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Preparation of photoactive chitosan–niobium (V) oxide composites for dye degradation

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Abstract

From an environmental standpoint, heterogeneous photocatalysis is a significant cutting-edge technology for application in water purification. Moreover, immobilising an appropriate catalyst onto the surface of a natural organic polymer presents a number of additional advantages including low-cost, high catalytic activity and extensive potential for reuse. In the present work, composites of niobium (V) oxide and chitosan (Chit/Nb) were prepared with semiconductor loadings in the range 0–13.9% attached to the polymer surface. Scanning electron microscopy (SEM) and niobium mapping with X-ray energy dispersive spectrometry showed that the niobium (V) oxide was homogeneously dispersed over the surface of the composites. Lewis and Bronsted acid sites were present on the biopolymer surfaces, the acidic character of which increased with the amount of semiconductor attached. The Chit/Nb composites were used to photocatalyse the degradation of indigo carmine dye in aqueous solution by UV irradiation. The kinetic constants were obtained by application of the Langmuir–Hinshelwood equation and determined to be 5.32, 5.90 and 9.10 μmol L^{-1} h^{-1}, respectively, for Chit/Nb composites with semiconductor loadings of 3.9, 9.3 and 13.9%, respectively. Whilst the thermal stabilities of the Chit/Nb composites were slightly lower than that of the pure biopolymer, the materials presented high catalytic efficiencies that remained unaltered after 15 cycles of reuse.

Keywords: Chitosan; Niobium; Photodegradation

1. Introduction

The immobilisation of a catalyst onto a matrix support offers a number of potential advantages presenting significant value in environmental applications, including facile incorporation within continuous reactors and ease of recovery and reuse [1]. Typically, inorganic polymers, such as silica, zeolites or metal oxide matrices, have been employed as solid supports in heterogeneous catalytic systems [2–4]. Recently, however, a number of studies [1,5] have focused on the use of natural organic polymers as support materials for catalytic compounds, and more especially in the preparation of homogeneous and heterogeneous catalysts [1,6–9].

In this context, the chitosans, a family of linear cationic, non-toxic, biodegradable polysaccharides obtained from chitin, appear to offer a number of distinct advantages. Chitin, the most abundant natural amino polysaccharide, is a low cost source material being present in plankton and the exoskeletons of crustaceans, such as crabs, lobsters and prawns [10]. Chitosan may be readily obtained from fishery wastes, and its large-scale production could represent, at least in Brazil, a much needed source of income through which to augment the quality-of-life in poorer fishing communities [11]. Chitosan is highly insoluble in water and in many organic solvents, shows low chemical reactivity and has a high amine content that makes it useful as a chelating agent [6,12,13]. Thus, transition metal ions and complexes have been immobilised onto this biopolymer in order to attain the advantages of homogeneous and heterogeneous catalysts in the form of a low cost product [14,15].

From an environmental point of view, heterogeneous photocatalysis is one of the most important of the new advanced oxidation technologies to be applied to water purification. Several reports have recently been devoted to this problem [16–19], and indicate that the immobilisation of a semiconductor onto chitosan can produce a new organic/inorganic composite material with photocatalytic properties that may be applied with great

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facility. Indeed, the low price and the ease with which chitosan-immobilised catalysts can be recovered and cleaned for reuse constitute major advantages of this material over alternative supports, such as inorganic oxides [20].

In the present paper, niobium (V) oxide, a catalyst with potential application in the photolysis of contaminants in water, was supported on a chitosan surface and applied to the photodegradation of indigo carmine dye in order to demonstrate the advantages of the proposed system.

2. Experimental

2.1. Chemicals

Chitin from shrimp shells was purchased from Fine Chemical Kito: ammonium niobium oxalate was obtained from CBMM and used without further purification. Chitosan was prepared by deacetylation of chitin in sodium hydroxide solution (50%, w/v) for 1 h at 110 °C as described previously [1,14].

