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Borohydride-Functionalized Polydopamine-Coated Open Cell Polyurethane Foam as a Reusable Soft Structured Material for Reduction Reactions: Application to the Removal of a Dye

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Open cell polyurethane foams coated with mussel-inspired polydopamine can be used as support for borohydride anions through their complexation by the catechol groups of the polydopamine layer. This strong interaction prevents borohydride hydrolysis and oxidation, and based on the redox mediator properties of polydopamine, the so-functionalized polydopamine-coated open cell polyurethane foams can act as efficient and reusable soft structured materials for the reduction of methylene blue in aqueous solution without additional sodium borohydride (NaBH₄). Very low amounts of released boron sub-products and very small potential of hydrogen (pH) increase are observed in comparison to previous processes using dissolved NaBH₄. This considerably reduces the environmental impact of the reducing structured material on the treated wastewater compared to the latter.

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Keywords: wastewater treatment, methylene blue, surface science

INTRODUCTION

The huge production of industrial dyes all over the world (700 000 t/year) and their use for textile applications are responsible of some of the main water contaminants [1]. Based on nitro- and amino-aromatic derivatives, some of

these compounds are highly toxic for human health and the natural environment [2,3]. Over the last decades, many water decontamination processes have been developed. Among them, adsorption systems that use activated charcoal have shown their efficiency but require the frequent renewal of the filter cartridge [2,4,5]. Recent advances in nanotechnologies have allowed the design of efficient photo-catalytic systems that can decompose organic contaminants into harmless end products [6–8]. However, the implementation of ultra-violet (UV) lamps into industrial depollution systems is not suitable because of the high-energy cost that would be required to treat large volumes of wastewater. Alternatively, metallic nanoparticles that use sodium borohydride (NaBH₄) instead of UV lamps as an electron provider have been reported [9–15]. In this approach, the nanocomposite relays electrons from NaBH₄ in an efficient way that leads to the degradation of dyes into non-toxic products. The main problem here is that NaBH₄ is sensitive to water hydrolysis and therefore must be used in large excess. Thus, even though the concentration of dyes to be reduced in wastewater is usually low, this causes an economic problem in addition to environmental issues as hydrolysis of NaBH₄ produces oxidized boron ions and considerably increases the potential of hydrogen (pH) of the treated water.

In order to develop concrete depollution systems that can be used for the decontamination of industrial wastewater, the following points must be taken into account: (i) nanomaterial-based catalysts should be strongly immobilized on a support to avoid the release of nano-objects in the environment, (ii) the chosen support must display an open cell structure to allow the treatment of wastewater with a reasonable flow [16–20], and to make sense (iii), no further

Additional Supporting Information may be found in the online version of this article.

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contamination caused by the depolluting process itself must be released in the treated water. Last but not least, the development of such decontamination tools must integrate the necessity to be built in an environmentally friendly fashion. In view of these requirements, a non-innocent flexible structured material that consists in an open cell polyurethane foam coated with mussel-inspired polydopamine (PDA@OCPUF) and fulfills all the above-mentioned requirements is reported here. The latter indeed acts both as a *protective support* and a *redox-mediator* of NaBH_4 through complexation of the borohydride anions by the catechol groups of the polydopamine (PDA) layer. Thus, the so functionalized structured support (NaBH_4 @PDA@OCPUF) allows the reduction of methylene blue (MB)—which, among the variety of cationic or azo dyes typically reduced by NaBH_4 in the presence of a redox mediator [9–15], was used as a model of dye contaminant—without addition of NaBH_4 in the reaction medium.

Thanks to its well-known redox properties [21,22], PDA indeed (i) stabilizes the grafted borohydride ions against hydrolysis and oxidation, (ii) plays the role of a redox mediator, and (iii) contributes to the reducing ability of the system. Furthermore, thanks to its strong binding abilities [23], PDA only releases a very low amount of borohydride into the medium, and thus allows a good pH control. The preparation of the reactive soft structured material, NaBH_4 @PDA@OCPUF, is described, as well as its reductive properties. The interaction of the borohydride salt with PDA is discussed.

EXPERIMENTAL SECTION

Materials and Methods

Commercial compounds were used as received. Polyurethane open cells foams (Regicell 20) were received 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 $\text{mg} \pm 20$ mg) were used without prior treatment. Dopamine hydrochloride, (99%, A11136), Tris base (99%, A18494), and methylene blue (high purity, A18174) were purchased from Alfa Aesar. NaBH_4 ($\geq 98\%$, 452882), sodium periodate (NaIO_4) ($\geq 99.9\%$, 311448), and benzaldehyde ($\geq 99\%$, B1334) were purchased from Sigma-Aldrich. Water purified by Synergy[®] Water Purification System (Millipore) was used for the preparation of the aqueous solutions and washing procedures. Scanning electron microscopy (SEM) was performed with a Hitachi S800 FEG microscope at the “Centre Technologique des Microstructures” (CT μ) of the University of Lyon I. Samples of NaBH_4 @PDA@OCPUF were deposited on a flat steel holder, coated under vacuum by cathodic sputtering with platinum, and observed under an accelerating voltage of 15 kV. UV-visible measurements for the methylene blue reductions were performed with a Varian Cary 50 Probe spectrophotometer. High Pressure Liquid Chromatography (HPLC) (Agilent 1100; SUPELCOSIL ABZ + PLUS column, 3 μm , 15 $\text{cm} \times 4.6$ mm (Sigma-Aldrich); isocratic eluent: $\text{H}_2\text{O} + 0.1\%$ TFA/acetonitrile 60/40; rate 1 $\text{mL}\cdot\text{min}^{-1}$) coupled to UV detection (250 nm) was used to follow the reduction of benzaldehyde to benzylic alcohol. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) measurements were performed by the “Plateforme Analytique” of the “Institut Pluridisciplinaire Hubert Curien” (CNRS, UMR 7178), Strasbourg, France.

