

Synthesis, characterization and applications of β -cyclodextrin coated $\text{Fe}_3\text{O}_4\text{-CeO}_2$

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ABSTRACT

Magnetic nanoparticles (MNPs) have emerged as excellent materials in many fields, such as biology, medicine, environment and material science due to their high specific surface area, biocompatibility, low toxicity and strong magnetic responsivity. In this work, we designed and fabricated β -cyclodextrin (β -CD) coated MNPs which could be used in various bio- and environmental applications. Cyclodextrins are natural oligosaccharides which have the molecular Inclusion / complexation capabilities through host-guest interactions with a wide variety of organic and inorganic molecules. Tagging cyclodextrins with magnetic stable nanoparticles makes them magneto-responsive and may lead to a new generation of catalysts which will provide good opportunities for applications in the fields of bio-separation / purification, contaminants removal from waste water in environment pollution cleanup and hydrophobic drug delivery. In this work Fe_3O_4 , CeO_2 , $\text{Fe}_3\text{O}_4\text{-CeO}_2$ β -cyclodextrin coated Fe_3O_4 , β -cyclodextrin coated CeO_2 and β -cyclodextrin coated $\text{Fe}_3\text{O}_4\text{-CeO}_2$ were prepared using different co-precipitation method. Functionalized nanoparticles were characterized with XRD and Raman analysis. The catalytic activities were tested for degradation of phenol and oxidation reactions. The degradation of phenol was monitored by change in colour of the reaction mixture from colorless to dark brown. The change in the concentration of phenol was monitored by using UV-Vis spectrophotometer.

Keyword: Magnetic Nanoparticles (MNPs), β -cyclodextrin, UV-Vis spectrophotometer.

INTRODUCTION

In Chemical Sciences, nano-structured materials in the form of nanotubes, nanowires, nanorods, nanoribbons and nanosheets [1] have attracted more attention in the last decades due to their unique optical, electrical and magnetic properties and their potential applications in nanodevices. It can be easily understood that metal nanoparticles chemistry differs from that of the bulk materials in terms of size reduction, high surface area to volume ratio which lead to enhanced catalytic activity. Among them magnetite (Fe_3O_4) nanoparticles due to their good biocompatibility, superior superparamagnetic property, nontoxicity and easy preparation process are becoming very popular and promising materials now a days. They have attracted increasing attention and enormous interest in various fields, such as environmental and biomedical applications including enzyme immobilization, protein separation, magnetic resonance imaging, hyperthermia, targeting drug delivery system [2].

Magnetite nanoparticles with superparamagnetism can be easily magnetized with an external magnetic field and demagnetized immediately once the external magnetic field is removed [3]. However, due to high specific surface energy and anisotropic dipolar attraction, magnetite nanoparticles tend to aggregate together into larger clusters which lead to a possible loss of superparamagnetism and limit their applications. Therefore, the surface modification of nanoparticles is necessary and can be modified by inorganic or organic coating to overcome the particles lack. Modification of the surface of MNPs prevents aggregation/agglomeration of the particles, leading to colloidal stability, renders them with water-solubility, biocompatibility, non-toxicity, nonspecific adsorption to cells, and bioconjugation. Moreover, magnetic nanoparticle-based materials can be re-collected by using an external magnet and avoiding conventional filtration or centrifugation processes. Considerable efforts have been made to modify the surface of magnetic nanoparticles and the preparation of organic-inorganic nanocomposites. The combination of inorganic and organic components in a single particle at the nano-sized level has made accessible an immense area of new functional materials [4].

Inorganic materials (silica, gold etc.) natural or synthetic polymers are frequently employed as coating materials to impart surface reactivity. Natural polymers include chitosan, dextran, gelatin, starch, cyclodextrin etc. and synthetic polymers are polyacrylic acid, polyvinyl chloride, poly vinyl alcohol etc.