2.2. Immobilisation of niobium (V) oxide

Organic–inorganic composite materials, containing between 0 and 13.9% of niobium (V) oxide dispersed on the organic structure, were obtained by adding appropriate amounts of ammonium niobium oxalate to suspensions of 1.0 g of chitosan in 26.0 cm^3 of acetic acid and maintaining the mixtures at 70 °C for 120 h in an hydrothermal system.

2.3. Characterisation of chitosan and composite materials

IR spectra (4000–400 cm^{-1}) of solid samples (KBr pellets) were measured on a Bomem MB-100 series spectrophotometer at a resolution of 4 cm^{-1} by accumulating 32 scans. The presence of Lewis and Bronsted acid sites on the surface of the composite material was assessed by IR spectroscopy using pyridine as a molecular probe. Composite materials were exposed to an atmosphere of dry pyridine at normal pressure for 4 h, the excess of pyridine was removed under vacuum at room temperature for 10 h and the IR spectra of the resulting material measured [21].

A thermogravimetric analyser model TA-2960 was employed to determine thermogravimetric curves using ca. 10 mg samples of Chito/Nb composite materials in a dynamic atmosphere, under a dry nitrogen flux, with heating from room temperature to 800 °C at a heating rate of 10 °C min^{-1}. Scanning electron microscopy (SEM) was performed on a JEOL model JSM-6360 LV coupled with a Thermo Electron Noran System Six X-ray EDS. Samples were coated with carbon using a Balzer model MED 020 metalliser.

2.4. Photocatalytic degradation of indigo carmine

The photolysis of indigo carmine dye was carried out in an in-house fabricated photo-reactor with 100.0 mL aliquots of dye solution (2.5 $\mu mol\,L^{-1}$) in the presence of 50.0 mg of the Chit/Nb composites each containing different amounts of niobium (V) oxide. The reaction solutions were illuminated with a 125 W mercury-vapour lamp and the temperature of the reactor was maintained at 30 °C during the reaction. The amount of dye degraded was followed by UV–vis spectrophotometer at 650 nm. After completion of the reaction, the solution was filtered to recover the catalyst, which was subsequently washed with water and used again.

2.5. Determination of niobium leached amount

The amount of leached niobium was determined after each photodegradation cycle by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Varian Liberty RL Series II spectrometer.

3. Results and discussion

The Nb_2O_5 presents a band gap (3.4 eV) similar to TiO_2 and ZnO (3.2 eV), which are extensively used in photocatalysis. Thus, it is expected that Nb_2O_5 has photocatalytic abilities, due to its band gap suggests that it must generate free hydroxyl radicals in water by UV irradiation. However, the application of this oxide in photodegradation is few reported in literature [22,23].

The problem of the Nb_2O_5 use is related to low stability in water of this hydrocolloid, as a consequence, it is usually precipitated in water. Indeed, the catalysis activity is damaged, and also it is difficult to reuse oxides to recycling the catalyst. In order to improve this material, the attachment of this oxide on chitosan allows the easy recuperation of the catalyst and increases its contact with water in order to generate more free hydroxyl radicals capable of degrading contaminants from water [24].

The new method employed in this work for the production of chitosan–niobium (V) oxide (Chit/Nb) composites was based on the co-condensation of ammonium niobium oxalate with the

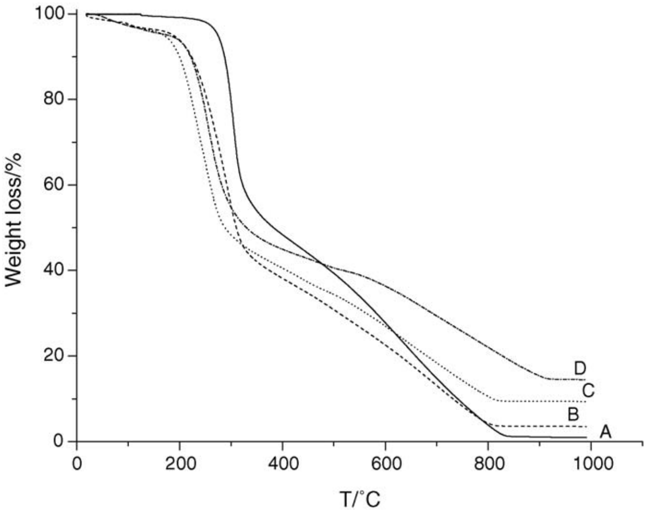

Fig. 1. Thermogravimetric curves obtained from the analysis of chitosan (A) and Chit/Nb composites with 3.0% (B), 9.3% (C) and 13.9% (D) of niobium (V) oxide supported on the biopolymer surface.