Open Cell Polyurethane Foam (OCPUF) Coating with Polydopamine (PDA)

With O_2 as oxidant: PDA- O_2 @OCPUF. PDA- O_2 @OCPUF foams were prepared according to the published procedure [24] with cubic samples of *ca.* 2 \times 2 \times 2 cm (180

$\text{mg} \pm 20$ mg) of OCPUF. The resulting samples of PDA- O_2 @OCPUF showed a mass increase of *ca.* 1.5 to 5 mg compared to pristine OCPUF.

With NaIO_4 as oxidant: PDA- NaIO_4 @OCPUF. The coating procedure was adapted from that published by V. Ball and collaborators [25]. Dopamine hydrochloride (180 mg) was dissolved in a 50 mM aqueous solution (90 mL) of sodium acetate containing sodium periodate as oxidant (dopamine/oxidant molar ratio of 1/2) and buffered to pH 5 with aqueous HCl (1 M). A cubic sample of OCPUF *ca.* 2 \times 2 \times 2 cm (180 $\text{mg} \pm 20$ mg) was dipped in the stirred solution for 24 h at room temperature. The solution rapidly turned dark brown. The resulting material was then taken out of the solution, and dried overnight in an oven at 67°C. After that, it was dipped again in vigorously stirred water (70 mL) for 10 min, and air-dried. This washing procedure was repeated 5 times, and the dark brown PDA- NaIO_4 @OCPUF was finally dried for two hours in an oven at 67°C, and characterized by SEM. Various samples showed a mass increase of *ca.* 10 to 12 mg compared to pristine OCPUF.

Functionalization of PDA@OCPUF with Sodium Borohydride (NaBH_4)

General procedure. NaBH_4 (567 mg, 15.0 mmol) was dissolved in water (150 mL). A cubic sample of PDA- O_2 @OCPUF or PDA- NaIO_4 @OCPUF (8 cm^3) was dipped in the stirred solution for 10 min at room temperature. The resulting borohydride-functionalized foam was taken out of the solution and dipped in vigorously stirred water (70 mL) for 30 min and air-dried. NaBH_4 @PDA- NaIO_4 @OCPUF was characterized by SEM, and the boron content of NaBH_4 @PDA- O_2 @OCPUF and NaBH_4 @PDA- NaIO_4 @OCPUF samples was determined by ICP-AES (Table S1, Supporting Information).

Regeneration of a “deactivated” NaBH_4 @PDA- NaIO_4 @OCPUF foam. NaBH_4 (567 mg, 15.0 mmol) was dissolved in water (150 mL). A “deactivated” sample of NaBH_4 @PDA- NaIO_4 @OCPUF (8 cm^3) was dipped in the stirred solution for 10 min at 20°C. The resulting borohydride-re-functionalized foam was taken out of the solution and dipped in vigorously stirred water (70 mL) for 30 min and air-dried.

Cyclic Voltammetry

Dopamine was dissolved in Tris buffer containing NaBH_4 at 50 mM. Immediately after the dissolution of dopamine, the solution was subjected to a cyclic voltammetry (CV) scan between -0.6 and $+1.0$ versus the Ag/AgCl reference electrode at a potential scan rate of 100 $\text{mV}\cdot\text{s}^{-1}$. A control experiment was performed with a pure dopamine solution at the same concentration without added NaBH_4 . Note that the pH of the NaBH_4 solution increased to about 10 after the dissolution and had to be readjusted to 8.50 before the dissolution of dopamine. These experiments were performed to investigate the interactions between BH_4^- and dopamine from an electrochemical point of view. The CV experiments were performed in a three-electrode configuration with an amorphous carbon working electrode (ref. CHI 104, CHI Instruments, Austin, TX), a Ag/AgCl reference electrode (ref. CHI 111) and a Pt wire auxiliary electrode (CHI 115). The potential difference between the working and the reference electrode was applied with a CHI 604B potentiostat. The carbon-working electrode was polished with SiC paper and then with alumina slurries of 1 and 0.1 μm (from Escil, Chassieu, France) in diameter before intensive sonication in water baths. The surface state of the amorphous carbon electrode was checked by performing a CV scan between -0.6 and $+1.0$ V versus Ag/AgCl in the presence of Tris buffer containing 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$ (ref. P9387, Sigma-Aldrich). The experiment was only continued if the oxidation peak

