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Polydopamine-coated open cell polyurethane foam as an efficient and easy-to-regenerate *soft structured catalytic support* (S_2CS) for the reduction of dye

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Graphical abstract

Inexpensive, easy-to-filtrate and easy-to-regenerate!

Abstract

Commercially available open cell polyurethane foams (OCPUF) are coated with polydopamine (PDA@OCPUF) and used as highly efficient Soft Structured Catalytic Support (S_2CS) for the removal of a methylene blue (MB) from aqueous solutions in the presence of sodium borohydride (NaBH_4). The process relies on the probable dual role of NaBH_4 that, on one hand, would allow MB to be adsorbed on the surface of OCPUF by forming an ionic pair, and on the other, would play the role of an electron-donor with the PDA layer acting as an electron relay toward the electron-acceptor dye. The catalytic activity of the PDA layer can be doped with Ag microparticules (MPs) by simple dipping the

structured PDA@OCPUF in a solution of silver nitrate. All S₂CS prepared (OCPUF, PDA@OCPUF and Ag@PDA@OCPUF) were then evaluated and compared. The readily prepared PDA@OCPUF has potential application in wastewater treatment in the presence of NaBH₄.

Keywords:

Polyurethane Open Cell Foam – Polydopamine – Methylene blue – Reduction – Adsorption

1. Introduction

Various industrial sectors such as the textile, paper, rubber, plastic, leather, cosmetic, food and drug industries use dyes to color their products [1]. The textile industry, in particular, is one of the biggest producer of dye-containing effluents. Removal of these pigments plays a significant role in wastewater treatment. Indeed dyes, such as methylene blue (MB) which is one of the most commonly used substance for dyeing cotton, wood and silk [2], interfere with the penetration of sunlight in water, retard photosynthesis, inhibit the growth of aquatic biota, and may be harmful to human health [3].

Various physicochemical methods have been developed to treat these dyes [4,5,6,7,8,9,10,11,12,13]. Among these processes, the adsorption technique is widely used in industry owing to its low cost and high removal rates [2,3,5]. The efficiency of an adsorption process is directly linked to the adsorption capacity, availability, cost, and potential for reuse of the chosen adsorbent [14]. Thus, most adsorbents are based on activated charcoal, which is highly efficient and inexpensive. However, because of its powdery nature, it is not a convenient choice for the treatment of high flows. There is therefore a growing demand for low-cost structured materials capable of removing dyes from water. In this context, R. J. Cassella *et al.* [15] have shown that polyurethane foams (PUF) can be used as an alternative adsorbent of MB in the presence of anionic surfactant; the latter forming a hydrophobic ionic pair with the cationic dye that has a high affinity for PUF. An open cell polyurethane foam (OCPUF; see Fig. 1) approach is exciting since an open cell foam allows an important surface over volume ratio, a small pressure loss (even at high flow) [16,17], efficient mass transfers, an intimate mixing of the reagents [18,19], and an easy separation of the adsorbent (OCPUF) from the solution; no filtration step is required in contrast to powdery adsorbents. Moreover, OCPUF are lightweight structures, commercially available at low cost due to the large variety of applications involving their physical and mechanical properties [20].

Figure 1. Commercially available polyurethane open cell foam used in this work

The chemical reduction of dyes is also a fast, efficient and commonly used method for water decontamination. In most cases, metal and metal oxide nanoparticles (NPs) are used as redox mediator (RM) catalysts to increase reduction rates in the presence of an electron source (usually an hydride) [21,22,23]. Indeed, RMs are composed of a redox couple with an intrinsically high electron transfer rate, which can assist the interaction between an electron donor and an electron acceptor by acting as an electron relay [23,24,25].

