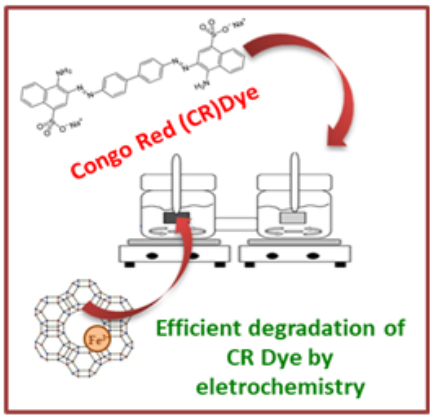
Fe(III)NaY$_{nano}$ as efficient electrocatalyst for electrodegradation of Congo Red dye

Z. Bencheqroun[1,3], M. Ferreira[1], H. Zaitan[3], M. Nawdali[4], A. M. Fonseca[1,2], P. Parpot[1,2], I. C. Neves[1,2]*
[1] CQUM, Center of Chemistry, University of Minho, Braga, 4710-057, Portugal; [2] CEB, Center of Biological Engineering, University of Minho, Braga, 4710-057, Portugal; [3] Laboratoire de Chimie de la Matière Condensée, Faculté des Sciences et Techniques, Fès- Maroc; [4] Laboratoire de Chimie de la Matière Condensée, Faculté de Polydisciplinaire, Université Sidi Mohamed Ben Abdellah, Taza- Maroc.
** contact_ parpot@quimica.uminho.pt*



Textile dyes are one of the most important contaminants of the superficial water resources. Their removal from water bodies constitutes a priority to guaranty water quality. Electrodegradation of Congo Red dye was carried out using modified electrodes prepared by the deposition of iron(III)-zeolite on Carbon Toray. The sample iron(III)-zeolite was prepared by ion-exchange method with a solution of iron(III) using NaY$_{nano}$ as parent zeolite, with small particles, 150 nm. Fe(III)NaY$_{nano}$ was characterized by SEM/EDX and XRD techniques. The introduction of iron by ion exchange method do not modified the morphology of the zeolite but affect the zeolite structure, as prove by the structural characterization results from XRD. However, cyclic voltammetry studies show that iron-zeolite modified electrode is stable in the experimental conditions. The complete degradation of Congo Red dye was achieved by electrochemical route without the use of acid and hydrogen peroxide in reactional medium.

Introduction

The discharge of textile dyes into water bodies is an environmental problem due their consequences for water quality. These compounds are usually toxic to aquatic life and they have a negatively impact to the food chain, because they are carcinogenic and mutagenic [1-2]. New emerging technologies have been recently proposed for the degradation of these organic pollutants [3]. Among various technologies, electrochemical oxidation appears as one of the most promising one for the treatment of wastewater containing organic pollutants, considering its environmental compatibility, low temperature and pressure requirements [5–6]. Thus the present work reports the study of the degradation of Congo Red ($C_{32}H_{22}N_6Na_2O_6S_2$) dye using iron-zeolite modified electrode. The results show that the electrocatalyst was very efficient for the degradation of the dye.

Methods

The dye was Congo Red (CR) from Sigma-Aldrich). NaY$_{nano}$ (NanoFAU-Y from NanoScape) was used as parent zeolite for preparing Fe(III)-NaY$_{nano}$ electrocatalyst. The ion-exchange method was achieved with a ratio of iron solution/zeolite weight to 35. So, 3.65 mmol of Fe(III) solution from $Fe(NO_3)_3.9H_2O$ (Sigma-Aldrich) with pH value of 5.0 was added to the zeolite parent at room temperature and mixing during 24 h. The suspension was filtrated off, washed and dried in oven at 80 °C for 24 h, following by a calcination step at 350 °C during 4 h in a static oven. Powder X-ray diffraction patterns were recorded on a Philips Analytical X-ray model PW1710 BASED diffractometer system. Scans were performed at room temperature, using Cu Kα radiation (λ=1.540598 Å) in the 2θ range between 5° and 70°. The samples were characterized using a desktop scanning electron microscope (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) analysis (Phenom ProX with EDX detector (Phenom-World BV, Netherlands)).
The preparation of the modified electrodes using Carbon Toray (CT) and the equipment used for electrochemical measurements were described in [6]. The dye concentrations used were 0.036 mM (25 ppm) for the cyclic voltammetry studies and 0.072 mM, 50 ppm for electrolyses in 0.10 M NaCl solution, at room temperature.

Results

Preparation and characterization of the samples. Fe(III)NaY$_{nano}$ was obtained by ion-exchange method. This usual method is the best for introduce cations in the zeolite structure, since the charge negative from the aluminum present in the structure need to be compensate with counter ions in order to maintain the neutrality of solid [7].
The presence of iron and the modifications provoked by the ion exchange method and thermal treatment in the sample were examined by different characterization techniques. SEM analysis show that the morphology and the average of the particles were the same as the parent zeolite. However, XRD analysis confirms that NaY was affected by the introduction of iron with a reduction of the crystallinity, 51%. The framework Si/Al ratios obtained are 3.68 for NaY and 1.72 for Fe(III)NaY$_{nano}$. The differences observed between the total Si/Al ratio (1.86 determined by ICP) and the framework Si/Al ratio for NaY are related to an irregular distribution of silicon and aluminum throughout the zeolite structure, with the presence of extra-framework alumina (EFAL) species. After the ion-exchange treatment, the framework Si/Al ratio of Fe(III)NaY$_{nano}$ decrease (Si/Al = 1.72) suggesting that the EFAL species were removed after the treatments. The presence of the iron also was detected by EDX analysis and it was 1.2 wt%.
Voltammetric study of Congo Red. The electrocatalyst, the iron-zeolite modified electrode, was prepared by deposition of Fe(III)NaY$_{nano}$ on Carbon Toray and their stability was confirmed by cyclic voltammetric study. For the range of the potential studied, in NaCl 0.10 M medium, the electrocatalyst was stable. The electroreactivity of Congo Red (0.036 mM) at iron-zeolite modified electrode, in NaCl 0.10 M medium was studied by cyclic voltammetry. The cyclic voltammograms of Pt/Fe(III)-NaY$_{nano}$ modified electrode in presence of Congo Red are given in Fig. 1.
The oxidation of CR starts at 0.5 V *vs.* SCE, after the oxidation of surface iron species. This result shows that the oxidation of CR is mediated by Fe(III). The oxidized CR is reduced during the negative variation of scan potential from -0.2 V *vs.* SCE.
High anodic and cathodic current densities were noticed in presence of Congo Red. During cyclic voltammetric study. For

