

Preparation and photocatalytic activity of chitosan-supported cobalt phthalocyanine membrane

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A chitosan-supported cobalt phthalocyanine membrane was prepared by deposition for use as a new environmentally friendly and economical photocatalyst. The structure and surface morphology of the polymer catalyst were analysed by Fourier Transform-infrared spectroscopy, ultraviolet-visible spectroscopy, X-ray diffraction, and scanning electron microscopy. The polymer photocatalyst was used for degradation of Rhodamine B, a stable dye material. Rhodamine B degradation reached 99% in aqueous solution at room temperature under ultraviolet irradiation. The influence of pH, the initial concentration of Rhodamine B, and the catalyst concentrations were investigated. The results revealed that the chitosan-supported membrane is an attractive photocatalyst for Rhodamine B degradation. It retained 60% of its initial catalytic activity after being reused five times.

Introduction

Textile dyeing is a major industry in China and produces large volumes of wastewater in different steps of the dyeing and finishing process [1]. Dye wastewaters can lead to water pollution and are a major concern [2,3]. Rhodamine B (RB), one of the most common xanthene dyes, has good stability as a dye material. It is used for dyeing various products, including cotton, silk, paper, bamboo, straw, and leather. In recent years, some new techniques have been applied in the textile and dyestuff industry, including biological and physicochemical processes. However, these processes are difficult to handle and are not always effective and economical, and can even cause new environmental pollution. Photodegradation has been widely used to remove organic pollutants under normal temperature and pressure. Thus, photodegradation of RB is an important model [4] for the purification of dye effluents [5,6]. Phthalocyanines (Pcs) are dyes of unique spectroscopic, photoelectric, and magnetic properties [7]. Since their synthesis in the early 1930s, a rich and varied chemistry and technology have been developed around these interesting materials [8]. They have been used as photosensitizers and show good catalytic activity under visible light (~500–700 nm) [9]. Phthalocyanine metal complexes with high thermal stability and effective catalytic degradation of organic pollutants have attracted great interest for environmental applications [10]. However, the main restricting factor of phthalocyanines is their rather low solubility in organic or aqueous solvents [11]. A typical method for improving their water solubility is to introduce carboxyl or amino groups into the skeleton [12]. Furthermore, immobilisation of metal phthalocyanines (MPcs) on nanometal oxides could improve their photocatalytic activity. For instance, an RB degradation rate of 32.5% was obtained for photocatalytic activity of CoPc/SnO₂ under visible-light irradiation, and the catalyst retained 48.8% of its initial

activity after being used 10 times [13]. After being immobilised on TiO₂, a copper(II) phthalocyaninetetrasulfonate (CuPcTs) showed strong photocatalytic activity [14] in the photodecomposition of methyl orange under visible light ($\lambda > 450$ nm) [1,13].

Chitosan is a very abundant biopolymer containing amino groups. Most studies focusing on the interactions of chitosan with metal ions have been carried out to recover strategic metals or remove hazardous metals from dilute solutions [15]. In recent years, chitosan has also been used to support catalysts [16,17] owing to its high sorption capacities, stability, and hydrophilicity [18]. The present authors found that the catalytic activity of metalloporphyrin or Schiff-base metal complexes [19], typical catalysts, could be improved by polymerisation [20] or by chitosan support [21]. Chitosan could also improve mechanical strength, hydrophilicity [22], and film-forming ability [23,24], and reduce costs. Although catalytic membrane reactor technology is one of the challenging research topics in membrane science and catalytic reaction engineering, there have been few reports on polymer membrane reactors [25]. In this paper, chitosan, a typical biopolymer, was used as an environmentally friendly and economical polymer carrier. Cobalt phthalocyanine (CoPc) was used as a photocatalytic active centre. A biopolymer functional membrane, a chitosan-supported CoPc membrane (CS/CoPc), was prepared by alternating deposition, which afforded a new environmentally friendly and economical photocatalyst. It was applied to the photocatalytic degradation of RB, a typical organic dye. It showed excellent photocatalytic activity for the degradation of RB in aqueous solutions under UV irradiation.

