Ammonium complex of niobium as a precursor for the hydrothermal preparation of cellulose acetate/Nb$_2$O$_5$ photocatalyst

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Abstract

Hydrothermal reaction by using ammonium niobium oxalate as a precursor was performed to prepare cellulose acetate/Nb$_2$O$_5$ catalyst with the following Nb$_2$O$_5$ loadings (in wt%) 3.9, 5.8, 6.7 and 10.9. These materials presented homogeneous dispersion of niobium on cellulose acetate surface with Bronsted and Lewis acid sites based on SEM/EDS microscopy and infrared spectroscopy. The thermal stability of these catalysts was at least 210 °C and these composites were applied as photocatalyst to degrade indigo carmine dye in water. This catalytic behaviour was followed though a kinetic series adjusted to a Langmuir–Hinshelwood equation. The kinetic constants obtained by application of this equation were 2.95, 3.47, 3.63 and 3.98 μmol L^{-1} h^{-1} for CA/Nb 3.6, 5.8, 7.4 and 10.9%, respectively. The materials were reused nine times more to degrade indigo carmine dye.
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1. Introduction

Cellulose acetate (CA) is a thermoplastic produced from cellulose, which presents mechanical and thermal resistance, thermal and dimensional stability, low cost and it is also a renewable feedstock [1]. CA can be easily molded in different forms, such as fibers, membranes and spheres, and it has many technological and scientific applications, such as supports for fibers, plastics, photographic films and coating for pharmaceuticals [2,3]. In order to increase the properties of polymers, hybrid organic/inorganic materials have been developed [4]. Polymer–metal oxide composite materials have been used as multitask materials, which have polymer mechanical properties combined with catalytic properties of the oxide, resulting in new materials that have been applied in ion-exchange [5], as supports for enzymes [6], in catalytic reactions [7], etc. Among the metal oxides have been used to produce composites, the Nb$_2$O$_5$ presents interesting properties [8]. Supported niobium oxides are extensively studied as heterogeneous catalysts in numerous reactions [9,10]. This oxide has a band gap energy of 3.4 eV, and therefore it would be expected to present photocatalytic properties [11]. On the other hand, there have been few reports on photocatalysis by Nb$_2$O$_5$ [11,12]. The band gap of Nb$_2$O$_5$ suggests that this oxide must generate free hydroxyl radicals in water by UV irradiation [11,12]. Thus, it must be capable of catalysing the contaminants degradation from water. On the other hand, the Nb$_2$O$_5$ hydrocolloid presents low stability in water, as a consequence, it usually is precipitated in water. Indeed, the catalysis activity is damaged, and also it is difficult to reuse oxides to recycling the catalyst. In order to solve this problem, the attachment of this oxide on cellulose acetate must allow the easy recuperation of the catalyst and increase its contact with water in order to generate more free hydroxyl radicals capable of degrading contaminants from water [13].

In this way, the present investigation reports a new synthetic route to obtain composite fibers of niobium (v) and

cellulose acetate and the application of these hybrids to photocatalyse the indigo carmine dye degradation.

2. Experimental

2.1. Chemicals

Cellulose acetate (Fluka) and ammonium niobium oxalate (CBMM) were used without purification.

2.2. Hydrothermal synthesis

Organic–inorganic hybrids were obtained by using 2.0 g of cellulose acetate suspended on a mixture with 6.0 mL of acetic acid and 14.0 mL of acetone. In this suspension, different amounts of ammonium niobium oxalate were added in order to obtain hybrids from 0 up to 10% of Nb_2O_5 dispersed on organic biopolymer surface. These mixtures were reacted into an autoclave with the internal Teflon bottle at 70 °C for 120 h.

2.3. Characterization

Thermogravimetric curves were followed from approximately 10 mg of CA/Nb samples on a thermogravimetric analyzer model TA-2960 in a dynamic atmosphere using dry nitrogen flux, with heating from room temperature up to 800 °C at heating rate of 10 °C min^{-1}.

Surface acid sites were determined by using infrared spectroscopy and pyridine as a molecular probe. The materials were reacted with dry pyridine atmosphere at normal pressure for 4 h. The pyridine excess was removed under vacuum at room temperature for 10 h. The samples were performed in KBr pellet on a Bomem MB-100 series spectrophotometer, with resolutions of 4 cm^{-1}, by accumulating 32 scans.

Scanning electron microscopy (SEM) was performed on JEOL JSM-6360 LV coupled with a Noran Sisten Six energy dispersive spectrometer (EDS). Samples were coated with carbon using a Balzer Model MED 020 metallizer.