Cyclodextrins (CDs) are a group of naturally cyclic oligosaccharides, with six, seven, or eight glucose subunits linked by α -(1, 4) glycosidic bonds in a torus shaped structure and are denominated as α -, β -, and γ -CD respectively. The cyclodextrin contains primary and secondary hydroxyl groups at the 2, 3 and the 6 position, respectively [5]. The cyclodextrin assumes a rigid structure because of the formation of a belt of intermolecular hydrogen bonds between hydroxyl groups at the 2 and 3 positions of adjacent glucose units. The rotation of the primary hydroxyl groups is possible, thus reducing the effective diameter of the cavity on the primary side of the molecule. The presence of the hydroxyl groups makes the upper and lower end of the molecule hydrophilic. The cavity of the cyclodextrins is rendered hydrophobic because of the presence of glycosidic oxygens and C-H units. Attention has recently been focused on cyclodextrin based polymeric materials in a wide variety of applications due to their unique sorption properties. Recently, a number of insoluble cyclodextrin polymer or co-polymers have been widely used for various applications such as contaminants removal from wastewater, protein refolding, drug delivery etc. However, the difficulty in separating those powdery cyclodextrin-based adsorbents, except high speed centrifugation, from treated effluent limits their practical applications. Magnetic assisted adsorption separation technology provides an alternative method to separate powdery adsorbents from solution effectively.

Metal-based nanomaterials have also emerged as efficient enzyme mimics. Among them, cerium oxide nanoparticles and magnetic nanoparticles are two most widely used metal oxide catalysts. CeO_2 is one of the most important rare-earth metal oxides and has a wide range of industrial applications, such as in catalysis and solid oxide fuel cells. CeO_2 nanoparticles, which exist in a mixed valence state

(Ce³⁺, Ce⁴⁺), possess many unique properties that have proven to be of high utility in biomedical and catalytic applications. Recently, they have been reported to possess multienzyme, such as SOD, catalase, oxidase, and phosphatase, mimetic properties. For instance, Perez's group reported that nanoceria has an intrinsic oxidase like activity at acidic pH values, as it can quickly oxidize a series of colorimetric dyes without any oxidizing agent. Most recently, it has been found that cerium oxide nanoparticles (nanoceria) possess antioxidant activity at physiological pH values, and the potential use of these materials in biomedical applications, such as protection against radiation damage, oxidative stress, and inflammation, has been reported. The ability of these nanoparticles to act as an antioxidant resides on their ability to reversibly switch from Ce³⁺ to Ce⁴⁺. Furthermore, the synthesis of biocompatible dextran-coated nanoceria and its enhanced stability in aqueous solution has been recently reported [6].

The electronic structure and chemical and physical properties of CeO₂ can be easily altered by introducing oxygen vacancies. Such defects can be rapidly formed and eliminated, giving rise to localized or delocalized 4f electron states. Another potentially important application is the diluted magnetic oxides with Curie temperature above room temperature which are a new class for spintronics. Magnetic ordering in a semiconductor depends on a small proportion of transition metal ion dopants that have partially filled d shells, which allow the unpaired electron to mediate ferromagnetism. Many other mechanisms have also been suggested. Introduction of Fe dopant, which normally has a valence of less than +4, may alter the crystal structure and the valence of the Ce ions, changing the chemical or physical properties. The electronic structures around the Ce and Fe sites provide valuable information. Several metals have been successfully used for this purpose, including ruthenium, cobalt, ruthenium-cobalt, palladium, and nickel. A few examples of mixed oxides (Fe₂O₃-CeO₂) have appeared, namely in dye degradation, oxidations, and synthesis of carbonyl compounds [7]. It is an important and urgent need to design magnetically recyclable nano-catalysts, to reduce their cost of preparation, and to show their efficacy in benign reaction media.

In view of the importance of this research area, we report here the preparation of Fe₃O₄, CeO₂, Fe₃O₄-CeO₂, β-cyclodextrin coated Fe₃O₄, β-cyclodextrin coated CeO₂ and β-cyclodextrin coated Fe₃O₄-CeO₂ and their characterization for catalytic activities for degradation of phenol and oxidation reactions with the following objectives.

METHODOLOGY

Preparation of CeO₂

The investigated CeO₂ were synthesized by coprecipitation method using ultra high dilute aqueous solutions. Coprecipitation was carried out from nitrate precursors Ce(NO₃)₃·6H₂O (Aldrich, AR grade). A dilute aqueous ammonia solution was used as the precipitating agent. The requisite quantities of precursors were dissolved in double distilled water under vigorously stirred condition and stirring continued until a clear solution obtained. The mixed solution was precipitated by drop-wise addition of aqueous ammonia solution over a period until the solution pH reached ~8.5. The resulting pale yellow colored slurry was decanted, filtered and washed several times with double distilled water until free from anion impurities. The obtained precipitate was oven dried at 393 K for 12 h and calcined at 773 K for 5 h at a heating rate of 5 K min⁻¹ in air atmosphere.