In 2007, Messersmith *et al.* [26] placed polydopamine (PDA) into the spotlight as a mussel-inspired coating material that can bind to virtually all kinds of inorganic and organic support, including three-dimensional materials such as OCPUF as shown by our recent works [27,28]. Furthermore, PDA is known as an environmentally friendly, non-toxic, and efficient redox mediator [29,30]. Thus, PDA possesses numerous catechol groups that are redox-active for a wide range of electrochemical applications [31,32,33,34], and can act as an electron acceptor at neutral and basic pH values because of the presence of semiquinone and quinone functional groups.

In this context, the work described herein illustrates the concept of *Soft Structured Catalytic Support* (S_2CS) modified by PDA in order to combine the remarkable features of OCPUF (elastic, lightweight, inexpensive) with both the strong adherence and redox properties of PDA. The resulting tool is evaluated for the decontamination of MB-containing wastewater in the presence of $NaBH_4$ [35,36,37,38].

2. Experimental

2.1. Materials and methods

Commercial compounds were used as received. Dopamine hydrochloride, sodium borohydride, Methylene Blue, Tris base and silver nitrate were purchased from Alfa Aesar. Polyurethane open cell foams (Fig. 1) were purchased from FoamPartner. Their characteristics are as follows: mean strut size: 220 μm ; mean window size: 779 μm ; mean

cell size: 2500 μm ; density: 0.027-0.033, porosity: 0.94-0.97. Cubic samples of 8 cm^3 (180 $\text{mg} \pm 20 \text{ mg}$) were used without prior treatment. The solutions are prepared with water purified by Synergy® Water Purification System (Millipore).

Polydopamine-coated open cell polyurethane foams (PDA@OCPUF) were prepared according to the reported procedure [27].

Scanning electron microscopy was performed with a Hitachi S800 FEG microscope at the “Centre Technologique des Microstructures” (CT μ) at the University of Lyon. Sample of OCPUF, PDA@OCPUF or Ag@PDA@OCPUF was 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 15 kV. Elemental analysis was performed with an EDS-SDD detector (SAMx) with an active area of 30 mm.

2.2. Ag-NPs doping of PDA@OCPUF: preparation of Ag@PDA@OCPUF

A cubic sample of PDA@OCPUF (8 cm^3) was immersed for 24 h at room temperature in a stirred aqueous solution (50 mL) of AgNO_3 (0.425 g, 50 mM) in the dark. The resulting Ag-functionalized open cell foam (Ag@PDA@OCPUF) was then taken out of the solution, rinsed thoroughly with water, immersed in vigorously stirred water (70 mL) for 10 min, and air-dried. This washing procedure was repeated 5 times, and Ag@PDA@OCPUF was finally dried overnight in an oven at 67 °C.

Ag@PDA@OCPUF materials were characterized by SEM micrographs combined to energy dispersive X-ray spectroscopy (EDX). The mass of Ag NPs immobilized on PDA@OCPUF was estimated to be of *ca.* 3 mg by simply weighing the foams before after silver doping.

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

In a typical experiment, an aqueous solution of MB (50 mL, $2.10^{-5} - 5.10^{-5}$ M) was stirred at room temperature (500-700 rpm) in the presence of NaBH_4 (945 g/250 mL, 0.1 M) and of cubic sample (8 cm^3) of OCPUF, PDA@OCPUF or Ag@PDA@OCPUF. The disappearance of MB was followed by measuring the decrease of its absorbance peak at 664 nm in the UV-visible spectra of the reaction solution in function of the time of reaction. The percentage of MB removed from the solution was calculated according to equation (1):

$$R (\%) = 100 \times [1 - (C(t)/C(0))] \quad (1)$$

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 reaction medium, washed with Milli-Q water and re-immersed in a fresh solution of MB and NaBH_4 .