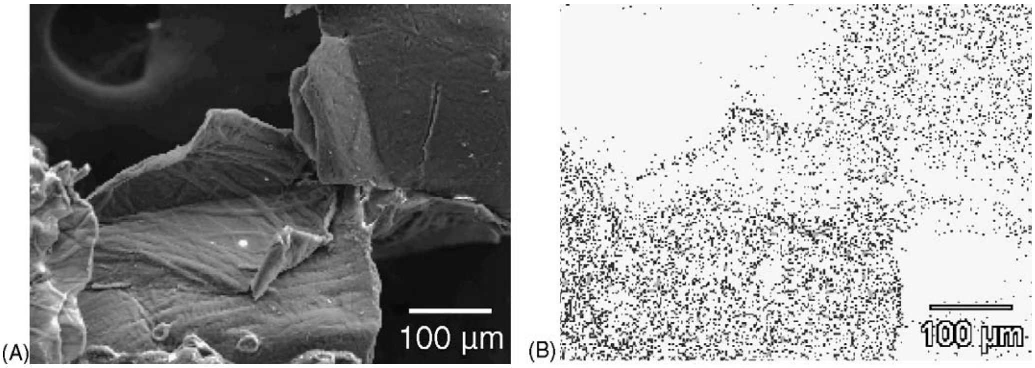

Fig. 2. Scanning electron micrograph of a Chit/Nb composite with 9.3% of niobium (V) oxide supported on the biopolymer surface (A) and the corresponding X-ray emission dot map (B) obtained with a X-ray fluorescence microprobe showing niobium as black points.

alcohol and/or amine groups of chitosan. The amount of niobium attached to the surface of the chitosan was determined from information concerning the residue remaining after thermogravimetric analysis, which could be related to the amount of niobium (V) oxide present in the original sample. Thermogravimetric curves of composite samples containing 0, 3.0, 9.3 and 13.9% of niobium (V) oxide are shown in Fig. 1, from which it may be seen that each presents two decomposition stages, one well-defined stage within the temperature range 250–400 °C and another above 400 °C. The thermogravimetric analyses also indicated that the presence of niobium (V) oxide produced a slight decrease in the thermal stability of the composite in relation to pure biopolymer but without reduction in the quality of the material.

Information concerning the morphology of the composite particles, and the dispersion of niobium on the composite surface, was obtained by scanning electron microscopy coupled with X-ray energy dispersive spectrometry (EDS). The SEM image of a Chit/Nb composite with 9.3% of niobium (V) oxide supported on the biopolymer surface is presented in Fig. 2A, and the corresponding X-ray emission map, obtained using the EDS detector at 0.32 keV, is shown in Fig. 2B in which black points of niobium can be observed. The images exhibit, within the magnification used to obtain the micrographs, a uniform dispersion of niobium and an absence of agglomerates. This may be taken as evidence that the semiconductor was immobilised homogenously onto the chitosan surface, thus confirming the high quality of the co-condensation reaction.

The presence of Lewis and Bronsted acid sites on the composite was verified by IR spectroscopy using pyridine as a molecular probe. As may be observed in Fig. 3, the IR spectra presented weak bands at 1540 cm^{-1}, assigned to the vibrational mode of pyridine in a Bronsted acid site, and further bands at 1606 and 1440 cm^{-1}, assigned to pyridine adsorbed on a Lewis acid site [21]. Fig. 3 also shows that the acid character of the composite increased with the amount of niobium (V) oxide anchored to the surface of the chitosan.