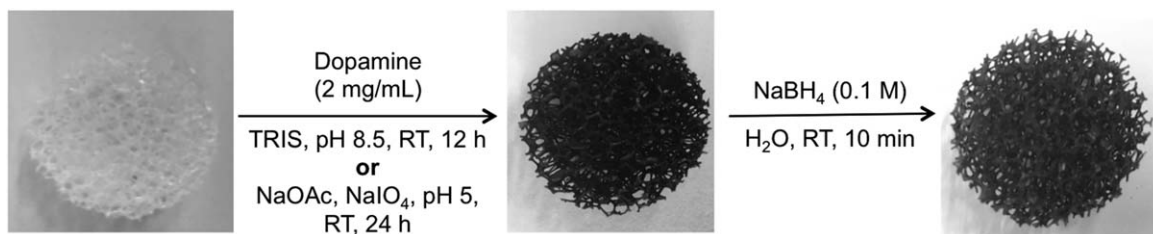


Figure 1. Two-step preparation of NaBH₄@PDA@OCPUF from OCPUF.

potential and the reduction peak potential of K₄Fe(CN)₆ were separated by less than 80 mV, the theoretical value being of 59 mV for a reversible one electron transfer process.

NaBH₄@PDA@OCPUF-Mediated Reduction of Benzaldehyde

A PDA-O₂@OCPUF sample (8 cm³) was functionalized by reaction with 10 mL of a freshly prepared aqueous solution of NaBH₄ (NaBH₄ 22 wt.%, NaOH 22 wt.%) for 1 min, washed with deionized water (10 mL), and subsequently dried with compressed air. The resulting NaBH₄@PDA-O₂@OCPUF material was then dipped in a vigorously stirred solution of benzaldehyde (0.200 mL, 1.97 mmol) in methanol (50 mL) at room temperature and the reaction was followed by HPLC. After 10 min, the conversion was found to be complete and the yield of benzyl alcohol was 100%.

NaBH₄@PDA@OCPUF-Mediated Reduction of Methylene Blue (MB)

In a typical experiment, an aqueous solution of MB (50 mL, 2.10⁻⁵ M) was stirred at room temperature (700 rpm) in the presence of a cubic sample (8 cm³) of NaBH₄@PDA-O₂@OCPUF or NaBH₄@PDA-NaIO₄@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 as a function of the reaction time. The percentage of MB removed from the solution was calculated according to Eq. (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 .

During some experiments, the evolution of the pH of the MB solutions was concomitantly monitored with a Mettler Toledo SG23-FK2 pH-meter. Between two successive runs, the foam was taken out of the reaction medium, washed with water and re-dipped in a fresh solution of MB.

RESULTS AND DISCUSSION

Preparation and Characterization of NaBH₄@PDA@OCPUF

PDA is a biomimetic coating inspired from the mussel adhesion mechanism that can form on almost all kind of materials from a simple, short and green process [23]. The oxygen from the air, naturally present in water, oxidizes dopamine that provides indole derivatives that are able to couple together through aryl-aryl oxidative coupling, thus leading to polydopamine structure [26]. A balance between catechol groups and their oxidized form (*i.e.* *o*-quinone) are disseminated all over the surface, underlying the reductive power of PDA [27,28]. Recently, PDA was shown to play the

role of redox mediator [29], thus allowing the use of soft structured materials such as PDA@OCPUF [24,30] for the efficient reduction of MB in the presence of a large excess of NaBH₄ [31,32]. Although being thermodynamically favorable, the reduction of MB with NaBH₄ is indeed kinetically restricted in the absence of a catalyst [9,10,29].

The molecular mechanism of this catalyzed reduction in the presence of PDA@OCPUF is not clear [31], but some borohydride ions were suspected to reduce the *o*-quinone groups of the PDA layer and then interact with the resulting catechols to lead to a NaBH₄-functionalized PDA@OCPUF material. This suspected behavior has been used to prepare borohydride-functionalized materials (NaBH₄@PDA@OCPUF) by simply dipping samples of PDA@OCPUF into a 0.1 M aqueous solution of NaBH₄ for 10 min (Figure 1). Then a second dipping step was carried out for 30 min in vigorously stirred deionized water to remove any excess of NaBH₄ eventually adsorbed onto PDA@OCPUF. Of note, the characteristic black color of the PDA coating had turned brownish after the dipping step into 0.1 M NaBH₄ solution (Figure S1, Supporting Information). Finally, the foams were dried under a nitrogen flow and stored under air. This procedure was carried out on two kinds of PDA@OCPUF materials: PDA-O₂@OCPUF and PDA-NaIO₄@OCPUF, which differ from each other by the nature of the oxidant used for the PDA coating (see Experimental Section), and thus by the thickness of the PDA coating; the stronger oxidant, NaIO₄, typically yielding the thicker PDA layer [25]. The investigation of these two processes was carried out to get a better understanding of the role of the PDA coating in the reduction reaction of MB.

