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Adsorption of dye with carbon media supported on polyurethane open cell foam

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ABSTRACT

The use of a combined polydopamine polyurethane open cell foam (OCPUF@PDA − recently introduced in open literature) with carbon media, is for the first time used for the dye (methylene blue) adsorption in an aqueous solution. The carbon media used in this work is activated charcoal and/or carbon nanotubes that are supported on the foam's surface. These new tools obtained (OCPUF@PDA@AC and OCPUF@PDA@CNT) are evaluated and compared to OCPUF@PDA and to the non-supported carbon media. The adsorption efficiency (245 mg_{MB}/g_{carbon} for OCPUF@PDA@AC *versus* 10 mg_{MB}/g_{PDA} for OCPUF@PDA) and easy-to-use of these new tools, open real perspective in wastewater treatment.

1. Introduction

Dyes are mainly used in food products, printing, cosmetics, but especially in the textile industries thanks to their chemical stability and their simplicity of synthesis [1]. Over the last decades, these dyes have contributed severely to water pollution once they have been discharged into the environment. A model dye is methylene blue (MB) which is composed of various highly carcinogenic and mutagenic amino-aromatic groups [2,3].

In order to treat these polluted waters, numerous methods have been developed in decontamination processes, such as photocatalytic discoloration [4,5], adsorption [6,7] and oxidation [8,9].

Among these processes, the adsorption technique is the most popular in the industry for economic reasons and its high rate of removing. The efficiency of the adsorption process is directly linked to the choice of the suitable support, particularly its adsorption capacity, its cost, its availability on the market and its potential for reuse.

Activated Carbon (AC) and Carbon Nanotubes (CNTs), which has been the subject of numerous studies [10–13], have proved to be a very effective adsorbent. However, they are essentially under powder form, which is not viable for the treatment of high flux effluent (e.g. pressure drop).

Polyurethane foams and polydopamine coated foams have been recently used for decontamination of water by adsorption [14] or reduction [15].

In this work, we propose to combine polyurethane foams characteristics (important surface over volume ratio, small pressure loss and good transport properties [16–19]) and adsorption efficiency of carbon media. This new tool (Fig. 1) which consists to carbon media supported on polydopamine open cell polyurethane foam (OCPUF@PDA@AC and OCPUF@PDA@CNT) is successfully used in order to improve the removing of a dye from water.

2. Experimental

2.1. Materials and methods

Dopamine hydrochloride, methylene blue and Tris base were purchased from Alfa Aesar and used without any further purification. carbon nanotubes (CNTs) were purchased from Nanocyl. Activated Charcoal (AC) was purchased from Arkopharma. Polyurethane open cell foams (Fig. 1) were purchased from FoamPartner (Regicell 20 PPI). Cubic samples of 8 cm^3 (180 mg ± 20 mg) were used without prior treatment. The solutions are prepared with water purified by Synergy® Water Purification System (Millipore).

Textural characterization of AC and CNT was determined from adsorption isotherms at 77 K using a Micrometrics ASAP 202 Surface Area Analyzer. The specific surface area was respectively 254 and 239 $m^2\ g^{-1}$.

Thermogravimetric analysis (TGA) of OCPUF, OCPUF@PDA, OCPUF@PDA@AC and OCPUF@PDA@CNT was performed with a TG 209 Netzsch apparatus. Alumina crucibles were filled with accurately weighted samples of about 20 mg. The temperature program ranged from 25 °C to 500 °C at a heating rate of 10 °C/min. All experiments were conducted under nitrogen atmosphere (flow: 20 mL/min). The weight loss was recorded as a function of temperature and time.

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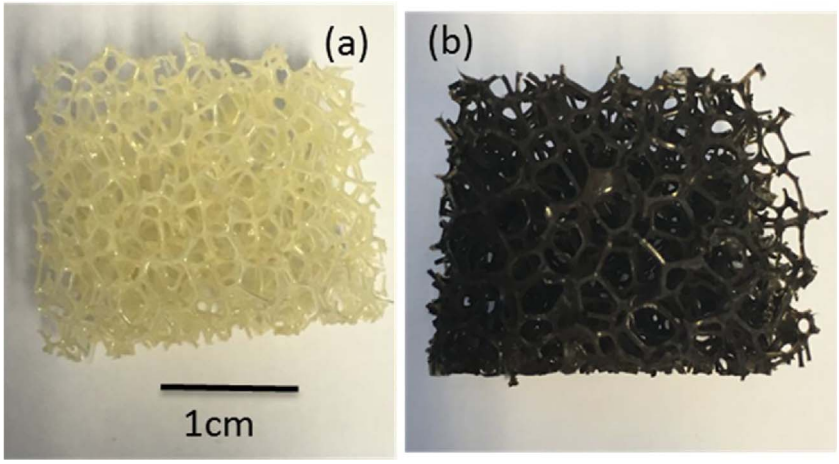


Fig. 1. Commercially available OCPUF (a) and OCPUF@PDA@AC (b) used in this work.