3. Results and discussion

3.1. Preparation and characterization of PDA@OCPUF

PDA@OCPUF were prepared by simple immersion of cubic samples of OCPUF at room temperature in an aqueous solution of dopamine buffered to a pH of 8.5 (Fig. 2), followed by thorough washings with water, according to our recently reported procedure [27]. Similarly to this work, low magnification scanning electron microscopy (SEM) images of PDA@OCPUF (Fig. 2 – 20 μm scale) revealed a coating of PDA on the whole surface of the 3D material at a macroscopic level. However, higher magnification SEM image (Fig. 2b – 2 μm scale) highlighted a rough film with the presence of dispersed aggregates as typically observed on flat surfaces [39]. The mass of PDA on a 8 cm^3 sample of OCPUF was evaluated to be of *ca.* 2 $\text{mg} \pm 0.5$ mg .

Figure 2. OCPUF coating with PDA (up), and SEM images of OCPUF (a) and PDA@OCPUF (b) (down)

3.2. OCPUF vs. PDA@OCPUF for the adsorption/reduction of MB in water

The activity of these PDA-coated foams were then evaluated and compared to that of uncoated OCPUF for the adsorption/reduction of MB in water. Experiments were conducted by simply immersing a sample of OCPUF or PDA@OCPUF in a stirred aqueous solution of MB (2.10^{-5} M) in the presence (or in the absence) of NaBH_4 as a hydride source (Fig. 3). The adsorption/reduction of MB was followed by the measure of the decrease of its absorbance peak at 664 nm in the UV-visible spectrum of the reaction medium. After a given time (25 min), the foams were reused by re-immersion in fresh solutions of MB and NaBH_4 . In Figure 4, we show the percentage of MB adsorbed and/or reduced on the support with OCPUF (a) and PDA@OCPUF (b) in function of the reaction time.

Figure 3. Degradation/removal of MB with OCPUF and PDA@OCPUF: solution and foam color after 3 runs with OCPUF (a, c) and after 5 runs with PDA@OCPUF (b, d)

Figure 4. Percentage of MB removal (50 mL, 2.10^{-5} M) in function of time: (a) with OCPUF, (b) with PDA@OCPUF. $[\text{NaBH}_4] = 0.1$ M

In the case of non-coated OCPUF (Fig. 4a), negligible disappearance of MB was observed after 25 min in the absence of NaBH₄, most probably in reason of the weak affinity of MB for polyurethane. In contrast, in the presence of a high concentration of NaBH₄ (0.1 M vs. 2.10⁻⁵ M of MB), about 70% of MB had been removed after 25 min (run 1). The amount of MB that was removed, however, decreased to *ca.* 50% in run 2, 40% in run 3, and 20% in run 4 (Fig. 4a). These results strongly suggest that a simple adsorption phenomenon occurs in these conditions. Thus, the amount of removed MB would dramatically decrease after 3 runs simply because the surface of OCPUF is saturated and the maximum adsorption capacity of MB has been reached (see the color of the OCPUF after 3 runs, Fig 3c). Similar results were observed by R. J. Cassella *et al.* [15] for the adsorption of MB on PUF in the presence of sodium dodecylsulfate, the latter presumably forming an ionic pair with MB that would be the substance sorbed onto PUF. Hence, we assume that a similar phenomenon would occur here, with the ionic pair formed from the cationic dye and BH₄⁻ being sorbed onto our OCPUF.

In the case of PDA@OCPUF also, negligible disappearance of MB was observed in the absence of NaBH₄ (Fig. 4b), thus showing that the presence of PDA on the OCPUF surface does not significantly affect the adsorption of MB onto polyurethane. However, in the presence of a high concentration of NaBH₄ (0.1 mol.L⁻¹), complete removal of MB was observed within 25 min (Fig. 4b, run 1), and the PDA-coated open cell foam could be reused at least 5 times with an almost constant activity (Fig. 4b, runs 2 to 5). This is in agreement with the recent work of F. Zuo *et al.*[30], which has shown that PDA microparticles (MPs) have only little effect on the decolorization of MB in the absence of NaBH₄, but can act as a good catalyst for the reduction of MB by NaBH₄.