Materials and Methods

Food-grade chitosan was purchased from Zhejiang Yuhuan Biochemical Co., China. It was purified by 2% acid



dissolution and vigorously stirred, and insolubles were removed by filtration and base precipitation. Its molecular weight was 525 kDa, as measured by gel permeation chromatography (GPC), and it had a degree of deacetylation of 95%. All other chemical reagents were of analytical grade. Distilled water was used in all experiments.

Infrared spectra were recorded using the KBr disc method on a Fourier Transform-infrared spectrometer (Excalibur FTS 3000; Digilab, USA). Ultraviolet-visible (UV-vis) spectra were observed in diffuse reflectance (DRUV-VIS) mode on a TU-1901 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China). Thermal analysis was carried out on a DT-40 thermal analyser (Shimadzu, Japan) ($15\text{ }^{\circ}\text{C min}^{-1}$). Scanning electron micrographs were recorded on a JSM-6701F instrument (JEOL, Japan).

The tetrachlorosulfonyl phthalocyanine cobalt complex (CoPc) was prepared according to the method described by Mifune *et al.* [26]. In brief, 1 g of phthalocyanine cobalt complex was dissolved in dichloromethane (CH_2Cl_2) in an ice bath under nitrogen. Then, 12 g of chlorosulphuric acid (HSO_3Cl) was added dropwise. After refluxing at $135\text{--}145\text{ }^{\circ}\text{C}$ for 4 h, the mixture was poured into ice and filtered. The precipitate was washed with dilute hydrochloric acid (HCl) solution. The product was evaporated under vacuum, and a dark-blue powder (CoPc) was obtained in a yield of 72%.

Double-layer chitosan-CoPc membranes (CS/CoPc) were prepared on glass slides. Firstly, the substrate was dipped into a solution of chitosan in acetic acid (6 mg ml^{-1}) for 15 min. Then, it was taken out and slowly dried under a nitrogen flow. Secondly, the obtained CS membrane was dipped into a CoPc solution in CH_2Cl_2 (10 mg ml^{-1}) for 15 min. After the layer of CoPc was deposited, the CS and CoPc double-layer membrane (CS/CoPc) was removed and washed with distilled water until the colour of the residual liquid was unchanged. Then, the CS/CoPc membrane was slowly dried under a nitrogen flow.

The photocatalytic activity of CS/CoPc membranes was evaluated for degradation of RB in aqueous solution. The light source was a 250 W high-pressure Hg lamp (365 nm , 30 W cm^{-2}). The general procedure was as reported by Soares *et al.* [27]. In brief, 20 ml of RB solution of different concentrations was placed in a water-jacketed reactor at a constant temperature ($25\text{ }^{\circ}\text{C}$). The CS/CoPc membrane was suspended in the solution. The suspension was stirred for 60 min in the dark, and was then irradiated for a predetermined time under UV light. Supernatant samples were periodically removed from the reactor and centrifuged. The UV absorbance of the supernatant was measured at 553 nm to determine the RB concentration. The RB degradation rate was calculated by means of the equation:

$$\text{Degradation rate}(\%) = (1 - A/A_0) \times 100 \quad (1)$$

where A_0 is the absorbance of the initial solution, and A is the absorbance of the solution after UV irradiation for a given time.

Results and Discussion

Characterisation

Figure 1 shows IR spectra of CS/CoPc and the raw materials. Phthalocyanine skeletal vibrations for the polymeric metal complex appear at $1502\text{--}759\text{ cm}^{-1}$ [28]. The peak attributed

to stretching vibrations of the S=O double bond of $-\text{SO}_2-\text{OH}$ at 1340 cm^{-1} is shifted to 1375 cm^{-1} for $-\text{SO}_2-\text{Cl}$ [29]. For CS/CoPc, the vibration peak for the $-\text{SO}_2-\text{N}-$ bond is shifted to 1398 cm^{-1} , which confirms that chitosan supported the phthalocyanine partly involved in sulfonamide bond formation.