The rate of photodegradation of an aqueous solution of indigo carmine dye, maintained at 30 °C in the presence of the Chit/Nb composite, was followed by UV–vis spectrophotometry and the results are depicted in Fig. 4A. The photodegradative ability (r_{LH}) of the Chit/Nb catalyst was evaluated by application of the Langmuir–Hinshelwood kinetic model [25] as given by:

$$r_{\mathrm{LH}} = \frac{-\mathrm{d}C}{\mathrm{d}t} = \frac{kKC}{1 + KC}$$

where k is the kinetic constant and K is the adsorption constant. This model assumes that, at equilibrium, the number of surface adsorption sites is fixed and only one molecule of substrate may bind at each surface site. Furthermore, it is implicit that the heat of adsorption by the substrate is identical for each site and is independent of the surface coverage, that there is no interaction between adjacent adsorbed molecules, and that there is no irreversible blocking of active sites by binding to the product. Indeed, photodegradation of the dye depends on the adsorption ability of the semiconductor as well as on the rate of the degradation reaction. Plots of the linearised form of the Langmuir–Hinshelwood kinetic model are shown in Fig. 4B, and the results obtained therefrom are listed in Table 1. The data show that the values of k and K increase with the amount of niobium (V) oxide attached to the surface of the chitosan, and this correlates with the efficiency of the composite to catalyse the

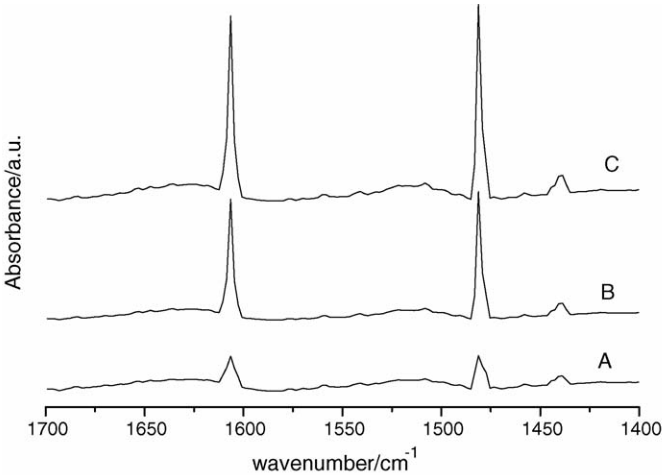

Fig. 3. Infrared spectra in the range 1700–1400 cm^{-1} of pyridine molecules adsorbed onto Chit/Nb composites with 3.0% (A), 9.3% (B) and 13.9% (C) of niobium (V) oxide supported on the biopolymer surface.