Simple weighing of several samples of OCPUF of 8 cm³ (ca. 180 mg) before and after the PDA coating revealed a mass difference of 1.5-5 mg for PDA-O₂@OCPUF and of 10-12 mg for PDA-NaIO₄@OCPUF in accordance with what was expected [25]. In contrast, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements on samples of NaBH₄@PDA-NaIO₄@OCPUF and NaBH₄@PDA-O₂@OCPUF revealed similar B contents of 22.4 ± 1.3 mg.kg⁻¹ (*i.e.* 2.07 ± 0.12 μmol.g⁻¹). Scanning electron microscopy (SEM) images of PDA-NaIO₄@OCPUF and NaBH₄@PDA-NaIO₄@OCPUF show aggregates of PDA, having micrometer size, randomly distributed on the whole surface of each foam, as previously reported (Figure 2) [24]. These aggregates appear comprised of several layers on both types of foams. However, a closer comparison of PDA-NaIO₄@OCPUF and NaBH₄@PDA-NaIO₄@OCPUF images indicates that the morphology of PDA seems slightly impacted by the 10 min of dipping step into the NaBH₄ solution. Indeed, the top of the aggregates of NaBH₄@PDA-NaIO₄@OCPUF appears rougher, which may indicate a partial degradation of the PDA layer during the dipping step. This would explain the observed lightening of the characteristic black color of PDA (Figure 1). Furthermore, no adsorbed macroscopic aggregates of NaBH₄ into the PDA plates can be observed on NaBH₄@PDA-NaIO₄@OCPUF (Figure 2b), which tends to indicate that borohydride ions would interact at the molecular scale with PDA.

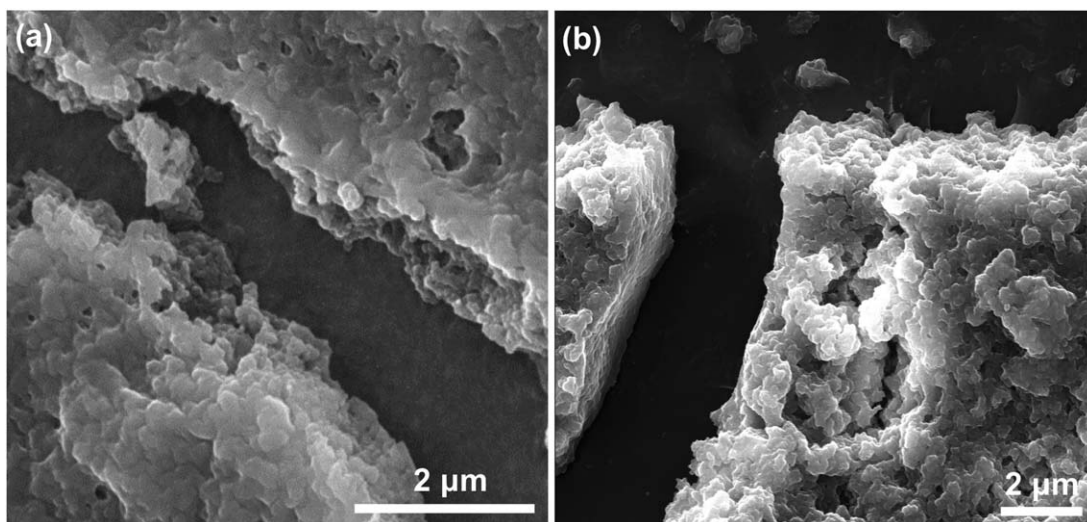


Figure 2. SEM images of PDA-NaIO₄@OCPUF (a) and NaBH₄@PDA-NaIO₄@OCPUF (b).

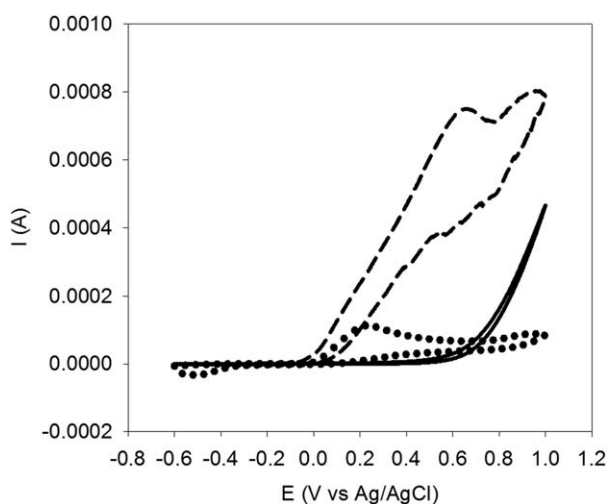


Figure 3. Cyclic voltammetry performed on a NaBH₄ solution (50 mM) (solid curve), a NaBH₄ solution (50 mM) containing dopamine (2 mg.mL⁻¹ or 10.6 mM) (dashed curve) and a dopamine solution (2 mg.mL⁻¹ or 10.6 mM) without added NaBH₄ (dotted curve). The potential scan rate was of 100 mV.s⁻¹. All solutions were made from 50 mM Tris buffer at pH 8.5.

To highlight the interaction between the catechols and the borohydrides, cyclic voltammetry (CV) experiments have been done on dopamine solutions (2 mg.mL⁻¹) to which NaBH₄ had been added to reach a final concentration of 50 mM. The obtained cyclo-voltammogram was compared to that of dopamine without NaBH₄ (Figure 3). The oxidation peak of dopamine was shifted to anodic potentials by about 0.4 V in the presence of NaBH₄, indicating that oxidation was less facile, and thus strongly suggesting the formation of complexes between the catechol moieties and borohydrides. This result is similar to those obtained by performing CV on catechol-boric acid mixtures [33]. In addition, these experiments were performed in the presence of Tris buffer at a pH of 8.5; conditions under which the dopamine solution rapidly turns brownish to its autoxidation in the presence of dissolved O₂. However in the presence of NaBH₄, even if the pH raised transiently above 10—which are conditions even more favorable to dopamine autoxidation—and was

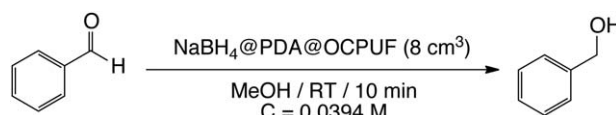


Figure 4. Reduction of benzaldehyde in benzyl alcohol by NaBH₄@PDA-O₂@OCPUF.

readjusted to 8.5, the dopamine solution remained transparent during hours, showing again that dopamine interacts strongly with NaBH₄ and is protected against spontaneous oxidation.