each measurement successive voltammograms were registered in order to check the absence of surface deactivation.

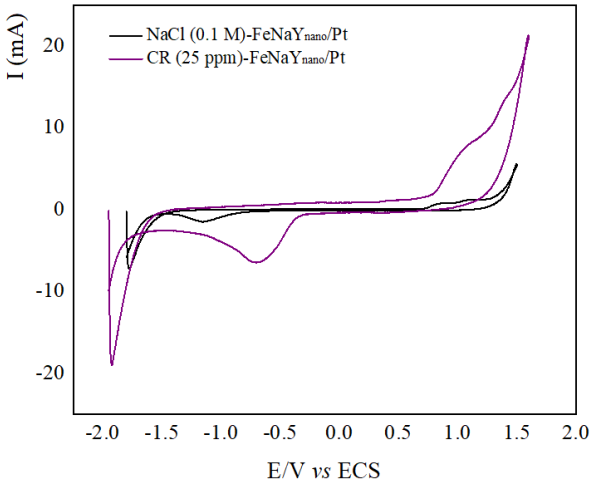


Figure 1. Cyclic voltammograms of Fe(III)NaY$_{nano}$ modified electrode with and without dye in 0.1 M NaCl medium registered with a scan rate of 50 mV/s.

Electrolysis of Congo Red dye in presence of chloride ions.
The electrolysis of CR dye (50 ppm) in 0.10 M NaCl medium was carried out on Fe(III)NaY$_{nano}$ modified electrode with an applied potential of 2 V *vs* SCE. After 2 h of electrolysis the initial concentration of CR was close to zero, which confirm that the CR dye was effectively degraded on the Fe(III)NaY$_{nano}$ modified electrode.

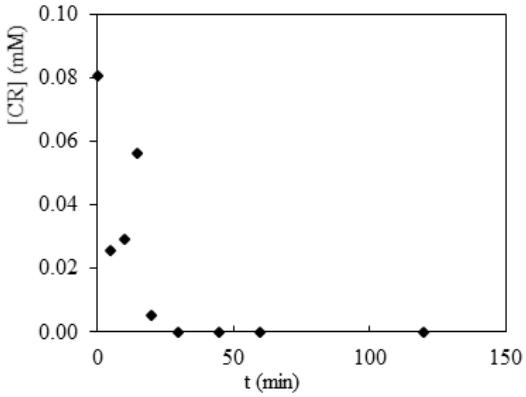


Figure 2. The variation of the concentration of the dye during the electrolysis of 50 ppm CR at Pt/Fe(III)NaYnano modified electrode, in 0.10 M NaCl medium.

Conversion rate for the first 15 min of electrolysis, which corresponds to the removal of 68% of the initial CR dye, was 97% at the end of electrolysis. A decrease of the conversion rate was noticed after this period due to the decrease of the reaction rate and, therefore, the more important contribution of the solvent oxidation to the overall current intensities.

Conclusion

The degradation of Congo Red dye in water was carried out by electrochemical methods using Fe(III)NaY$_{nano}$ zeolite modified electrodes. The results show that the modified electrode was very stable in the experimental conditions and it was very efficient for the degradation of the dye. The concentration of Congo Red dye at the end of the electrolysis was closer to zero.

Acknowledgements

Z. Bencheqroun thanks for her Erasmus grant. This work has been developed under the scope of the projects: BioTecNorte (operation NORTE-01-0145-FEDER-000004), PTDC/AAGTEC/5269/2014, and Centre of Chemistry (UID/QUI/00686/2013 and UID/QUI/0686/2016).

References

[1] M.M.F. Silva, M.M. Oliveira, M.C. Avelino, M.G. Fonseca, R.K.S. Almeida, E.C. S. Filho, Chem. Eng. J., 203 (2012) 259–268.

[2] Th. Ngulube, J.R. Gumbo, V. Masindi, A. Maity, J. Environ. Management, 191 (2017) 35-57.

[3] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, Appl. Catal. B Environ., 79 (2008) 237–243.

[4] C.A. Martínez-Huitle, S. Ferro, Chem. Soc. Rev., 35 (2006) 1324–1340.

[5] C. Comninellis, Electrochim. Acta, 39 (1994) 1857–1862.

[6] M. Ferreira, M.F. Pinto, O.S.G.P. Soares, M.F.R. Pereira, J.J.M. Órfão, J.L. Figueiredo, I.C. Neves, A.M. Fonseca, P. Parpot, Electrochim. Acta, 60 (2012) 278– 286.

[7] M. Dusselier, M.E. Davis, Chem. Rev., 118 (2018) 5265−5329.