Preparation of Fe₃O₄

The Fe₃O₄ were synthesized by coprecipitation method using FeCl₂·4H₂O (Fluka, AR grade) and FeCl₃·6H₂O (Aldrich, AR grade). A dilute aqueous ammonia solution was used as the precipitating agent. The requisite quantities of precursors were dissolved in double distilled water separately, mixed together under vigorously stirred condition and stirring continued until a clear solution obtained. The mixed solution was precipitated by drop-wise addition of aqueous ammonia solution over a period until the solution pH reached ~8.5. The resulting black colored slurry was decanted, filtered and washed several times with double distilled water until free from anion impurities. The obtained precipitate was oven dried at 363 K for 12 h.

Preparation of β -cyclodextrin coated $\text{Fe}_3\text{O}_4\text{-CeO}_2$ nanoparticles:

Prepared $\text{Fe}_3\text{O}_4\text{-CeO}_2$ nanoparticles were mixed with distilled water to make a colloidal solution. The colloidal solution was mixed with β -cyclodextrin (0.2, 0.5, 0.8 and 1wt% of catalyst) under intense stirring at 40°C . The formed nanoparticles were collected by filtration. The particles were washed with distilled water repeatedly and dried for 24 h in oven at 90°C .

Catalyst characterization

Powder X-ray diffraction analysis: Powder X-ray diffraction data were acquired on a Rigaku Multiflex diffractometer utilizing nickel-filtered $\text{Cu K}\alpha$ (0.15418 nm) radiation source and a scintillation counter detector. The samples were scanned from $2\text{--}80^\circ 2\theta$ in 0.02° steps with a counting rate of 1 s/step. The mean crystallite size of the solid solution phases was estimated with the help of Scherrer equation from the line broadening, and the lattice parameter was calculated by a standard cubic indexation method using the intensity of most prominent peak.

The Raman spectra: The Raman spectra of investigated samples were collected on a Horiba Jobin-Yvon HR800 Raman spectrometer equipped with a liquid-nitrogen cooled charge coupled device (CCD) detector and a confocal microscope. A line at 325 nm from a He-Cd laser is used as excitation source of the UV Raman spectroscopy. Visible Raman spectra were recorded with a 632-nm Ar^+ ion (Spectra Physics) laser. The lasers were focused keeping the sample under a microscope with the diameter of the analyzed spot being $\sim 1 \mu\text{m}$, under the ambient conditions. The acquisition time was adjusted according to the intensity of Raman scattering. The wave number values reported from the spectra are accurate to within 1 cm^{-1} .

RESULTS AND DISCUSSION

Characterization of catalysts

The XRD patterns of Fe_3O_4 (prepared at 60°C), Fe_3O_4 (prepared at 90°C) and β -cyclodextrin coated Fe_3O_4 samples are illustrated in Fig. 1, 2 and 3 respectively .

In Fig. 1 & 2 all characteristic peaks at 30.20, 35.51, 43.32, 53.71, 57.21 and 62.94° were corresponding to the (220), (311), (400), (422), (511) and (440) crystal planes of a pure Fe_3O_4 with a spinal structure (JCPDS file PDF no.65-3107) [8].