Based on these results and on those obtained with uncoated OCPUF, as well as on the above cited literature precedents [15,30], we believe that NaBH₄ plays a dual role here: on one hand BH₄⁻ would allow MB to be adsorbed on the surface of OCPUF by forming an ionic pair, and on the other, it would play the role of an electron-donor with the PDA layer acting as an electron relay toward the electron-acceptor dye (Scheme 1). Although being thermodynamically favorable, the reduction of MB with NaBH₄ is indeed kinetically restricted in the absence of a catalyst (or redox mediator) [30], as confirmed by the absence of decolorization of MB by NaBH₄ in the absence of PDA@OCPUF (Fig. 5).

Scheme 1. OCPUF@PDA-catalyzed reduction of MB by NaBH_4

Figure 5. UV-Vis spectra of aqueous solutions of MB (2.10^{-5} M) and NaBH_4 (0.1 M) in the absence and in the presence of PDA@OCPUF after various reaction times

For the PDA@OCPUF samples, the catalytic activity can be then quantitatively estimated. As the initial concentration of NaBH_4 was in large excess compared to that of MB, pseudo-first order reaction kinetics can be applied. Considering a simplified model, the concentration evolution ($C(t)$) of BM can be given by the following relations:

$$\begin{cases} \frac{dC(t)}{dt} = -v_{ads} + v_{des} - v_{PDA} \\ \frac{dC_{ads}(t)}{dt} = v_{ads} - v_{des} - v_{PDA} \end{cases} \quad (2)$$

$$v_{ads} = k_{ads}[C(t)], \quad v_{des} = k_{des}[C_{ads}(t)], \quad v_{PDA} = k_{PDA}[C_{ads}(t)]$$

with $C(t)$ and $C_{ads}(t)$ being the concentration of MB in the solution and that adsorbed on the open cell foam, respectively, and k_{ads} (adsorption constant) and k_{des} (desorption constant) being directly obtained from the adsorption measurement with OCPUF sample (Fig. 6).

Figure 6. Kinetic simplified model vs. experiments

In a first approximation, the agreement between the experimental values and the simplified model is satisfying in order to estimate the catalytic activity of the PDA layer. The best fit for the apparent rate constant of PDA (k_{PDA}) was found to be 0.33 min^{-1} , which is in very good agreement with the value of 0.328 min^{-1} found for the activity of unsupported PDA microparticles [30].

3.3. Stability and recyclability of the soft structured PDA@OCPUF

From an industrial point of view, the stability and recyclability of a catalytic material are key features. In this context, based on work of the F. Zuo *et al.* [30], which demonstrated (i) that quinone groups such as those of anthraquinone-2-sulfonate accelerate the electron transfer between NaBH_4 and MB, (ii) that the decrease in quinone content of PDA MPs (probably owing to an incomplete reduction/oxidation cycle between quinones and catechols during the electron transfer process) was the main reason for their deactivation, and (iii) that the quinone content, and hence the activity, of the PDA MPs can be increased by oxidation with NaIO_4 , we present here a simple procedure, *i.e.* air re-oxidation at room temperature, in order to ensure recyclability of our soft structured redox mediator catalyst, PDA@OCPUF.

Indeed, similarly to what was observed with PDA MPs, the removal rate of MB gradually decreased during the successive runs conducted with PDA@OCPUF (Fig. 4). Assuming that this was also due to a decrease of the amount of quinone moieties, we decided to attempt to re-oxidize the resulting catechol groups by simple exposure of the foams to air. Gratifyingly

after 8 h exposure at 67 °C, the activity re-increased from 31% removal after 25 min in run 10 to *ca.* 50% removal in run 11, but decreased again quickly in runs 12 and 13 (Fig. 7a). Novel exposure to air for then 6 days at room temperature between run 13 and 14 proved even more efficient since the activity of re-oxidized PDA@OCPUF was this time almost quantitatively recovered with over 81% removal of MB after 25 min (*vs.* 91% removal in run 1), and then decreased gradually in the successive runs (see Fig. 7b, run 13 to 18) at a rate similar to that observed in the first runs. These results unambiguously indicate that a dynamic equilibrium exists between quinone and catechol, and thus that the PDA@OCPUF RM can be efficiently regenerated by simple exposure to air at room temperature for several days.