Reduction of Benzaldehyde

The activity of the functionalized foam was first investigated for the reduction of benzaldehyde. When a cubic sample of 8 cm³ of NaBH₄@PDA-O₂@OCPUF was dipped into a 3.94 × 10⁻² M solution of benzaldehyde in methanol (50 mL), the monitoring by HPLC coupled with UV detection showed a complete conversion in benzyl alcohol after 10 min of stirring at room temperature (Figure 4), thus demonstrating the reducing ability of the borohydride-functionalized foam.

Removal of Methylene Blue

The activity of the borohydride-functionalized foam was next evaluated for the reduction of MB in *leuco*-methylene in water. Experiments were conducted by simply immersing a sample of NaBH₄@PDA-NaIO₄@OCPUF (OCPUF: 195 mg; PDA: 12 mg; B: 21.1 mg.kg⁻¹, *i.e.* 0.40 μmol) in a stirred aqueous solution of MB (50 mL, 2 × 10⁻⁵ M, 1 μmol) at room temperature. The reduction of MB was followed by the measure of the decrease of the absorbance peak at 664 nm in the UV-visible spectrum of the reaction medium as a function of time. After 25 min, the functionalized foam was removed from the treated MB solution, rinsed with distilled water, and reused by re-immersion in a fresh solution of MB. Over 97% removal was observed after 25 min in the first run (Figure 5a—NaIO₄ Run 1), leading to a colorless solution (Figure S2, Supporting Information). Remarkably no deactivation was observed in the 2nd and 3rd runs, with discoloration ratios over 95% in 25 min (Figure 5a—NaIO₄ Runs 2 and 3), and only a slight decrease in activity was observed in the 4th and 5th runs with degradation ratios of *ca.* 89 and 87% after 25 min, respectively (Figure 5a—NaIO₄ Runs 4 and

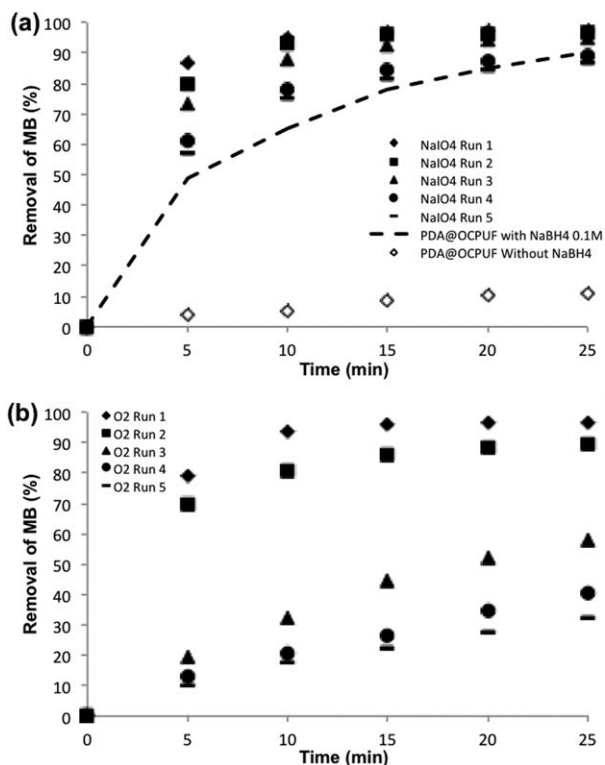


Figure 5. (a) Percentage of MB removal (50 mL, 2×10^{-5} M, $1 \mu\text{mol}$) as a function of reaction time with (i) NaBH₄@PDA-NaIO₄@OCPUF (OCPUF: 195 mg; PDA: 12 mg; B: 21.1 mg/kg, *i.e.* $0.40 \mu\text{mol}$), runs 1 to 5, (ii) PDA@OCPUF with added NaBH₄ in the medium (0.1 M); average activity of 5 consecutive runs [31], and (iii) PDA@OCPUF in the absence of NaBH₄ [31]. (b) Percentage of MB removal (50 mL, 2×10^{-5} M, $1 \mu\text{mol}$) as a function of reaction time with NaBH₄@PDA-O₂@OCPUF (OCPUF: 170 mg; PDA: 4.7 mg; B: 23.7 mg/kg, *i.e.* $0.38 \mu\text{mol}$), runs 1 to 5.