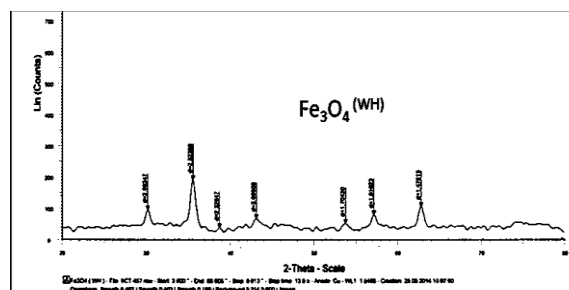


Fig 1: XRD pattern of Fe_3O_4 prepared at 60°C

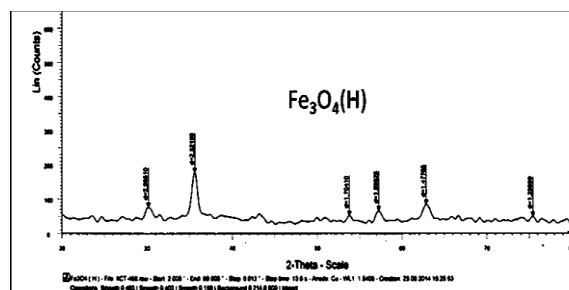


Fig 2: XRD pattern of Fe_3O_4 prepared at 90°C

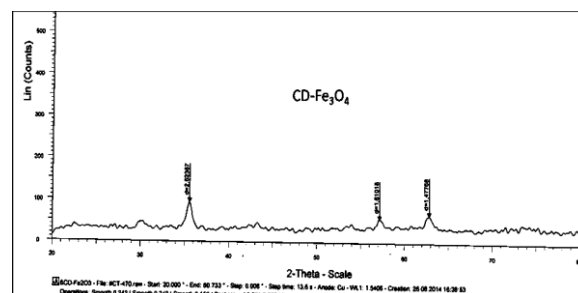


Fig 3: XRD pattern of β -cyclodextrin coated Fe_3O_4

It indicates that the samples are in single phase. The peaks indicate that Fe_3O_4 with a spinal structure and no characteristic peak of impurities are detected in the XRD pattern. This success in fabricating high quality Fe_3O_4 nanoparticles is essential for further research work. All diffraction peaks and positions for Fe_3O_4 match well with those for the β -cyclodextrin coated Fe_3O_4 . The peak intensity in the β -cyclodextrin coated Fe_3O_4 was less as compared to the pure Fe_3O_4 due to the coating of β -cyclodextrin on the surface of Fe_3O_4 .

Raman Analysis

Raman scattering is an inelastic phenomenon. Although its cross section is very small, recent advances in electronics, lasers, optics, and nanotechnology have made Raman spectroscopy suitable in many areas of application. With the advent of Raman enhancement mechanisms and the progress being made in metal nanomaterials and nanoscale metal surfaces fabrications, surface enhanced Raman scattering spectroscopy has become an extra sensitive method applicable for analysis of foods, drugs and for intracellular and intercellular imaging. Raman spectra are usually used to identify the phase of materials. Figure 4 illustrates the Raman spectra of magnetite nanoparticle Fe_3O_4 . As we can see the peaks at 226 cm^{-1} , 496 cm^{-1} , 607 cm^{-1} , and 651 cm^{-1} were observed. Among them 226 cm^{-1} and 496 cm^{-1} peaks attributed to T_{2g} vibration mode of Fe_3O_4 . The peaks at 291 and 819 cm^{-1} were mainly due to the M=O and M-O-M bonding [9]

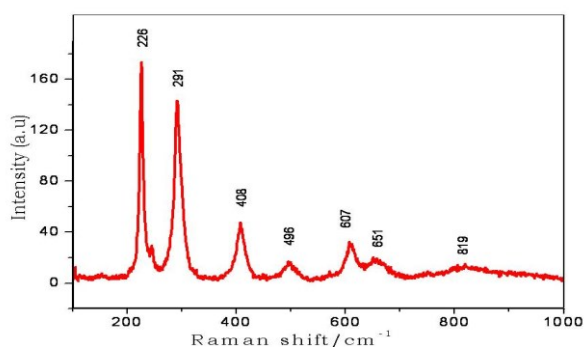


Fig 4: Raman spectra of Fe_3O_4

Phenol degradation studies

Industrial activities generate large amounts of organic hazardous substances in many industries as by-products such as petroleum refining, petrochemical, pharmaceutical, plastic, pesticides, chemical industries, agrochemicals, and pulp and paper industries [10]. The organic pollutants e.g. phenol, are toxic and cause considerable damage and threat to the ecosystem in water bodies and to the human health even at low concentrations. The organics in wastewaters from chemical and related industries cannot be well treated by conventional processes due to degradation of these pollutants being very slow or ineffective and not environmentally compatible.