The thermal stability of the polymer CS/CoPc membrane was measured by thermal analysis (Figure 2). The chitosan exhibited *ca.* 60% weight loss at $550\text{ }^{\circ}\text{C}$, which could be ascribed to water evaporation, decomposition of polymer with low molecular weight, and splitting of the saccharide rings. The thermal decomposition of CoPc mainly occurred between 220 and $500\text{ }^{\circ}\text{C}$; 40% of the amount was retained. This is due to the fact that the thermal decomposition of CoPc will produce a mass residue composed of sulphate and Co oxide. However, the CS/CoPc showed the same tendency of decomposition as CoPc, and the degradation temperature was lower. This result indicated that the thermal stability of CS/CoPc was not as strong as that of

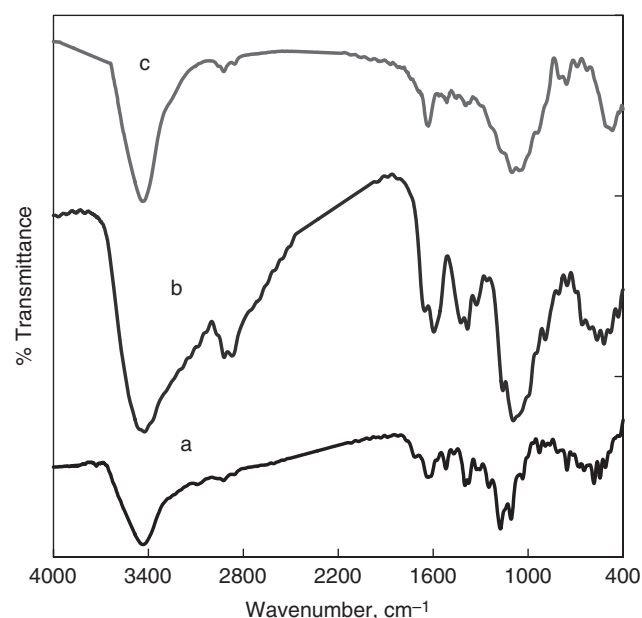


Figure 1 FTIR spectra of CS/CoPc and the raw materials. a: CoPc; b: CS; c: CS/CoPc

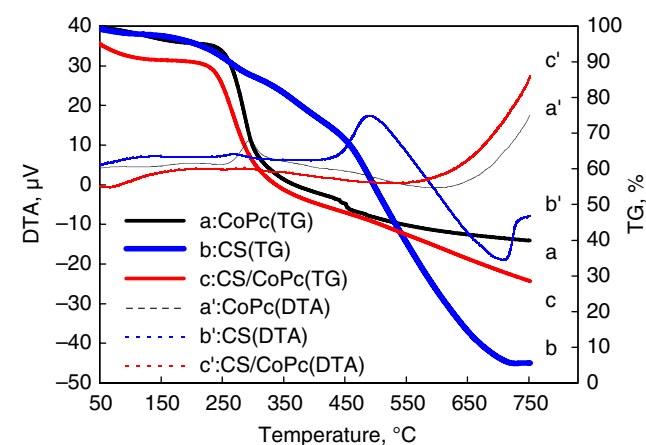


Figure 2 Thermogravimetric curves of CS/CoPc and the raw materials [Colour figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CoPc because the introduction of the chitosan decreased the crystallinity of CoPc.

UV-vis spectra of the polymer CS/CoPc membrane and its materials (CS and CoPc) were measured, and the results are shown in Figure 3. A strong absorption peak (Q-bands) appeared in the visible region at 550–750 nm [30]. The CS/CoPc exhibits a band of medium intensity around 679 nm, corresponding to the Q-band, which was similar to the band of cobalt phthalocyanine derivatives [CoPc(SO₂Cl)₄] at 677 nm. This means that the phthalocyanine cobalt complex was mainly physically combined with chitosan.