5). Even more remarkably, these results compare advantageously, both in terms of kinetics and efficiency, with the average activity observed for five consecutive runs with PDA@OCPUF (180 mg) in the presence of a large excess of NaBH₄ (0.1 M); a fresh solution of NaBH₄ being used at each run (Figure 5a—PDA@OCPUF with NaBH₄ 0.1 M) [31]. Furthermore, in the absence of NaBH₄, only 11% MB removal was observed after 25 min (Figure 5a—PDA@OCPUF without NaBH₄), which shows that PDA is unable to reduce MB efficiently by itself and that MB adsorption onto PDA is not predominant here.

The influence of the amount of PDA coating was next examined by studying the activity of a sample of NaBH₄@PDA-O₂@OCPUF (OCPUF: 170 mg; PDA: 4.7 mg; B: 23.7 mg.kg⁻¹, *i.e.* $0.38 \mu\text{mol}$) that shows a lower PDA content under similar conditions. About 97% and 90% MB reduction were observed after 25 min in the two first runs, but the activity quickly decreased in the following runs (Figure 5b—O₂ Runs 1 to 5).

Considering (i) that the amount of immobilized boron is similar on both types of NaBH₄@PDA@OCPUF ($0.39 \pm 0.01 \mu\text{mol}$), (ii) that the maximum possible amount of hydrides (*ca.* $1.56 \mu\text{mol}$ if one considers that each B atom corresponds to a BH₄⁻ anion) is too low for the amount of MB to be reduced in the five consecutive runs ($5 \mu\text{mol}$), especially when one considers that these reductions are carried out in water, this clearly shows the importance of PDA in the redox

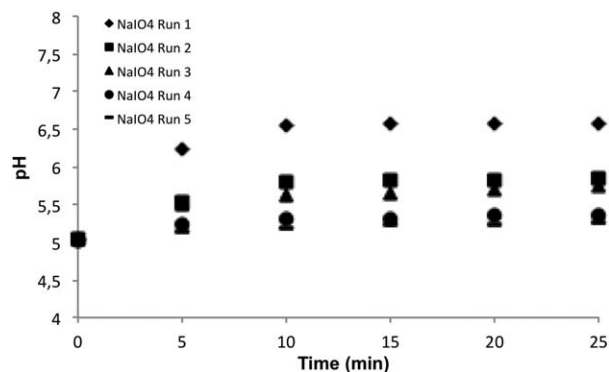


Figure 6. pH variation of the MB solutions treated with NaBH₄@PDA-NaIO₄@OCPUF as a function of reaction time.

process. Thus, in addition to playing the role of a redox mediator (or electro-catalyst) that allows the efficient reduction of MB by borohydrides [29,31,32], PDA presumably prevents the hydrolysis and oxidation of the immobilized borohydrides, and somehow participates to the reduction of MB: the reduced *o*-quinone functionalities (to catechols) that were generated during the NaBH₄-functionalization serving as an additional source of electrons. This would explain that the thicker the PDA layer, the higher the reducing ability of the resulting NaBH₄@PDA@OCPUF material.

The protecting ability of PDA was further confirmed by the behavior of a NaBH₄@PDA-NaIO₄@OCPUF material that was stored for one week in the air before use. Indeed, no significant difference was observed compared to a freshly prepared material (Figure S3, Supporting Information).

As can be inferred from the lower B content of the foams after the five runs ($8 \pm 1 \text{ mg.kg}^{-1}$, Table S1, Supporting Information), some B leaching to the medium was however observed by ICP-AES of the filtrates. This leaching, which may explain the progressive loss of activity of the borohydride-functionalized foams, varies from 4.4×10^{-3} wt.% in the 1st run to 8.0×10^{-4} wt.% in the 5th run with NaBH₄@PDA-NaIO₄@OCPUF and from 6.8×10^{-3} wt.% in the first run to less than 6.0×10^{-4} wt.% in the 5th run with NaBH₄@PDA-O₂@OCPUF. It thus remains very low when compared to the use of a 0.1 M solution of NaBH₄ (0.108 wt.% B) to treat the same amount of MB with PDA@OCPUF [31], which considerably reduces the environmental impact of boron sub-products on the treated wastewater. Furthermore, the low borohydride release into the solutions has also positive consequences on the pH variation of the treated solutions. Whereas the pH of a 0.1 M aqueous solution of NaBH₄ rapidly reaches values ≥ 10 , the pH of the MB solutions treated with a NaBH₄@PDA-NaIO₄@OCPUF material only varies from 5 to 6.6 in the 1st run and from 5 to 5.3 - 5.8 in the following runs (Figure 6). A similar behavior is observed with NaBH₄@PDA-O₂@OCPUF (Figure S4, Supporting Information).

Since the deactivation of the functionalized foam seems to be due to the leaching of borohydrides species, a used NaBH₄@PDA-NaIO₄@OCPUF material was re-functionalized (after 5 runs) by simple dipping in a fresh 0.1 M NaBH₄ solution for 10 min. The reducing activity of the thus re-functionalized foam was next examined under the same conditions as before. Satisfyingly, the first run of the 2nd series led again to over 97% reduction of MB in 25 min. However, in the following runs, the activity decreased a little more quickly than in the 1st series (Figure S5, Supporting Information). This may be due to the possible degradation of the PDA coating during the NaBH₄ dipping treatment as suggested by

the SEM images (Figure 2). This problem may however be circumvented by using recently described PDA deposition processes that should lead to more chemically robust coatings [34,35].