Heterogeneous catalytic oxidation systems have recently attracted much interest in the waste water treatment processes due to easily recovery and reuse of the catalysts. The Fe_3O_4 MNPs has peroxidase-like activity and could activate H_2O_2 , yielding over 85% removal of phenol and about 30% mineralization within 3 h. Also cerium exhibits a redox cycle between the $3+$ and $4+$ oxidation states, providing a high oxygen storage capacity. This property enhances the performance of transition metal catalysts used in automotive exhaust treatment and waste water treatment. The nanoscaled Fe-Ce oxide hydrate catalyst showed a relatively low rate in heterogeneous Fenton reaction for decolorization of reactive brilliant red X-3B, which was assisted by UV irradiation to achieve almost complete removal of dye within 30 min. We anticipate that nanoscaled cerium oxide (CeO_2) can enhance the catalytic activity of Fe_3O_4 MNPs, and this novel composite is a fascinating and competitive candidate for the catalytic activation of H_2O_2 . Furthermore, Heckert et al. suggested that cerium might be capable of redox cycling in the presence of H_2O_2 and behaved similar to iron in a Fenton-like reaction [11]. Based on this we studied the phenol degradation by magnetic nanoscaled Fe_3O_4 - CeO_2 and β -cyclodextrin coated Fe_3O_4 - CeO_2 composite prepared by the methods described above.

Degradation Experiment

Batch degradation experiments of phenol were carried out in a conical flask (25 mL) placed on a magnetic stirrer with the constant stirring. The reaction suspension was prepared by adding the required amount of catalyst into 5 mL of phenol. A known concentration of H_2O_2 was added to the solution to initiate the reaction. Then, samples were taken at set intervals using a $5\ \mu\text{L}$ syringe and quenched with excess methanol. The reaction mixture was analyzed with the help of a UV-Vis spectrophotometer in the range of 200-800 nm.

Catalytic Activity of Fe_3O_4 - CeO_2 Composite

Control experiments were conducted to compare the removal efficiencies of phenol by various processes at pH 7.0. The change in the absorbance of phenol in the reaction mixture was analyzed by JASCO, V650 UV-

Vis spectrophotometer. The change in intensity of peak at λ_{\max} for phenol at 270 nm was shown in the Fig. 5.

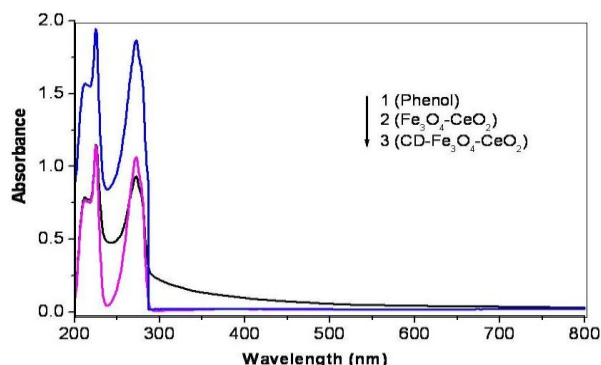


Fig.5: UV-Vis spectra of phenol degradation by using $\text{Fe}_3\text{O}_4\text{-CeO}_2$ and β -cyclodextrin coated $\text{Fe}_3\text{O}_4/\text{CeO}_2$

In the presence of H_2O_2 , the decrease in absorbance of phenol using β -cyclodextrin coated $\text{Fe}_3\text{O}_4\text{-CeO}_2$ composite as the heterogeneous Fenton-like catalyst was notably higher than that for pure $\text{Fe}_3\text{O}_4\text{-CeO}_2$, implying that the catalytic activity was enhanced by the introduction of β -cyclodextrin. The phenol degradation study was also conducted by using CeO_2 , β -cyclodextrin coated CeO_2 , Fe_3O_4 and β -cyclodextrin coated Fe_3O_4 . For CeO_2 and Fe_3O_4 catalyst the observed decrease in absorbance for phenol (λ_{\max} 270 nm) was negligible at the specified reaction conditions in presence of H_2O_2 [12, 13].

In Fig 6 the change in colour of phenol in the solution from colour less to dark brown is shown which is attributed to the formation of intermediates like catechol, resorcinol and glycerol etc. during the degradation of phenol in presence of catalyst and H_2O_2 after 1h. Fig 7 shows the easy separation of catalyst from the reaction mixture by using external magnet. The separation of the catalyst was better in case of CD coated MNP than the Fe_3O_4 nanoparticles [14]. This magnetic separation of catalyst was more convenient than the conventional filtration methods and may be used for different Industrial separation processes.



Figure 6 Photographs of phenol degradation after 1 h,



Fig. 7 Separation of catalyst using an external magnet.