Scanning electron microscopy (SEM), was performed with a Hitachi S800 FEG microscope at the "Centre Technologique des Microstructures" (CTμ) at the University of Lyon. Sample of OCPUF, OCPUF@PDA, OCPUF@PDA@AC and OCPUF@PDA@CNT were deposited on a flat steel holder and coated under vacuum by cathodic sputtering with platinum. The samples were observed by SEM under an accelerating voltage of 10 kV.

Transmission Electron Microscopy (TEM), was performed with a Philips CM120 microscope A small drop of suspension was deposited of a microscope grid (copper support covered with carbon) and slowly dried in open air. The dry samples were observed by TEM under 120 kV acceleration voltage. Observations were made directly on the aqueous suspensions diluted with water.

2.2. Preparation of the carbon media

Before the deposition on the foam, the carbon media (CM) was treated in order to insure a better grip on the foam's surface. According to Serp et al. [20], acidic treatment is realized in order to functionalize the surface of the CM. The standard procedure is the following: five grams of carbon media was reacted with 250 mL of nitric acid (65%) at 120 °C for 8 h under stirring. Then the media was filtered on a hot fritted glass funnel and washed with distilled water until a stable pH value was obtained. The media are then dried at 120 °C during 2 days and crushed to a powder.

2.3. Deposition of the CM

The deposition of the CM was made in two steps:

First, a deposition of the CM was made at the same time as the deposition of polydopamine on the foam. This method, namely 'combined method' consists to do an immersion of cubic samples of OCPUF at room temperature in an alkaline aqueous solution of dopamine buffered to a pH of 8.5 [21] completed with 2 g of CM functionalized, followed by thorough washings with water, according to our recently reported procedure [15].

Next, a new deposition of CM functionalized was realized on the polydopamine-coated foam surface (see for instance [21]). This second step allows to increase the mass of the CM deposited on the OCPUF. These steps were followed by washing with water and sonication to remove all CM not well gripped.

These procedures are summarized in Scheme 1.

2.4. General procedure for the removal of methylene blue in water

According to Lefebvre et al. [15], an aqueous solution of MB (50 mL, 2.10^{-5} M) was stirred at room temperature (700 rpm) with cubic sample (8 cm^3) of OCPUF, OCPUF@PDA, OCPUF@PDA@AC or OCPUF@PDA@CNT. The disappearance of MB was measured by the decrease of its absorbance peak at 664 nm in the UV–vis spectra in the solution as a function of the time [see for instance 15]. The dye percent removal (R (%)) was calculated using the following Eq. (1):

$$R(\%) = \left[100 \times \left[1 - \frac{C(t)}{C(0)}\right]\right] \pm 2\% \quad (1)$$

Where *R* is the removal percentage, *C(0)* the initial concentration of MB in the solution, and *C(t)* the concentration in the solution at time t.

Between two successive runs, the foam was taken out of the solution and re-immerged in a fresh solution of MB.

3. Results and discussion

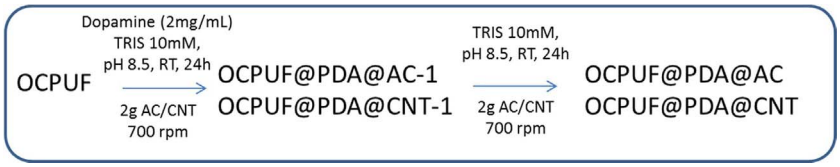
3.1. Characterization of the CM supported on the open cell foam

3.1.1. Thermo gravimetric analysis

The deposition of the CM on the foam is analyzed by the Thermo Gravimetric Analysis (TGA). This method consists in heating 20 mg of our samples up to 500 °C. At this temperature, OCPUF and OCPUF@PDA are almost entirely decomposed while the CM deposited on the foam does not decompose (Fig. 2). Table 1 shows mass increase of PDA and carbon media on our samples. Higher amount of CNT can be explained by aggregates of CNT with PDA during the first deposition step.

3.1.2. Scanning electron microscopy

The catalyst layer was characterized by scanning electron microscopy (SEM). Images of OCPUF@PDA, OCPUF@PDA@AC and



Scheme 1. Deposition method of carbon media.