂.

Surface area for the samples were obtained by BET method which are reported in Table 1. The samples which are not deposited on SiO₂, has a surface area of about 110 m²/g , but deposition of TiO₂ on SiO₂, leads to increaseing the surface area significantly(150 m²/g).

The pores in the sample were in the range of 2–30 nm which are in mesopore range. The formation of mesoporous structure in the samples can be attributed to the aggregation of TiO₂ particles which can be seen in SEM image.

SEM image of the TiO₂ (Fig. 3) shows that the particle sizes of the TiO₂ are about 40-70 nm and the particle size distribution is not in wide
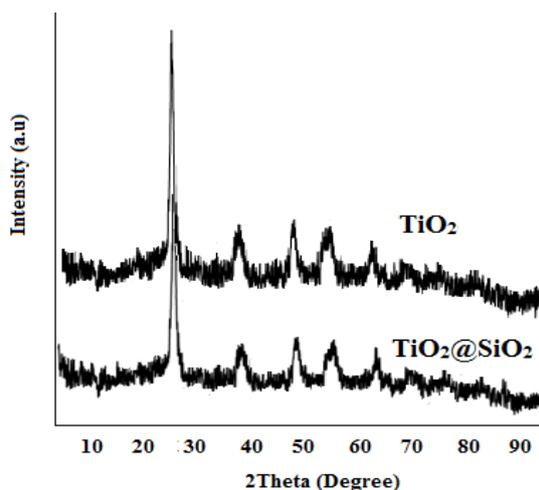
Fig. 2. XRD pattern of TiO₂ and TiO₂@SiO₂
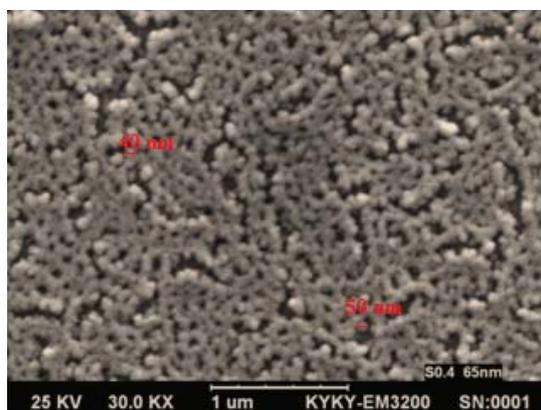
Fig. 3. SEM image of TiO₂

range. The pores are formed because of particle aggregation. TEM image is given for TiO$_2$@SiO$_2$ nanocomposite (Fig. 4). Particle sizes are between 20 to 40 nm. Spherical particles of SiO$_2$ are seen in the image which TiO$_2$ particles are deposited on their surface. The darker points show the SiO$_2$ particles.

The synthesized catalysts were applied for

degradation of methylorange. The results (Fig. 5) indicates that the un-doped TiO$_2$ has the lowest activity among synthesized samples. As mentioned previously the low activity of TiO$_2$ is because of electron-hole recombination and low surface area. Doping the TiO$_2$ with metal ions solve the first problem to some extend as can be seen in Fig. 5. The metal ions enhanced the activity significantly but the enhancement was equal by all of them. Among the ions Nd doping had the maximum effect and Ni the minimum. Adding the SiO$_2$ to the catalyst composition led to increase the activity because of increasing the surface area, so the doping was done with best ion and addition of SiO$_2$ to have the both promotion. Sequence of

