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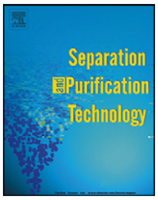

Electrochemical-switchable polymer film: An emerging technique for treatment of metallic ion aqueous waste

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ABSTRACT

The present work aims at using grafted polyacrylic acid (PAA) films as active surfaces for heavy metal waste removal. We focus first on grafting PAA onto carbon felt surfaces by means of an economical and simple preparation method compatible with real industrial applications. XPS, SEM results and interfacial electrochemistry allow us to confirm the grafting of PAA films on carbon felts. Metal ion uptake inside the PAA film is discussed in detail. The final part of the work is then devoted to the application of carbon felt grafted PAA electrodes to remove metal ions from aqueous waste according to the electrochemical-switchable process. Primary treatments of real industrial effluents are performed with a lab-made semi-pilot system. Such electrochemical-pH-switchable PAA films can be considered within the field of aqueous effluent treatments in order to reach very low concentration in heavy metal ions.

1. Introduction

Polymer-modified electrodes have received considerable attention in areas such as biosensors, enzyme immobilization, separation membranes, surface patterning, nano-composites because of many advantageous properties of polymers [1,2]. In the environmental field, although several electrochemical technologies such as electrodialysis, electrocoagulation, electrooxidation or electrodisinfection have become an indispensable step in treating waste water containing refractory pollutants [3], polymer-coated electrodes are generally used for the detection and characterization of organic compounds in waste water since they exhibit high sensitivity, good selectivity, rapid response and are relatively easy to use [4]. Application of conducting polymer-modified electrodes to remove heavy metal ion waste has been reported as an emerging technology [5]. The principle of heavy metal ion treatment by polymer films relies on the intrinsic chelating or ion exchange properties of the chosen polymers toward the metals ions. Polyvinylpyridine, polyvinylpyrrolidone or polyacrylic acid can be given as representative examples [6–11]. Due to their chelating properties, such polymer films can capture heavy metal ions at very low concentration that cannot be reached with conventional electrodialysis using ion exchange membranes. However, heavy metal ions accumulated in the polymer films are generally released by acidic washing where the metal cations from the film are exchanged for H^+ ions from the acidic medium [12]. Use of electrochemically pH-switchable polymer films as active surfaces is thus a new concept for heavy metal ions liquid waste treatment [13]. Indeed, the release of the metal ions from the grafted polymer film can be obtained easily under electro-induced-acidification by applying an anodic potential at the electrode to promote localized water electrolysis. So far, such results were obtained with grafted poly-4-vinylpyridine films initially prepared by cathodic electro-polymerisation in highly stringent conditions (using distillated monomers, glove-box conditions, highly cathodic potentials, etc.). In our recent work [14], polyacrylic acid (PAA) has been directly grafted onto gold substrates at open air and room temperature. The ability of PAA-grafted gold electrodes to reversibly bind or release metal ions was confirmed by means of electrochemistry. Our results lead to a promising technique for efficient treatment of waste water in order to reach very low concentration in heavy metal ions without production of secondary effluents. It is thus important to find the electrode materials suitable for the requirement of real industrial applications. The purpose of this work is, therefore, to obtain grafted PAA films on carbon felts which have significantly higher surface per volume ratio than flat substrates. Our recently published GraftFast [15,16] that provides grafted polymer films on any surface through a simple chemical process will be taken into account in the first section of the work. The second part deals with removal of metal ions from real industrial waste water by means of a semi-pilot system using the PAA-grafted carbon felt electrodes in accordance with the electrochemically pH-switchable process.

2. Experimental

Main characteristics of the carbon felt used in this work are presented in Table 1.

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Table 1
Main characteristics of commercial carbon felt.

Name	RVC—Carbone Lorraine (France)
Thickness (mm)	6
Tolerance on thickness (mm)	4.80–6.40
Density (g/cm^3)	0.088
Water absorption in 90% relative humidity (% weight)	1
Surface area (via nitrogen) (m^2/g)	0.6

The grafting of PAA on carbon felts was carried out at open air and room temperature as already described [16]: first, p-phenylenediamine was solubilised as a 0.1 M solution in water at pH = 0.3. To generate the mono-aryldiazonium salt, 160 mL of sodium nitrite (0.1 M) was added dropwise to the same volume of the p-phenylenediamine solution. Then, we introduced 160 mL of commercial acrylic acid (Aldrich, ≥99%) in the flask. After homogenizing the solution, 10 g of iron powder was added to reduce the diazonium salt in solution. Once the solution bubbled because of dihydrogen and dinitrogen evolution, we introduced the carbon felt samples. The surface area and thickness of the disk-shaped samples were 314 cm^2 and 0.6 cm, respectively. The average weight of each disk was 10 g. The samples were taken from the solution after the reaction time of 120 min and carefully rinsed with deionised water.

XPS studies were performed with a KRATOS Axis Ultra DLD spectrometer, using the monochromatized Al Kα line at 1486.6 eV. Fixed analyzer pass energy of 20 eV was used for C_{1s} core level scans.