CONCLUSIONS

In summary, an open cell polyurethane foam coated with mussel-inspired polydopamine has been used as both a redox mediator (or electro-catalyst) and a protective support for borohydride ions, neither PDA nor BH_4^- being able to reduce MB efficiently by itself. The borohydrides have been shown by cyclic voltammetry to interact strongly with the catechol groups of polydopamine. This interaction provides protection from water hydrolysis and air oxidation to the borohydride anions, and the thicker the PDA layer, the better the stabilization; the excess catechols (compared to the classical balance of PDA between catechols and *o*-quinones) that were generated during the NaBH_4 -functionalization serving as an additional source of electrons. Thus, without addition of NaBH_4 in solution, which allows important cost savings compared to decontamination processes using solutions of NaBH_4 , the functionalized support can quickly reduce MB (or benzaldehyde) and can be re-used at least three times without loss of its reductive property. In addition, the amount of released boron sub-products and the pH variations are much lower compared to processes using dissolved NaBH_4 , which considerably reduces the environmental impact of the current process on the treated wastewater compared to the latter. Finally, dipping of a deactivated foam into a fresh solution of NaBH_4 partly regenerates its reductive property. Hence, NaBH_4 @PDA@OCPUF appears as highly efficient, reusable, economically advantageous, and environmentally friendly.

Furthermore, it must also be pointed out that PDA@OCPUF is a soft structured material particularly well adapted to industrial applications because of its low cost, light weight, easiness to handle, elastic properties and most importantly here, because water can flow through at high speed with small pressure loss. This work should be useful for further development of decontamination systems of industrial wastewater.

LITERATURE CITED

- Wu, Z., Zhong, H., Yuan, X., Wang, H., Wang, L., Chen, X., Zeng, G., & Wu, Y. (2014). Adsorptive removal of methylene blue by rhamnolipid-functionalized graphene oxide from wastewater, *Water Research*, 67, 330–344.
- Rafatullah, M., Sulaiman, O., Hashim, R., & Ahmad, A. (2010). Adsorption of methylene blue on low-cost adsorbents: A review, *Journal of Hazardous Materials*, 177, 70–80.
- Hu, L., Yang, F., Lu, W., Hao, Y., & Yuan, H. (2013). Heterogeneous activation of oxone with CoMg/SBA-15 for the degradation of dye Rhodamine B in aqueous solution, *Applied Catalysis B*, 134–135, 7–18.
- Paulino, A.T., Guilherme, M.R., Reis, A.V., Campese, G.M., Muniz, E.C., & Nozaki, J. (2006). Removal of methylene blue dye from an aqueous media using superabsorbent hydrogel supported on modified polysaccharide, *Journal of Colloid and Interface Science*, 301, 55–62.
- Ali, I. (2012). New generation adsorbents for water treatment, *Chemical Reviews*, 112, 5073–5091.
- Khan, M.M., Ansari, S.A., Amal, M.I., Lee, J., & Cho, M.H. (2013). Highly visible light active Ag@TiO_2 nanocomposites synthesized using an electrochemically active biofilm: a novel biogenic approach, *Nanoscale*, 5, 4427–4435.
- Thomas, J., & Yoon, M. (2012). Facile synthesis of pure $\text{TiO}_2(\text{B})$ nanofibers doped with gold nanoparticles and solar photocatalytic activities, *Applied Catalysis B*, 111–112, 502–508.
- Rauf, M.A., & Ashraf, S. (2009). Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution, *Chemical Engineering Journal*, 151, 10–18.
- Gupta, N., Singh, H.P., & Sharma, R.K. (2011). Metal nanoparticles with high catalytic activity in degradation of methyl orange: an electron relay effect, *Journal of Molecular Catalysis A*, 335, 248–252.
- Khan, M.M., Lee, J., & Cho, M.H. (2014). Au@TiO_2 nanocomposites for the catalytic degradation of methyl orange and methylene blue: an electron relay effect, *Journal of Industrial and Engineering Chemistry*, 20, 1584–1590.
- Ali, N., Awais, Kamal, T., Ul-Islam, M., Khan, A., Shah, S.J., & Zada, A. (2018). Chitosan-coated cotton cloth supported copper nanoparticles for toxic dye reduction. *International Journal of Biological Macromolecules.*, 111, 832–838.
- Zhou, X., Wan, J., Liu, Y., Liu, D., Wang, H., Lai, X., Zou, Y., Lin, G., & Chen, J. (2017). Size-controlled silver nanoparticles confined in ordered mesoporous silica and their enhanced catalytic activities. *Nano*, 12, 1750104.
- Wang, N., Hu, Y., & Zhang, Z. (2017). Sustainable catalytic properties of silver nanoparticles supported montmorillonite for highly efficient recyclable reduction of methylene blue, *Applied Clay Science*, 150, 47–55.
- Kohantorabi, M., & Gholami, M.R. (2017). $\text{M} = \text{Ag}$, and Co) nanoparticles supported on CeO_2 nanorods derived from Ce–metal organic frameworks as an effective catalyst for reduction of organic pollutants: Langmuir-Hinshelwood kinetics and mechanism, *New Journal of Chemistry*, 41, 10948–10958. MxNi100
- Mallikarjuna, K., Raju, B.D.P., Park, S., & Kim, H. (2017). Synthesis and catalytic activity of alkylamine-capped ultra-small palladium nanoparticles for organic pollutant degradation, *Journal of Cluster Science*, 28, 2833–2846.
- Bakker, J.J.W., Groendijk, W.J., de Lathouder, K.M., Kapteijn, F., Moulijn, J.A., Kreutzer, M.T., & Wallin, S.A. (2007). Enhancement of catalyst performance using pressure pulses on macroporous structured catalysts, *Industrial & Engineering Chemistry Research*, 46, 8574–8583.
- Edouard, D., Lacroix, M., Pham Huu, C., & Luck, F. (2008). Pressure drop modeling on SOLID foam: state of the art correlation, *Chemical Engineering Journal*, 144, 299–311.
- Truong Huu, T., Lacroix, M., Pham Huu, C., Schweich, D., & Edouard, D. (2009). Towards a more realistic modeling of solid foam: use of the pentagonal dodecahedron geometry, *Chemical Engineering Science*, 64, 5131–5142.
- Richardson, J.T., Remue, D., & Hung, J.-K. (2003). Properties of ceramic foam catalyst supports: mass and heat transfer, *Applied Catalysis A*, 250, 319–329.
- Giani, L., Groppi, G., & Tronconi, E. (2005). Mass-transfer characterization of metallic foams as supports for structured catalysts, *Industrial & Engineering Chemistry Research*, 44, 4993–5002.
- Liu, Y., Ai, K., & Lu, L. (2014). Polydopamine and its derivative materials: synthesis and promising applications in energy, environmental, and biomedical fields, *Chemical Reviews*, 114, 5057–5115.
- Kim, J.H., Lee, M., & Park, C.B. (2014). Polydopamine as a biomimetic electron gate for artificial photosynthesis, *Angewandte Chemie International Edition*, 53, 6364–6368.
- Lee, H., Dellatore, S.M., Miller, W.M., & Messersmith, P.B. (2007). Mussel-Inspired Surface Chemistry for Multifunctional Coatings, *Science*, 318, 426–430.