2.4. Indigo carmine photocatalytic degradation

Photolyses of indigo carmine dye were carried out in a homemade photo-reactor using 100.0 mL of a 2.5 μmol L^{-1} dye solution and 50.0 mg of CA/Nb composites with different amounts of Nb_2O_5. These solutions were illuminated with mercury-vapour lamp 125 W with temperature being monitored during the reaction. The dye degradation was followed on a Beckman DU-650 UV–vis spectrophotometer.

2.5. Recycling of CA/Nb

After indigo carmine photodegradation, CA/Nb composite was filtrated and washed with water and then added to photo-reactor to be reused in another indigo carmine dye solution, in order to perform the same photodegradation.

2.6. 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 incorporation of Nb_2O_5 on cellulose acetate is based on hydrolysis of ammonium niobium oxalate and polycondensation of metal oxides on polysaccharide surface through strong interaction between Nb–OH and alcohol and acetyl groups of cellulose acetate [2].

Thermogravimetric curves obtained for all samples presented a well-defined decomposition stage range between 250 and 400 °C (Fig. 1). The amount of niobium anchored on polymer surface was determined from the residual data of thermogravimetric curves. The obtained composites presented 0, 3.9, 5.8, 6.7 and 10.9% of Nb_2O_5 dispersed on polymeric surface. These curves show a softly decrease in thermal stability in relation to pure cellulose acetate. However, the modified materials present a thermal stability of at least 210 °C. Indeed, the attachment of niobium on surface do not decrease significantly the thermal quality of material [8,14].

SEM/EDS images were followed to check morphology of the obtained materials and to know how the niobium particles were dispersed on cellulose acetate surface. SEM image of 6.7% CA/Nb is presented in Fig. 2A. Fig. 2B corresponds to niobium mapping on surface with the EDS detector. The
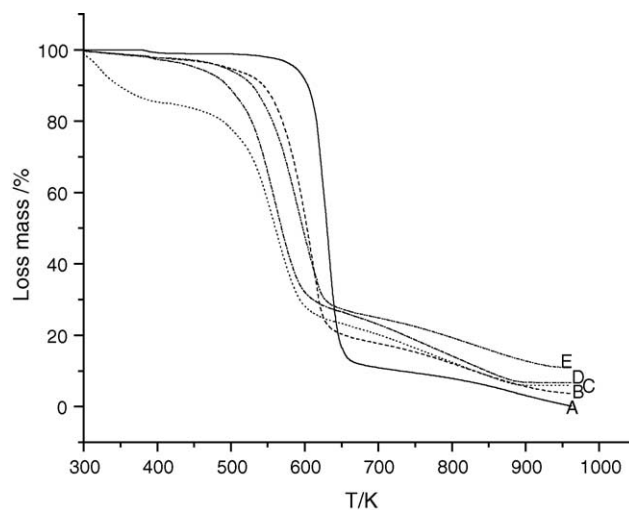

Fig. 1. Thermogravimetric curves of pure cellulose acetate (A) and CA/Nb with 3.9% (B), 5.8% (C), 7.4% (D) and 10.9% (E) of Nb_2O_5 supported onto CA.
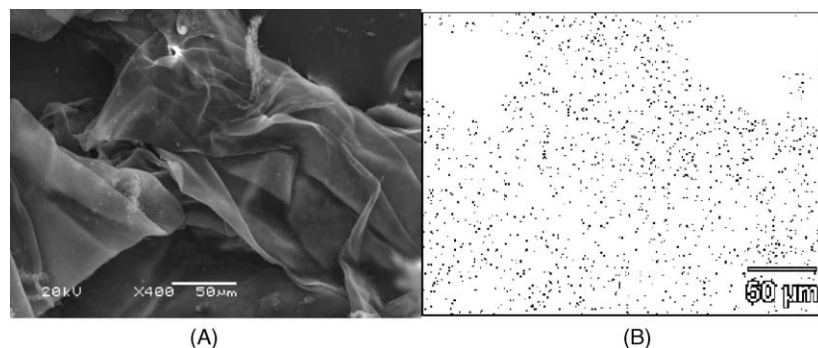
Fig. 2. Scanning electron micrographs of CA/Nb 6.7% sample (A), and corresponding (B) X-ray emission dot map obtained with X-ray fluorescence microprobe niobium are the black points.

black niobium points are observed at 0.32 keV. The images show clearly, within the magnification used to obtain the micrographs, that niobium particles are uniformly dispersed on surface without detectable agglomerates. This fact indicates that the niobium was immobilized homogenously onto the cellulose acetate surface, attesting the high quality of the reaction.