Fig.4. TEM image of TiO$_2$/SiO$_2$/Nd
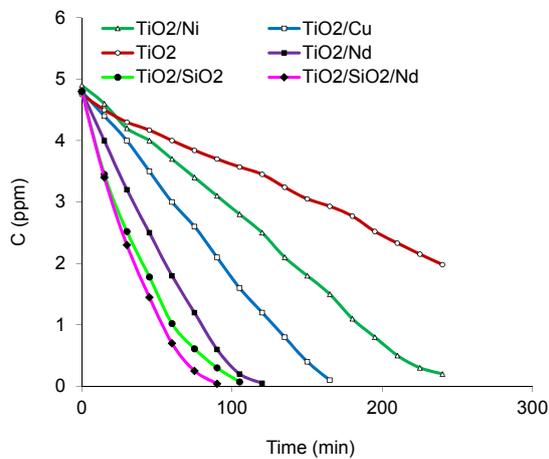
Fig.5. Comparing the photodegradation rate by different catalysts
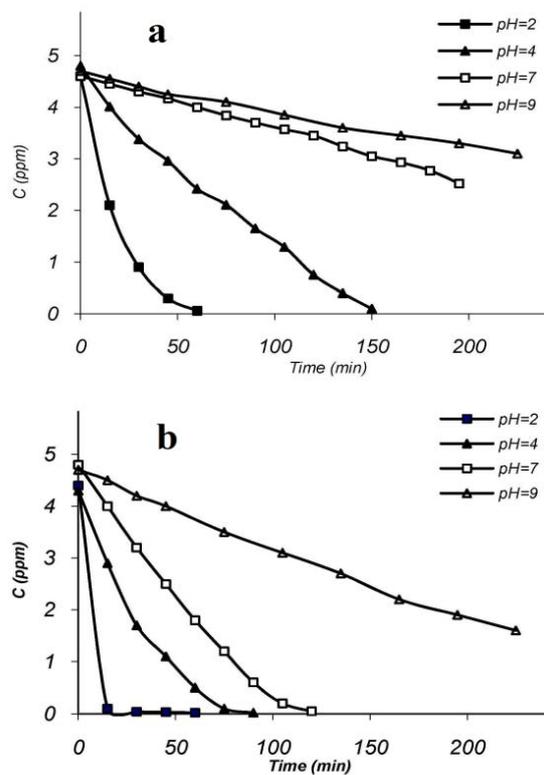
Fig. 6. The pH effect on TiO$_2$ (a) and Nd-doped TiO$_2$ (b) catalyst activity

Table 1. Surface area of the samples obtained by BET

Sample name	TiO$_2$	TiO$_2$@Nd	TiO$_2$@Ag	TiO$_2$@Cu	TiO$_2$@Ni	TiO$_2$@SiO$_2$@Nd	TiO$_2$@SiO$_2$
Surface area (m²/g)	110	112	114	111	110	150	148
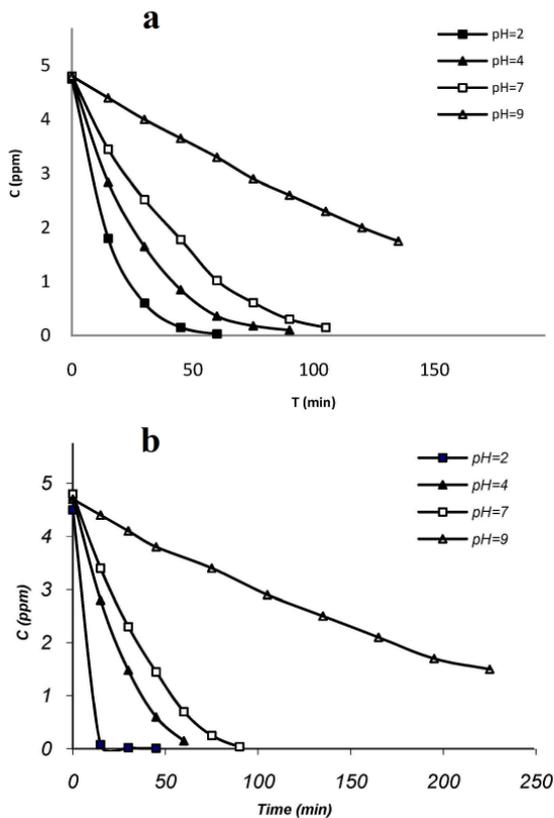
Fig. 7. pH effect on degradation time by TiO$_2$/SiO$_2$ (a) and TiO$_2$/SiO$_2$/Nd (b)
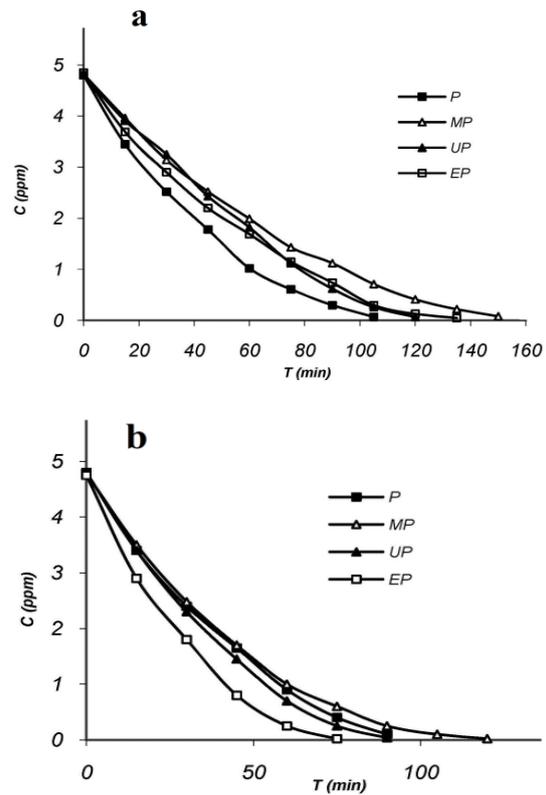
Fig. 8. Coupling systems effect on degradation rate of TiO$_2$/SiO$_2$ (a) and TiO$_2$/SiO$_2$/Nd (b) in pH=7

catalytic activity for all synthesized catalysts was as below:

