On the behavior of reduced graphene oxide based electrodes coated with dispersed platinum by alternate current methods in the electrochemical degradation of reactive dyes
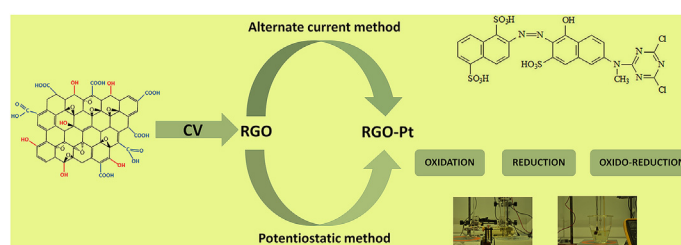
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HIGHLIGHTS

- Enhanced electrochemical properties of dispersed Pt by an AC method is applied.
- Electrolyses of a reactive dye solutions were performed with these electrodes.
- Reduced graphene oxide (RGO) based electrodes show the best results.
- The configuration of the electrochemical cell showed an important role.

GRAPHICAL ABSTRACT

ABSTRACT

The electrochemical behavior of different carbon-based electrodes with and without nanoparticles of platinum electrochemically dispersed on their surface has been studied. Among others, reduced graphene oxide based electrodes was used to determine the best conditions for the decolorization/degradation of the reactive dye C.I. Reactive Orange 4 in sulfuric medium. Firstly, the electrochemical behavior was evaluated by cyclic voltammetry. Secondly, different electrolyses were performed using two cell configurations: cell with anodic and cathodic compartments separated (divided configuration) and without any separation (undivided configuration). The best results were obtained when reduced graphene oxide based anodes were used. The degree of decolorization was monitored by spectroscopic methods and high performance liquid chromatography. It was found that all of them followed pseudo-first order kinetics. When reduced graphene oxide-based electrodes coated with dispersed platinum by alternate current methods electrodes were used, the lowest energy consumption and the higher decolorization kinetics rate were obtained. Scanning Electronic Microscopy was used to observe the morphological surface differences.

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1. Introduction

In 2010 the Nobel Prize in Physics was granted to Andre Geim and Konstantin Novoselov, not for the discovery of graphene, but for the "groundbreaking experiments regarding the two-dimensional material, graphene" (Nobel Prize Official Web, 2010), based on their study published in 2004 (Novoselov et al., 2004).

Graphene exhibits a theoretical surface area of 2630 m^2 g^{-1}, which is much greater than that of graphite (~10 m^2 g^{-1}) and even that of carbon nanotubes (1315 m^2 g^{-1}) (Pumera et al.,

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2009). Moreover, the electrical conductivity of graphene is excellent.

Several synthetic methods have been established to prepare graphene, but each one of them, besides possessing different scalability, generates graphene with very different characteristics, which strongly influences the resulting properties. Electrochemical methods represent an interesting approach, since they can be easily controlled, can be performed under ambient conditions, do not require toxic or dangerous chemical agents (the only reactive used is the electron), and require only simple instrumentation. In this case, the limitations of electrochemical methods are that the electrode or sample where the reduction takes place must be conductive, be electrochemically active and be in contact with the solution. In literature, electrochemically reduced graphene oxide (RGO) has been obtained on different electrode materials such as glassy carbon (Chen et al., 2011; Hilde et al., 2011; Bonanni and Pumera, 2012), gold (Hilde et al., 2011; Bonanni and Pumera, 2012; Sheng et al., 2012), indium tin oxide (ITO) (Hilde et al., 2011) or Pt (Bonanni and Pumera, 2012).

Moreover, due to their high surface area, these electrodes can be used as a support with anchoring sites for metal nanoparticles such as Pt nanoparticles, to produce graphene-nanoparticle hybrids. This combination lead to materials which have enhanced electro-catalytic activity and interesting properties for a variety of applications as methanol oxidation in fuel cells (Zhang et al., 2013; Hsieh et al., 2013), counter electrodes for dye sensitized solar cells (Yeh et al., 2014), hydrogen gas sensing (Shafiei et al., 2010), oxalic acid sensing (Chen et al., 2013), DNA detection (Yin et al., 2012), among others. In the case of Pt, there is a great dependence of the degradation of pollutants on the presence of chloride. The presence of a relatively small amount of chloride ions seems to inhibit the oxygen evolution reaction (OER), causing an increase of the anode potential. Therefore, there is a higher reactivity of oxychloro compounds and the performance of Pt electrodes can be significantly improved in the presence of NaCl.

Although the dispersion of Pt nanoparticles on graphene surface has been done mainly using chemical methods, currently, electrochemical methods have arisen great interest within the scientific community. As reported in recent studies carried out by our research group (Molina et al., 2014), the synthesis of Pt nanoparticles on the surface of reduced graphene oxide can be accomplished potentiostatically or using alternating current methods such as electrochemical impedance spectroscopy (EIS) technique. With the EIS synthesis technique, a lower effective synthesis time was required to obtain an optimum coating of Pt nanoparticles (Molina et al., 2014).