The morphology of the product was observed by scanning electron microscopy (SEM). Figure 4 shows surface images of the CS/CoPc membrane. Compared with pure chitosan membranes, there are some islands and pores on the surface of CS/CoPc. It is likely that the pores in CS/CoPc membranes were formed during deposition of the CoPc complex. In other words, there are interstices between the polymeric layers. Small molecules can easily permeate through such polymer layers, which is advantageous in increasing the photocatalytic efficiency of the sample.

Photocatalytic degradation

To investigate the photocatalytic activity of CS/CoPc, RB degradation was carried out in aqueous solution at room temperature. Using CS/CoPc membrane as a photocatalyst, the RB degradation rate reached 99%. The colour of the RB

solution changed to colourless after a short irradiation time (60 min) in the presence of CS/CoPc. This is higher than the RB degradation rate observed for P₂₅TiO₂ [31], which was 93% under optimised conditions. RB degradation in the presence of chitosan without a catalyst was also investigated and was only *ca.* 1%. Thus, chitosan alone showed negligible photocatalytic activity. The effects of the catalyst dosage, initial RB concentration, and pH on RB degradation were also investigated.

The influence of pH on RB degradation was investigated, and the results are shown in Figure 5. Solutions were adjusted to the desired test pH using an acid (1 mol l⁻¹ nitric acid, HNO₃) or base solution (1 mol l⁻¹ sodium hydroxide, NaOH). According to the literature [32], it was reported that RB exists in two forms (acid and lactone), and the lactone form is not coloured. The authors had measured visible spectra (400–800 nm) of the RB solution at different pH values. The results showed that the characteristic absorption peak of RB and its intensity at 553 nm did not change with different pH values (from 3 to 11). This means that the RB in the present experiment is in acid form. It was found that RB degradation decreased with increasing pH value. This trend is similar to ultrasonic degradation of RB in aqueous solution [33]. Sreelatha *et al.* [34] and Namasivayam *et al.* [35] also found that the degradation of dyes is easier in a weakly acidic medium. If the pH value was < 6, the decrease in the amplitude of catalytic activity was

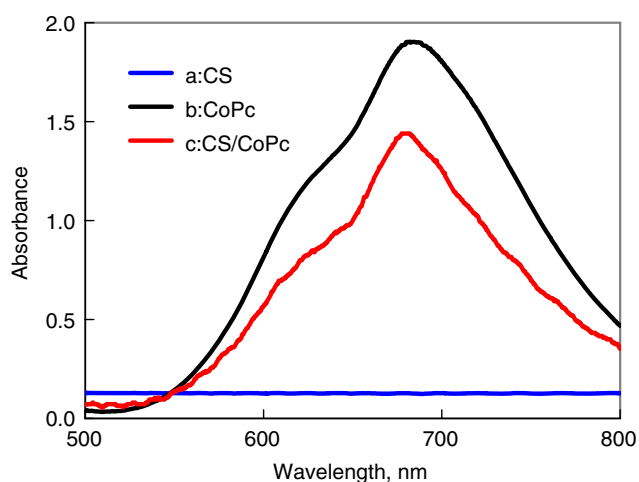


Figure 3 UV-vis spectra of the CS/CoPc membrane and its materials. a: CS; b: CS/CoPc; c: CoPc [Colour figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