24. Pardieu, E., Chau, N.T.T., Dintzer, T., Romero, T., Favier, D., Roland, T., Edouard, D., Jierry, L., & Ritleng, V. (2016). Polydopamine-coated open cell polyurethane foams as an inexpensive, flexible yet robust catalyst support: a proof of concept, *Chemical Communications*, 52, 4691–4693.
 25. Ponzio, F., Barthès, J., Bour, J., Michel, M., Bertani, P., Hemmerlé, J., d'Ischia, M., & Ball, V. (2016). Oxidant control of polydopamine surface chemistry in acids: a mechanism-based entry to superhydrophilic-superoleophobic coatings, *Chemistry of Materials*, 28, 4697–4705.
 26. Kang, X., Cai, W., Zhang, S., & Cui, S. (2017). Revealing the formation mechanism of insoluble polydopamine by using a simplified model, *Polymer Chemistry*, 8, 860–864.
 27. Zangmeister, R.A., Morris, T.A., & Tarlov, M.J. (2013). Characterization of polydopamine thin films deposited at short times by autoxidation of dopamine, *Langmuir*, 29, 8619–8628.
 28. Bernsmann, F., Ponche, A., Ringwald, C., Hemmerlé, J., Raya, J., Bechinger, B., Voegel, J.-C., Schaaf, P., & Ball, V. (2009). Characterization of dopamine-melanin growth on silicon oxide, *The Journal of Physical Chemistry C*, 113, 8234–8242.
 29. Du, S., Liao, Z., Qin, Z., Zuo, F., & Li, X. (2015). Polydopamine microparticles as redox mediators for catalytic reduction of methylene blue and rhodamine B, *Catalysis Communications*, 72, 86–90.
 30. Edouard, D., Ritleng, V., Jierry, L., Chau Dalencon, N.T.T. (2016). Method for modifying the surface properties of elastomer cellular foams. WO 2016012689 A2.
 31. Lefebvre, L., Kelber, J., Jierry, L., Ritleng, V., & Edouard, D. (2017). Polydopamine-coated open cell polyurethane foam as an efficient and easy-to-regenerate soft structured catalytic support (S2CS) for the reduction of dye, *Journal of Environmental Chemical Engineering*, 5, 79–85.
 32. Edouard, D., Lefebvre, L., Jierry, L., Ritleng, V., Kelber, J. (2018). Reduction kit, reducing composition and use of said kit and composition. WO 2018020146 A1.
 33. Rafiee, M., & Nematollahi, D. (2008). Electrochemical study of catechol-boric acid complexes, *Electrochimica Acta*, 53, 2751–2756.
 34. Zhang, C., Ou, Y., Lei, W.-X., Wan, L.-S., Ji, J., & Xu, Z.-K. (2016). CuSO₄/H₂O₂-induced rapid deposition of polydopamine coatings with high uniformity and enhanced stability, *Angewandte Chemie International Edition*, 55, 3054–3057.
 35. Yang, H.-C., Liao, K.-J., Huang, H., Wu, Q.-Y., Wan, L.-S., & Xu, Z.-K. (2014). Mussel-inspired modification of a polymer membrane for ultra-high water permeability and oil-in-water emulsion separation, *Journal of Materials Chemistry A*, 2, 10225–10230.
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