TiO$_2$/SiO$_2$/Nd > TiO$_2$/SiO$_2$ > TiO$_2$/Nd > TiO$_2$/Cu > TiO$_2$ / Ni > TiO$_2$

pH effect was investigated by four catalysts of TiO$_2$, TiO$_2$/Nd, TiO$_2$/SiO$_2$ and TiO$_2$/SiO$_2$/Nd. Fig. 6 shows the results for TiO$_2$ and TiO$_2$/Nd. Decreasing the solution pH led to decrease in degradation time(the degradation time by TiO$_2$/Nd is 15 minutes in pH=2). In acidic solution the surface is positively charged so the adsorption of dyes is facilitated and the degradation is proceeds faster. In alkaline pH the activity decreased significantly because of low efficiency in hydroxide radical production which is come from repulsion between the hydroxide ion and negatively charged surface.

Fig. 7 also shows the pH effect on degradation rate by TiO$_2$/SiO$_2$ and TiO$_2$/SiO$_2$/Nd. As previous, these catalysts are more active in the acidic media , but the activity is higher comparing with the previous catalysts.

Coupling effect of the mentioned field for TiO$_2$/ SiO$_2$ and TiO$_2$/SiO$_2$/Nd are investigated in Fig.8. The photocatalytic activity in coupling system for TiO$_2$/ SiO$_2$ was as: P > UP ~ EP > MP. The best degradation time was about 105 minutes. The activity for TiO$_2$/ SiO$_2$/Nd catalyst was as: EP > P ~ UP > MP, which was different from TiO$_2$/SiO$_2$. The best degradation time was about 75 minutes. The results show that the deposition of TiO$_2$ on SiO$_2$ leads to significant increase in activity and electric field has increased significantly the degradation rate.

LC MS analysis shows the fragmentation of methylorange before complete degradation and also confirms the complete degradation. Fig. 9 (a) shows that there is just un-fragmented methylorange in starting point. After 30 minutes when a fraction of methyorange is decomposed, the methylorange and some other masses which are formed by its fragmentation are observed; and finally at the end there is no fragment with considerable concentration in the solution and just two peaks in noise range are seen.
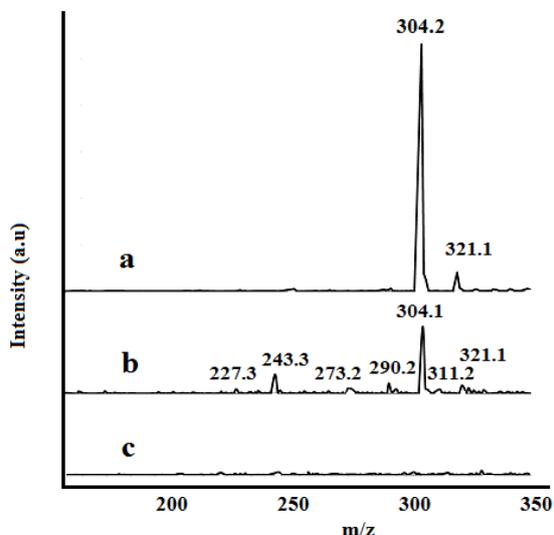
Fig. 9. LC-Mass analysis of methylorange before degradation (a), after 30 min (b) and after degradation (c) by TiO$_2$/SiO$_2$/Nd in pH=7

CONCLUSION

Nd-TiO$_2$@SiO$_2$ was synthesized by sol-gel method. It was characterized by XRD, TEM and XRF methods. It was found that the TiO$_2$ was deposited on the surface of the SiO$_2$. The particle sizes were between 30 and 40 nm. Deposition of TiO$_2$ on SiO$_2$ surface and doping it by Nd led to increase the activity of catalyst significantly. In acidic solution the degradation rate was much better than alkaline or neutral solutions and the best result was in pH=2. Coupling the photochemical process with different fields was studied. the electro-photochemical coupling system had promising effect on degradation rate. LC-MS analysis showed the fragmentation of methylorange before the end of process. The complete decomposition at the end of process was also confirmed by LC MS analysis.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