Figure 7. Recyclability of the PDA@OCPUF by simple exposure to air: (a) for 8 h at 67 °C, (b) for 6 days at RT. [MB] = $5 \cdot 10^{-5}$ M, [NaBH₄] = 0.1 M, PDA@OCPUF: m = 173 mg (0.5 mg PDA).

3.4. Silver NPs doping of the soft structured PDA@OCPUF redox mediator: catalytic activity of Ag@PDA@OCPUF

The ability of PDA to reduce some noble metal ions such as Ag⁺ is well known [40]. This property has been used recently to prepare uniformly distributed multilayer Ag NPs on the surface of a PDA-coated polyethylene film by simple alternative immersion in silver nitrate and dopamine solutions [41]. The obtained material demonstrated interesting catalytic activity for the decoloration of MB in the presence of NaBH₄.

On this basis, we doped our structured PDA@OCPUF redox mediator with Ag NPs by simple dipping a sample in a stirred 50 mM silver nitrate solution for 24 h at room

temperature (Fig. 8a). The presence of Ag NPs on the obtained Ag@PDA@OCPUF material was confirmed by SEM micrographs combined to energy dispersive X-ray spectroscopy (EDX) (Fig 8b and 8c). The SEM images showed that the Ag NPs were not uniformly distributed but were rather present as nanometric clusters (30 – 50 nm) randomly dispersed all over the surface of the modified 3D material, similarly to what we observed with TiO₂ NPs in previous works [27,28]. The mass of Ag NPs immobilized on PDA@OCPUF was estimated to be of *ca.* 3 mg by simply weighing the foams before after silver doping.

Figure 8. PDA@OCPUF doping with Ag NPs (a), SEM images of Ag@PDA@OCPUF (b), and the EDX spectra (c)

The activity of these soft structured catalytic Ag@PDA@OCPUF materials were then evaluated and compared to that of uncoated OCPUF and PDA@OCPUF for the adsorption/reduction of MB in water. Experiments were conducted similarly than for the latter. As can be seen from Fig. 9, a net beneficial effect of Ag NPs on the removal of the MB was observed. Thus, over 95% removal of MB was observed after 25 min for 6 consecutive runs. Moreover, until the third run, the use of Ag@PDA@OCPUF led to about 90% decontamination after only 15 min instead of 25 min for PDA@OCPUF. From run 4 to 6, the rate of MB decontamination observed with Ag@PDA@OCPUF became however similar to that observed with PDA@OCPUF, which may suggest a deactivation of the Ag NPs at this stage.

Figure 9. Percentage of MB removal (50 mL, 2.10^{-5} M) in function of time with Ag@PDA@OCPUF. $[\text{NaBH}_4] = 0.1$ M

4. Conclusion

In summary, we have demonstrated that our recently introduced *Soft Structured Catalytic Support* (S_2CS) [27,28] based on a bioinspired coating of OCPUF by PDA is an efficient support for the reduction of dye. The thin film of PDA onto the OCPUF surface provides RM properties to the open cell foam. Moreover, the RM properties of the PDA@OCPUF S_2CS can be efficiently regenerated by simple exposure to air at room temperature. Finally, it is possible to dope the catalytic activity of the S_2CS after immobilization of Ag NPs on the PDA@OCPUF's surface by simple dipping in a AgNO_3 solution. In conclusion, the strategy presented in this work provides a facile, green approach towards designing *Soft Structured Catalytic Supports* for biological and environmental applications.

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