Considering these previous results, the present work deals with two new approaches in the environmental field. Firstly, the study of the electrochemical behavior of different carbonaceous materials with different structures in solutions containing the dye C.I. Reactive Orange 4, commercially known as Procion Orange MX2R (PMX2R). The carbonaceous materials studied in this part are: glassy carbon (GC), GC with Pt dispersed on its surface (GC-Pt), reduced graphene oxide deposited on a Pt support (RGO) and reduced graphene oxide deposited on a Pt support with Pt dispersed on its surface using a potentiostatic method (RGO-Pt/POT) and a current alternating method (RGO-Pt/EIS). Secondly, considering the voltammetric results as an initial reference for the efficiency of these electrodes, different electrolyses under different conditions were performed to evaluate the degradation and decolorization of PMX2R. In this part, RGO-Pt/POT and RGO-Pt/EIS were studied and later compared to other carbonaceous materials. These materials were activated carbon textile (ACT) and activated carbon textile with Pt dispersed on its surface (ACT-Pt), also studied in previously published works (del Río et al., 2015). In

all cases, special attention was paid to the influence of the synthesis method.

The dye selected for these studies, PMX2R, it is a monofunctional reactive dye with a 1, 3, 5-triazinyl group as a functional group and an azo group as chromophore. Reactive dyes are widely employed in the textile industry. However, during the dyeing with reactive dyes, they undergo a secondary reaction consisting on their hydrolysis. These dyes are not easily biodegradable and thus even after extensive treatment, color from unexhausted reactive dyes may still remain in textile wastewater. For this reason, this dye was chosen as a representative model of recalcitrant dyes.

2. Experimental

2.1. Reagents and materials

All reagents used were of analytical grade. For the synthesis: Monolayer graphene oxide (GO) powders were acquired from Nanoinnova Technologies S.L. (Spain). Lithium perchlorate ($LiClO_4$) was purchased from Merck. Pt wires (0.5 mm diameter, 99.99% purity) were acquired from Engelhard-Clal. The area of the electrodes was controlled with Teflon®.

For the characterisation: Sulphuric acid (H_2SO_4), CH_3OH (methanol) and $H_2PtCl_6 \cdot 6H_2O$ (hexachloroplatinic acid hexahydrate) were purchased from Merck. Iron (III) sulfate pentahydrate (($Fe_2SO_4)_3 \cdot 5H_2O$) was used as received from Acrōs Organics. C.I. Reactive Orange 4 (PMX2R) was purchased from Zeneca. NaCl was from Fluka. When needed, solutions were deoxygenated by bubbling nitrogen (N_2 premier X50S). Ultrapure water was obtained from an Elix 3 Millipore-Milli-Q Advantage A10 system with a resistivity near to 18.2 MΩ cm.

2.2. Solutions

Voltammetric measurements were performed using the following solutions: 0.5 M H_2SO_4 containing 3.9 g L^{-1} PMX2R and 0.5 M H_2SO_4 as blank solution.

Electrolysis analyses were performed using 0.08 g L^{-1} dye concentrations in 0.5 M H_2SO_4, according to real concentrations in wastewaters (Zaharia and Suteu, 2012). When adding NaCl to the solutions, the concentration was 0.3 g L^{-1}.

2.3. Electrodes. Pretreatment and/or preparation

Pt electrodes were pretreated with a flame treatment to clean their surface according to the method developed by Clavilier (1979). GC electrodes were also pretreated by polishing the electrode with 1.0, 0.3 and 0.05 μm alumina slurry. For the preparation of ACT electrodes, the company Carbongen S.A. (Spain) supplied a hydrophilic activated carbon fabric (ref HST 1110). To discard the presence of impurities on the surface of the fabric, a previous analysis (not included) by FTIR-ATR was carried out. The ACT electrodes were prepared by cutting strips of 1 cm × 2 cm area from the textile. To ensure a proper electric contact between the textile samples and the 2 mm copper rods used as a support, they were glued (the tip was flattened to improve the electrical contact) using CircuitWorks conductive epoxy resin by Chemtronics. The resin was cured in an oven at 90 °C and wrapped with Teflon tape to protect it from the solution. The dispersion of Pt on GC and ACT electrodes (to obtain GC-Pt and ACT-Pt electrodes) was performed in 5 mM $H_2PtCl_6 \cdot 6H_2O$ and 0.5 M H_2SO_4 aqueous solution by CV from −0.25 to + 0.4 V at 10 mV s^{-1} during 20 scans with a stainless steel (SS) as counter electrode (CE) and Ag/AgCl (3.5 M KCl) as the reference electrode. The pretreatment for the CE of SS electrodes was described by del Rio et al. (del Río et al., 2009a, 2009b).