The scanning electron microscopy images were recorded by a Hitachi S4500 equipped with a Field Emission Gun (FEG-SEM).

A multiparameter bench colorimeter (Spectrophotometer HI 83200 from Hanna Instrument Corporation) was used to measure copper and zinc amounts in the solutions. Measurements are performed in two successive steps, on 10 mL of the solution filling the cuvette. The first one is the calibration (zeroing) with the unknown solution and the second is the proper measure and consist to add a specific reagent to create absorbing specie which are detected at a specific wavelength. Latter is automatically selected through the method.

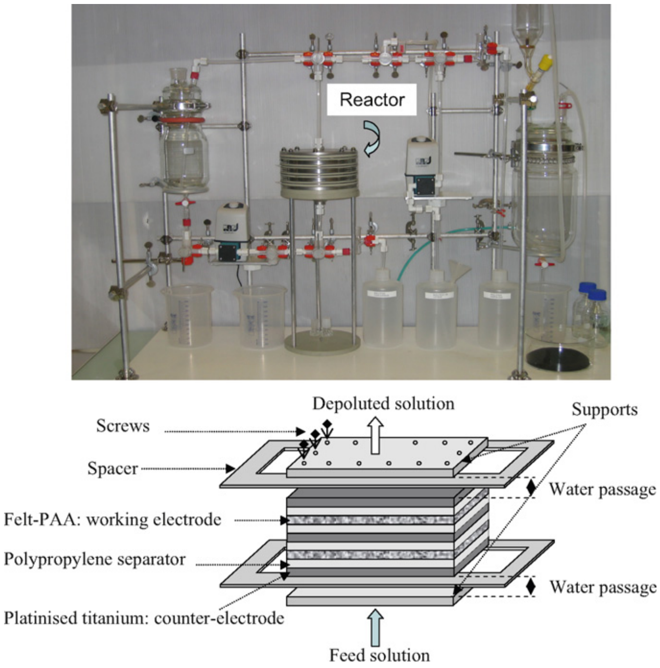

Fig. 1. Generalised schematics of the semi-pilot system.

Electrochemistry was carried out with a SOLARTRON 1255 frequency analyzer controlled by a computer with the Corrware and Zplot softwares. For impedance spectroscopy, the frequency analyzer was equipped with an electrochemical interface (SI1286) and the measurements were realized in a range of frequencies extending from 0.01 Hz to 100 kHz.

Fig. 1 presents a generalised schematic of the semi-pilot system used in this work (pumps, solution reservoirs, reactor, etc.). PAA-grafted carbon felt samples and disk-shaped platinised titanium nets were placed alternatively in the reactor to play the roles of working and counter electrodes respectively, when current is applied through the system. The reactor volume was 1.0 dm^3. The solution was pumped vertically through the reactor by an electrical pump at a range of velocity from 0.6 to 3.0 dm^3/min.

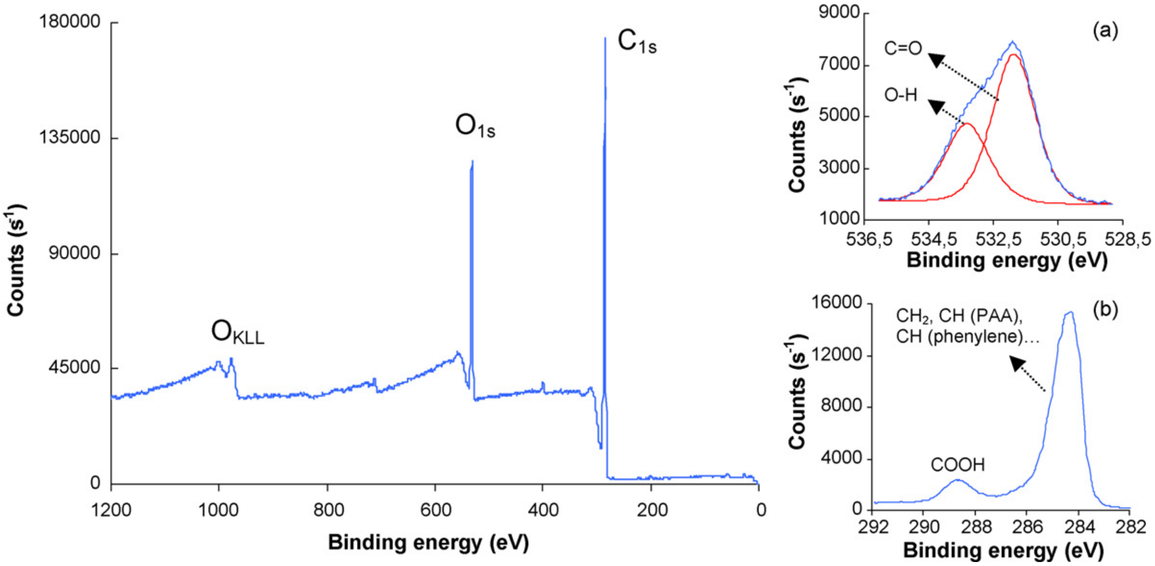

Fig. 2. XPS survey spectrum of the PAA-grafted carbon felt.