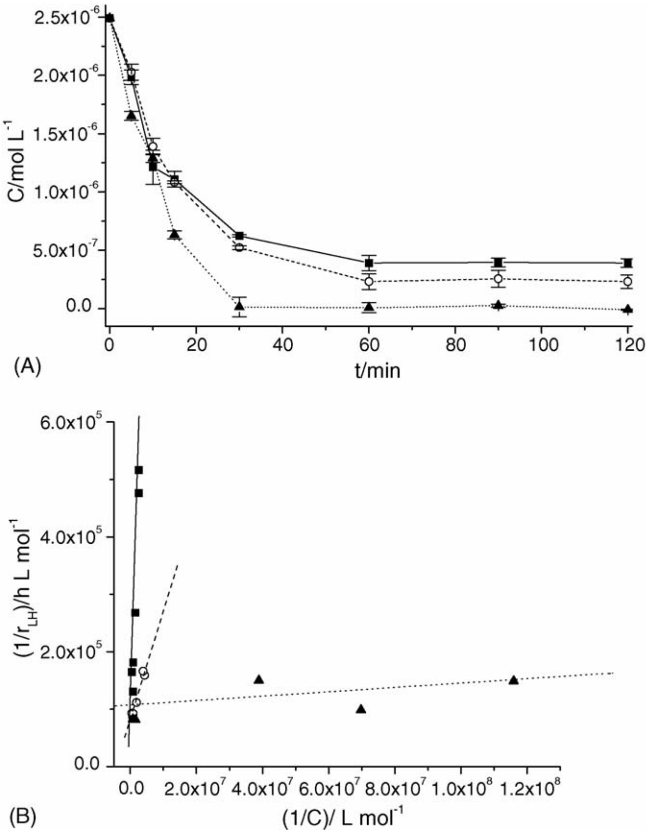

Fig. 4. Rates of photocatalysed degradation (A) and the linearised form (obtained using the Langmuir–Hinshelwood kinetic model) of the degradation (B), of indigo carmine dye in the presence of Chit/Nb composites with 3.0% (■), 9.3% (○) and 13.9% (▲) of niobium (V) oxide supported on the biopolymer surface.

photodegradation of indigo carmine dye. The photodegradation of indigo carmine did not observed in absence of catalyst and in presence of crude chitosan.

Following the catalytic photodegradation of each batch of indigo carmine dye, the Chit/Nb composite was recovered from the reaction mixture by filtration, washed and reused. Fig. 5 shows that no change in the catalytic activity of the composite could be observed even after 15 cycles of reuse, and niobium leached amount was not detected by ICP-OES apparatus.

The process of catalytic photodegradation of a contaminant in water is usually based on the excitation of a semiconductor by UV irradiation to generate the free radicals involved in the degradation reaction. The semiconductor niobium (V) oxide has a band gap energy of 3.4 eV but does not exhibit good photocatalytic activity [22,26]. The hydrocolloid formed by this semiconductor in water has low stability leading to precipitation of the oxide and thus perturbing the adsorption of the substrate onto its surface [24]. In order to avoid this problem, niobium (V) oxide was attached to the surface of chitosan biopolymer by a co-condensation reaction. The biopolymer composites thus formed showed good dispersion of semiconductor on the surface of the chitosan and presented typical Lewis and Bronsted acid sites. Furthermore, Chit/Nb composites exhibited high catalytic efficiencies for the degradation of indigo carmine dye in aqueous solution, were readily recovered from the reaction mixture and maintained high catalytic capacity after many cycles of reuse. In terms of the principles of clean technologies and green chemistry, the low cost, catalytic efficiency similar to TiO_2 photocatalyst as described before [27] and excellent reutilisation potential of Chit/Nb composites suggest that these materials could play a key role as environmentally acceptable catalysts in water purification processes. And besides, the Chit/Nb is much easier to recovery than Nb_2O_5 and the large use of chitosan can present social improvement to poor fishermen from Brazil and others developing countries. As well as, new scientific, technological and environmental applications of niobium are very important to Brazil development, due to Brazil is the main producer of niobium compounds of the world.

Table 1
Values of *k* and *K* obtained from the application of the Langmuir–Hinshelwood equation to the photodegradation of indigo carmine dye in the presence of Chito/Nb composites

Percentage of niobium (V) oxide associated with the Chit/Nb composite	*k* (μmol L^{-1} h^{-1})	*K* (L μmol^{-1})
3.0	5.32	2.04
9.3	5.90	3.04
13.9	9.10	5.64

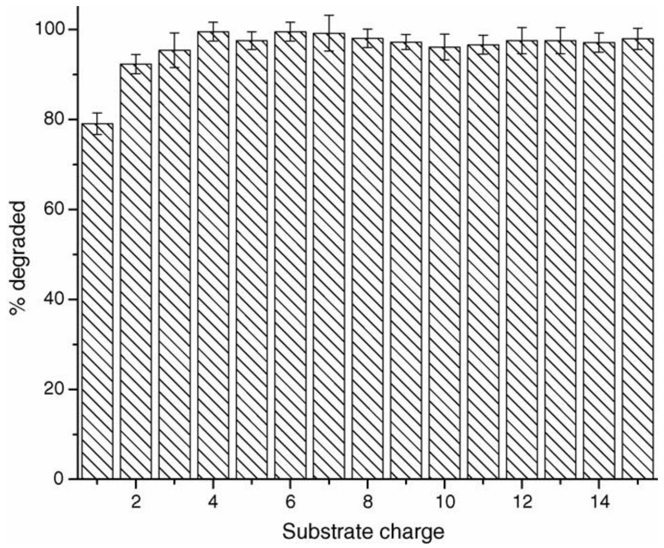

Fig. 5. The percentage photolysis (after 30 min reaction time at 30 °C) obtained for 15 aliquots of indigo carmine dye reacted in the presence of the same sample of Chit/Nb composite with 9.3% of niobium (V) oxide supported on the biopolymer surface.