The presence of Lewis and Bronsted acid sites in the catalyst were followed by using pyridine as a molecular probe. The infrared spectra obtained for the catalysts treated with pyridine (Fig. 3) present a weak-band at $1540\,cm^{-1}$, which is assigned to the vibrational mode of pyridine in a Bronsted acid site, and two other bands at 1606 and $1440\,cm^{-1}$, which are assigned to pyridine adsorbed on Lewis acid sites. Another aspect that can be observed in these spectra is the increase of acid character with niobium amount attached on surface. This acid characteristic corroborates with the best photocatalytic activity in acid medium. Low pH values make easy hydrogen bonds between dye and Nb–OH of the material surface.

This new synthetic route using ammonium niobium oxalate as precursor in hydrothermal system shows a material as good as reported before through other synthetic method-

ologies. Furthermore, this route is very promising due to the fact that it is very simple and it is based on reactants more stable than traditional methods. The other synthetic procedures have been used $NbCl_5$ as a precursor to obtain the material [1,2,8,15]; however, this compound reacts strongly with O_2, which hinders the composite obtaining processes.

The photodegradation of indigo carmine dye was followed as a function of time, as represented in Fig. 4A.

The attachment of niobium facilitates the adsorption of contaminants by niobium due to the particles of Nb_2O_5 is more available when incorporated on surface, which is suspended in water, while Nb_2O_5 free is in precipitated form. Another great advantage of composite is the easy recycling, which is one of the key principles of green chemistry.

This photodegradation ability of CA/Nb catalyst was evaluated by applying Langmuir–Hinshelwood kinetic model [16–18], as represented in Fig. 4B:

$$r_{LH} = \frac{-dC}{dt} = \frac{kKC}{1 + KC}$$

This model assumes that at equilibrium the number of surface adsorption site is fixed, and only one substrate may bind at each surface site. Thus, the heat of adsorption by substrate is equal for each site and it is independent of surface coverage, and there is no interaction between adjacent adsorbed molecules. The rate of surface adsorption of the substrate is greater than the rate of any subsequent chemical reactions, and no irreversible blocking of active sites by binding to product occurs [19]. Indeed, The dye photodegradation depends on adsorption ability of the semiconductor, as well of the degradation reaction rate [16,17]. The kinetic degradation results obtained from curves of Fig. 4B are listed in Table 1.

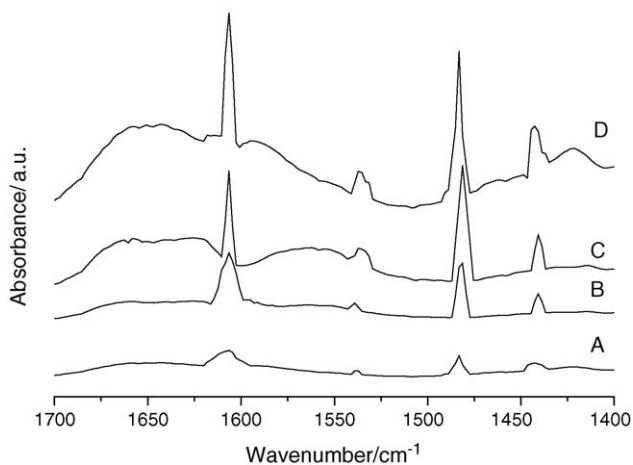Fig. 3. Infrared spectra of pyridine molecule adsorbed on CA/Nb with: 3.9% (A), 5.8% (B), 6.7% (C) and 10.9% of Nb_2O_5 supported onto CA (D).
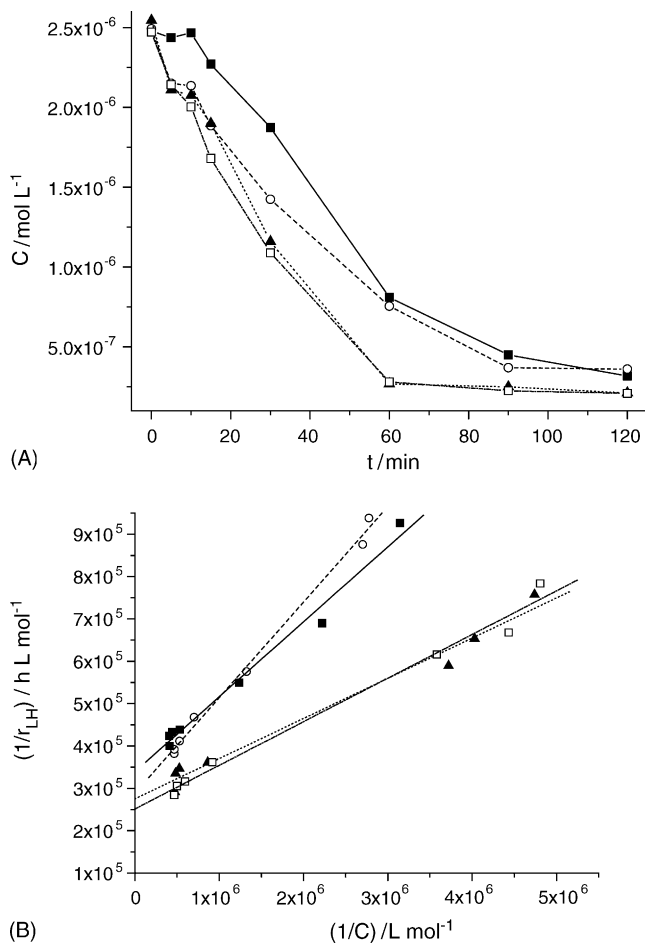
Table 1
k and K values obtained from application of Langmuir–Hinshelwood equation in indigo carmine dye photodegradation by using as catalyst CA/Nb composites