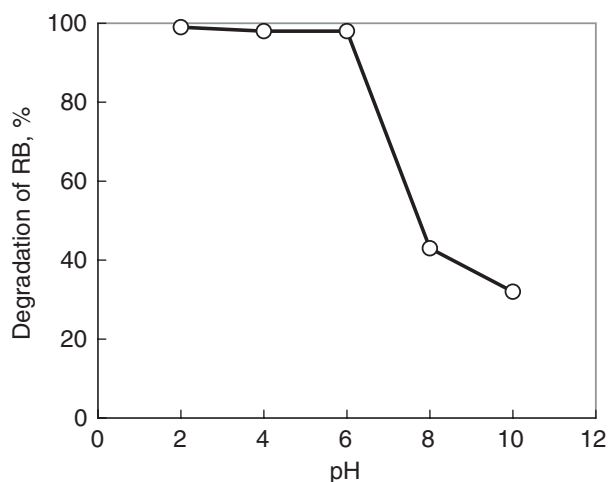


Figure 5 Effect of the pH value on the photocatalytic activity of the polymer photocatalyst (CS/CoPc) (conditions: [RB] = 1.0 × 10⁻⁵ mol l⁻¹; [Cat] = 0.50 g l⁻¹; 25°C; 60 min)

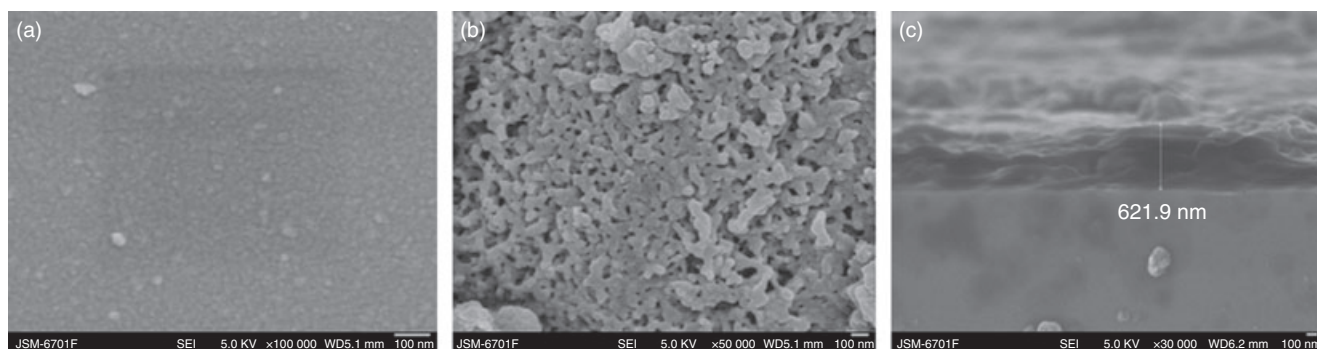


Figure 4 SEM images of CS/CoPc and chitosan membranes: (a) chitosan membrane; (b) CS/CoPc membrane; (c) a section of the CS/CoPc membrane

negligible. The reason for this is that CoPc is dispersed as chitosan is gradually dissolved in acidic solution. However, catalyst recycling would be difficult if the chitosan membrane were dissolved completely, especially at $\text{pH} < 4$. Hence, efficient treatment of organic contaminants with a molecular structure like that of RB requires a near-neutral medium.

The effects of RB concentration, catalyst dosage, and reaction time on photocatalytic degradation were also investigated. The RB degradation rate first increased with the initial RB concentration up to $1 \times 10^{-5} \text{ mol l}^{-1}$ and decreased thereafter. The active sites of the photocatalyst (CoPc) were considered to be occupied and covered by RB molecules and its decomposition products if the initial RB concentration was too high. Therefore, the degradation of higher concentrations of RB decreased with increasing initial RB concentration. The RB photodegradation rate gradually increased with increasing CS/CoPc, and the highest catalyst efficiency was observed for 0.5 g l^{-1} of photocatalyst. The suggested reason for this is as follows. Firstly, the catalyst absorbed light energy. It caused photon excitation at the appropriate wavelength, and an oxidation–reduction reaction occurred. The catalyst generated holes and produced strong free radicals in solution. The free radicals may be singlet oxygen ($^1\text{O}_2$) and/or superoxide radicals ($\text{O}_2^{\cdot-}$) [36]. It is generally accepted that singlet oxygen contributes undoubtedly to the photooxidation of chlorophenols sensitised by metallosulphophthalocyanines [37]. The production of superoxide radicals by irradiation of photosensitiser ZnPc has also been reported [38]. Organic matter was adsorbed on the catalyst surface and was then degraded by the superoxide radical. As the dosage of catalyst was increased, the chances of photodegradation increased. However, light transmission was reduced if the dosage of catalyst was too high, which affected light absorption and photolysis efficiency.