CONCLUSION

$\text{Fe}_3\text{O}_4\text{-CeO}_2$ was successfully prepared by coprecipitation method. The resulting nanoparticles were coated with β -cyclodextrin, the reactivity and the magnetic separation property of β -cyclodextrin coated $\text{Fe}_3\text{O}_4\text{-CeO}_2$ can be used in catalysis and adsorption with high efficiency. The degradation of phenol and separation of catalyst by using external magnet was more pronounced with CD- $\text{Fe}_3\text{O}_4\text{-CeO}_2$ than the $\text{Fe}_3\text{O}_4\text{-CeO}_2$. The interaction between the Fe_3O_4 and β -cyclodextrin results in the formation of a complex with enhanced aqueous solubility. The use of β -cyclodextrin can improve the magnetic properties of the Fe_3O_4 . The growth and the particle size distribution of the inorganic materials may be restricted by the use of the β -cyclodextrin. Furthermore due to the high activity of β -cyclodextrins in the resulting product, they have promising applications in much more extensive fields.

REFERENCES

1. Zhang N, J. Li, Z. He, K. Sun, Preparation and characterization of nano-tube and nano-rod structured $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}/\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_2$ composite cathodes for solid oxide fuelcells, *Electrochem. Comm.* 2011;13: 570-573.
2. Gupta AK, Gupta M, Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications, *Biomaterials.* 2005; 26 :3995-4021.
3. Bruce IJ, Sen T, Surface modification of magnetic nanoparticles with alkoxy silanes and their application in magnetic bioseparations, *Langmuir.* 2005; 21:7029-7035.
4. Liao MH, Chen DH, Preparation and characterization of a novel magnetic nanoadsorbent, *J. Mater. Chem.* 2002; 12 :3654-3659.

5. Zhao D, Zhao L, Zhu CS, Huang WQ, Hu JL, Water insoluble β -cyclodextrin polymer crosslinked by citric acid synthesis and adsorption properties toward phenol and methylene blue, *J. Inclusion Phenom. Macrocyclic Chem.* 2009; 63: 195-201.
6. Asati A, Santra S, Kaittanis C, Nath S, Perez J M, Oxidase- Like Activity of Polymer-Coated Cerium Oxide Nanoparticles. *Angew. Chem., Int. Ed.* 2009; 48: 2308–2312.
7. Lejin Xu, Jianlong Wang, Magnetic Nanoscaled $\text{Fe}_3\text{O}_4/\text{CeO}_2$ Composite as an Efficient Fenton-Like Heterogeneous Catalyst for Degradation of 4-Chlorophenol, *Environ. Sci. Technol.* 2012; 46: 10145–10153
8. G. L. Li, Y. R. Jiang, K. L. Huang, P. Ding, and I. I. Yao, Kinetics of adsorption of *sacharomyces cereviceae* mandelated dehydrogenase on magnetic Fe_3O_4 -chitosan nanoparticles, *Journal Colloid Interface Sci.* 2008;320: 11-18.
9. D. L. A. De Faria, S. V. Silva, et al., Raman Microspec-troscopy of Some Iron Oxides and Oxyhydroxides, *Journal of Raman Spectroscopy* 1997; 28: 873-878.
10. Saputraa E, Muhammada S, Suna H, Anga H, Tadea MO, Wanga S, Manganese oxides at different oxidation states for heterogeneous activation of peroxy monosulfate for phenol degradation in aqueous solutions, *App Cat B: Env*2013; 142– 143:729– 735.
11. S. Yu, H.J. Yun, Y. H. Kim, J. Yi, Carbon-doped TiO_2 nanoparticles wrapped with nanographene as a high performance photocatalyst for phenol degradation under visible light irradiation, *App Cat B: Env* 2014; 144: 893– 899
12. Ayati A, Ahmadpour A, Bamoharram FF, Tanhaei B, Manttari M, Sillanpaa M, A review on catalytic applications of Au/TiO_2 nanoparticles in the removal of water pollutant, *Chemosphere* 2014; 107:163–174.
13. Y. Zhang, X. M. Dou, J. Liu, M. Yang, L. P. Zhang, Y. Kamagata, Decolorization of reactive Brilliant Red X-3B by heterogeneous photo-Fenton reaction using an Fe–Ce bimetal catalyst, *Catal. Today* 2007; 126: 387–393.
14. Heckert EG, Seal S, W. T. Self, Fenton-like reaction catalyzed by the rare earth inner transition metal cerium, *Environ. Sci. Technol.* 2008; 42: 5014–5019.