CA/Nb	k ($\mu mol\,L^{-1}\,h^{-1}$)	K ($L\,\mu mol^{-1}$)
3.6	2.95	1.92
5.8	3.47	1.28
6.7	3.63	2.91
10.9	3.98	2.44

Fig. 4. Indigo carmine dye degradation photocatalised by CA/Nb 3.9% (■); 5.8% (○), 6.7% (▲) and 10.9% of Nb_2O_5 supported on CA (□) (A) and linearization of this degradation by using Langmuir–Hinshelwood kinetic model (B).

These data show the k increase with amount of the niobium present on cellulose acetate surface; however, the adsorption constant data presented unexpected results. The CA/Nb 3.9 and 5.8% samples showed lower K values than CA/Nb 6.7 and 10.9% samples, which presented very similar photodegradation results. Furthermore, the dye degradation by CA/Nb 7.4 and 10.9 is very similar, as showed in Fig. 4A. This fact can be explained by niobium saturation of the cellulose acetate surface above 6.7% of niobium present on biopolymer.

The catalyst was reapplied in the photodegradation reaction in order to obtain data to test the recycling capacity of CA/Nb materials. The recycling experiments are presented in Fig. 5.

The percentage photodegradation studies suggests the excellent ability of this material in catalyzing this reaction. Photocatalytic activity decrease to 45% yield of dye degradation in second charge. On the other hand, this activity maintains constant after nine cycles.

The activity reduction observed from second cycle must be occurred by leaching of part of niobium attached on cellulose acetate according to Fig. 5, which shows that 23% of
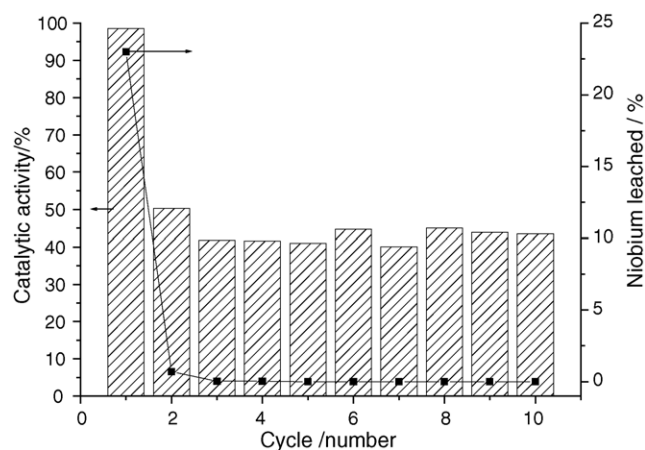

Fig. 5. Conversion rate for recycle experiments of catalyst at 30 °C for 30 min of reaction by using 6.7% CA/Nb and niobium leached amount of each recycle.

niobium was leached after first cycle. However, from second application of catalyst only 0.7% of niobium was lost, after that, the photoactivity was constant and the release of niobium was not detected, which contributes with ability of this material to be applied to degrade contaminants from water.

4. Conclusion

The methodology used to obtain Nb_2O_5/cellulose acetate catalyst is much easier than traditional methods; thus, it is a very promising synthetic route, and the materials presented a good dispersion of niobium on cellulose acetate, and showed typical acid sites on surface. Moreover, these materials show high quality to degrade indigo carmine dye in aqueous solution, they were easily recovered and loss activity after second charge and maintain the half-catalytic ability after nine runs.

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