1. Coleman M, Eggins BR, Byrne JA, Palmer FL, King E, Photocataytic degradation of 17-β-oestradiol on immobilized TiO$_2$, Appl Catal B. 2000;24: L1-L5.
2. Hong CS, Wang Y, Bush B, , Kinetics and products of the TiO$_2$, photocatalytic degradation of 2-chlorobiphenyl in water, Chemosphere. 1998;36: 1653–166.
3. Ohko Y, Ando I, Niwa C, Tatsuma T, Yamamura T, Nakashima T, Kubota Y, Fujishima A, Degradation of bisphenol A in water by TiO$_2$ photocatalyst, Environ Sci Technol. 2001; 35: 2365–2368.
4. Rui X, Jia L, Jun W, Xiaofang W, BinLiu BW, Xiaoyu L, Xiangdong Z, Photocatalytic degradation of organic dyes under solar light irradiation combined with Er^{3+}:YAlO$_3$/Fe- and Co-doped TiO$_2$ coated composites. Sol Energ Mat Sol Cells. 2010;94: 1157–1165
5. Wu X, Qin W, Ding X, He W Jiang Z, Dopant influence on the photo-catalytic activity of TiO$_2$ films prepared by micro-plasma oxidation method, J Molecul Catal A. 2007;268: 257-263.
6. Shaoqi ZW, Titania deposited on soft magnetic activated carbon as a magnetically separable photocatalyst with enhanced activity, Appl Surf Sci. 2010;256:6191-6198.
7. Ioannis KK, Triantafyllos AA, TiO$_2$-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations A review. Appl Catal B. 2004;49:1–14.
8. . Bouras, P, Stathatos E, Lianos P, Pure versus metal-ion-doped nanocrystalline titania for photocatalysis, Appl Catal B. 2007, 73: 51–59.
9. Ding X, An T, Li G, Zhang S, Chen J, Yuan J, Zhao H, Chen H, Sheng G, Fu J, Preparation and characterization of hydrophobic TiO$_2$ pillared clay: the effect of acid hydrolysis catalyst and doped Pt amount on photocatalytic activity, J Colloid Interf Sci; 2008;320 (2): 501–507.
10. Li Y, Peng S, Jiang F, Lu G Li S. Effect of doping TiO$_2$ with alkaline-earthmetal ions on its photocatalytic activity. J Serbian Chem Soc. 2007;72 (4): 393–402
11. Liao D L., Badour CA, Liao BQ, Preparation of nanosized TiO$_2$/ZnO composite catalyst and its photocatalytic activity for degradation of methyl orange. J Photochem Photobiol A. 2008;194: 11–19.
12. Rengaraj S, Li, XZ, Photocatalytic degradation of bisphenol A as an endocrine disruptor in aqueous suspension using Ag-TiO$_2$ catalysts. J Environ Pollut. 2006; 27 (1/2/3): 20–37
13. Xu AW, Gao Y, Liu HQ, The preparation, characterization, and their photocatalytic activities of rare-earth-doped TiO$_2$ nano-particles. J Catal. 2002 207:151–157.
14. Ranjit KT, Willner I, Bossmann SH, Braun AM, Lanthanide oxide doped titanium dioxide photocatalysts: effective photocatalysts for the enhanced degradation of salicylic acid and t-Cinnamic acid. J Catal. 2001;204: 305-313.
15. Ranjit KT, Willner I, Bossmann SH,. Braun AM, Lanthanide oxide doped titanium dioxide photocatalysts: novel photocatalysts for the enhanced degradation of p-Chlorophenoxyacetic acid. Environmental Science& Technology.2001;35: 1544-1549
16. Ding Z, Lu GQ, Greenfield PF, A Kinetic Study on Photocatalytic Oxidation of Phenol in Water by Silica-Dispersed Titania Nanoparticles J Colloid Interf Sci, 2000;232, 1-9.
17. Meltem A, Funda S, Ertugrul A, Effect of Fe^{3+} ion doping to TiO$_2$ on the photocatalytic degradation of Malachite Green dye under UV and vis-irradiation, J Photochem Photobiol A. 2009; 203: 64–71
18. Aberoomand AP, Moradi DSH, Samadi S, Tehrani MS, Kamyar S, Givianrad MH, Effect comparision of Nd^{3+}, pectin and poly(ethylene glycol) on the photocatalytic activity of TiO$_2$/SiO$_2$ film. Asian J Chem. 2010;22(10):1619-1627.