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References

[1] J.E. Hardy, S. Hubert, D.J. Macquarrie, A.J. Wilson, Green Chem. 6 (2004) 53.

[2] A.G.S. Prado, C. Airoldi, J. Mater. Chem. 12 (2002) 3823.

[3] V. Sage, J.H. Clark, D.J. Macquarrie, J. Catal. 227 (2004) 502.

[4] R. Bouarab, O. Cherif, A. Auroux, Green Chem. 5 (2003) 209.

[5] T. Vicent, E. Guibal, Ind. Eng. Res. Chem. 41 (2002) 5158.

[6] J. Zhang, C.G. Xia, J. Mol. Catal. A 206 (2003) 59.

[7] M.Y. Yin, G.L. Yuan, Y.Q. Wu, M.Y. Huang, Y.Y. Jiang, J. Mol. Catal. A 147 (1999) 93.

[8] X.B. Zeng, Y.F. Zhang, Z.Q. Shen, J. Polym. Sci. A 35 (1997) 2177.

[9] N.V. Kramareva, A.Y. Stakheev, O.P. Tkachenko, K.V. Klementiev, W. Grunert, E.D. Finashina, L.M. Kustov, J. Mol. Catal. A 209 (2004) 97.

[10] A.G.S. Prado, J.L. Macedo, S.C.L. Dias, J.A. Dias, Colloid Surf. B 35 (2004) 23.

[11] A.G.S. Prado, J.D. Torres, E.A. Faria, S.C.L. Dias, J. Colloid Interface Sci. 277 (2004) 43.

[12] N.V. Majeti, R. Kumar, React. Funct. Polym. 46 (2000) 1.

[13] M. Aslam, H.C. Linstid, K.G. Davenport, Hoechst Cleanese Corp., US Patent, 5,087,769, 1999.

[14] A.V. Kucherov, N.V. Kramareva, E.D. Finashina, A.E. Koklin, L.M. Kustov, J. Mol. Catal. A 198 (2003) 377.

[15] E. Guibal, Prog. Polym. Sci. 30 (2005) 71.

[16] C. Guillard, J. Disdier, C. Monnet, J. Dussaud, S. Malato, J. Blanco, M.I. Maldonado, J.M. Herrmann, Appl. Catal. B 46 (2003) 319.

[17] J.M. Herrmann, Catal. Today 24 (1999) 157.

[18] O. Legrini, E. Oliveros, A. Braun, Chem. Rev. 93 (1993) 671.

[19] J.M. Herrmann, C. Guillard, P. Pichat, Catal. Today 17 (1993) 7.

[20] F. Quignard, A. Choplin, A. Domard, Langmuir 16 (2000) 9106.

[21] E.A. Campos, Y. Gushikem, J. Colloid Interface Sci. 193 (1997) 121.

[22] H. Kominami, K. Oki, M. Kohno, S. Onouc, Y. Kera, B. Ohtani, J. Mater. Chem. 11 (2001) 604.

[23] M.K. Silva, R.G. Marques, N.R.C.F. Machado, O.A.A. Santos, Braz. J. Chem. Eng. 19 (2002) 359.

[24] N. Daneshvar, D. Salari, A.R. Khataee, J. Photochem. Photobiol. A 162 (2004) 317.

[25] M.A. Fox, M.T. Dulay, Chem. Rev. 93 (1993) 341.

[26] A.G.S. Prado, E.A. Faria, J.R. SouzaDe, J.D. Torres, J. Mol. Catal. A 237 (2005) 115.

[27] M. Vautier, C. Guillard, J.M. Herrmann, J. Catal. 201 (2001) 46.