The stability of the polymer photocatalyst was investigated by measuring its reusability. Repeated experiments were carried out under the same conditions. After the experiment, the residue solution was poured out, and the photocatalyst was used again for degradation of RB. Figure 6 shows that the photocatalytic activity decreased with an increasing number of catalytic cycles. It is clear that

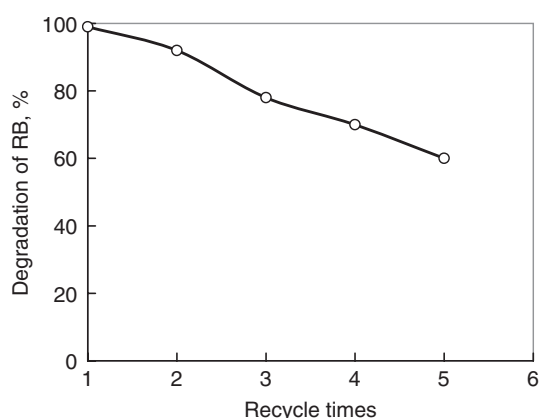


Figure 6 The recycling stability of the polymer photocatalyst (CS/CoPc) (conditions: $[\text{RB}] = 1.0 \times 10^{-5} \text{ mol l}^{-1}$; $[\text{Cat}] = 0.50 \text{ g l}^{-1}$; $\text{pH}=6.0$; 25°C ; 60 min)

the RB photodegradation efficiency was highest for the fresh catalyst. After being reused 5 times, 60% of the initial catalytic activity was retained. The change in activity was ascribed to deactivation of the active sites with increasing use, although the mechanism of deactivation of CS/CoPc was complicated. A possible mechanism is as follows. Firstly, the active sites on the surface of the photocatalyst were partly occupied by decomposition products. Secondly, the CoPc skeleton was destroyed during the photocatalytic reaction. On the other hand, part of the CS/CoPc was lost during pouring of the residue solution. Therefore, the active sites decreased in number with repeated use.

Conclusions

A chitosan–phthalocyanine membrane was successfully prepared by deposition. The polymer membrane was used for catalytic photodegradation of RB in aqueous solution at room temperature. It showed high catalytic activity for RB degradation, which reached 99%. The catalyst was stable and could be reused more than five times. In addition, chitosan is a cheap and abundant natural resource. Therefore, this novel biopolymer membrane catalyst is an attractive candidate for treatment of dye wastewater.

Acknowledgements

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References

1. J Zhang, S Z Wang, Y Guo, D H Xu, Y M Gong and X Y Tang, *Color. Technol.*, **128** (2012) 323.
2. I Arslan, I A Balcioglu and D W Bahnemann, *Dyes Pigm.*, **47** (2000) 207.
3. T L Xing, H Kai and G Q Chen, *Color. Technol.*, **128** (2012) 295.
4. K Shakir, A F Elkafrawy, H F Ghoneimy, S G E Beheir and M Refaat, *Water Res.*, **44** (2010) 1449.
5. Z He, C Sun, S G Yang, Y C Ding, H He and Z L Wang, *J. Hazard. Mater.*, **162** (2009) 1477.
6. R Jain, M Mathur, S Sikarwar and A Mittal, *J. Environ. Manage.*, **85** (2007) 956.
7. A Biadasz, B Bursa, B Barszcz, A Bogucki, B Laskowska, A Graja and D Wróbel, *Dyes Pigm.*, **89** (2011) 86.
8. R Singh and A S Hay, *Macromolecules*, **25** (1992) 1025.
9. X Tao, W H Ma, T Y Zhang and J C Zhao, *Angew. Chem. Int. Ed.*, **40** (2001) 3014.
10. P Kluson, M Drobek, A Zsigmond, J Baranyi, P Bata, S Zarubova and A Kalaji, *Appl. Catal. B*, **91** (2009) 605.
11. A M Sevim, C Ilgün and A Gül, *Dyes Pigm.*, **89** (2011) 162.
12. A Kalkan and Z A Bayör, *Monatsh. Chem.*, **134** (2003) 1555.
13. H B Pan, F Wang, J L Huang and N S Chen, *Acta Phys. Chim. Sin.*, **24** (2008) 992.
14. Z Y Wang, W P Mao, H F Chen, F Zhang, X P Fan and G D Qian, *Catal. Commun.*, **7** (2006) 518.
15. E Guibal, *Prog. Polym. Sci.*, **30** (2005) 71.
16. J H Tong, Y Zhang, Z Li and C G Xia, *J. Mol. Catal. A Chem.*, **249** (2006) 47.
17. G Huang, Y A Guo, H Zhou, S K Zhao, S Y Liu, A P Wang and J F Wei, *J. Mol. Catal. A Chem.*, **273** (2007) 144.
18. A V Kucherov, N V Kramareva, E D Finashina, A E Koklin and L M Kustov, *J. Mol. Catal. A Chem.*, **198** (2003) 377.
19. H X Feng, R M Wang, Y F He, Z Q Lei, Y P Wang, C G Xia and J S Suo, *J. Mol. Catal. A Chem.*, **159** (2000) 25.
20. Y F He, R M Wang, Y P Wang and C G Xia, *Eur. Polym. J.*, **38** (2002) 2129.

21. Y Chang, Y P Wang, F Zha and R M Wang, *Polym. Adv. Technol.*, **15** (2004) 284.
22. A B Sorokin, F O Quignard, R Valentin and S Mangematin, *Appl. Catal. A Gen.*, **309** (2006) 162.
23. E Humeres, E P de Souza, N A Debacher and A E Aliev, *J. Phys. Org. Chem.*, **15** (2002) 852.
24. M Gouda and S M A S Keshk, *Carbohydr. Polym.*, **80** (2010) 504.
25. J S Choi, I K Song and W Y Lee, *J. Memb. Sci.*, **198** (2002) 163.
26. M Mifune, Y Shimoura, Y Saito, Y Mori, M Onoda, A Iwado, N Motohashi and J Haginaka, *Bull. Chem. Soc. Jpn.*, **71** (1998) 1825.
27. E Soares, M Lansarin and C Moro, *Braz. J. Chem. Eng.*, **24** (2007) 29.
28. S Singh, S K Tripathi and G S S Saini, *Spectrochim. Acta Part A Mol. Biol.*, **69** (2008) 619.
29. F Yuksel, D Atilla and V Ahsen, *Polyhedron*, **26** (2007) 4551.
30. S Seelan, M S Agashe, D Srinivas and S Sivasanker, *J. Mol. Catal. A Chem.*, **168** (2001) 61.
31. L H Zhao, S M Sun, Z J Kang, Z F Wei and G H Xu, *J. Yanbian Univ. (Nat. Sci.)*, **29** (2003) 190.
32. Q Y Qi and J H Sun, *Water Resour. Prot.*, **22** (2006) 56.
33. M A Behnajady, N Modirshahla, S B Tabrizi and S Molanee, *J. Hazard. Mater.*, **152** (2008) 381.
34. G Sreelatha, V Ageetha, J Parmar and P Padmaja, *J. Chem. Eng. Data*, **56** (2011) 35.
35. C Namasivayam and D Kavitha, *Dyes Pigm.*, **54** (2002) 47.
36. M A Zanjanchi, A Ebrahimian and M Arvand, *J. Hazard. Mater.*, **175** (2010) 992.
37. K Ozoemena, N Kuznetsova and T Nyokong, *J. Photochem. Photobiol. A Chem.*, **139** (2001) 217.
38. L Wu, A Li, G Gao, Z Fei, S Xu and Q Zhang, *J. Mol. Catal. A Chem.*, **269** (2007) 183.