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Continuous adsorption of metal ions based on an elastic and reusable polydopamine-modified foam

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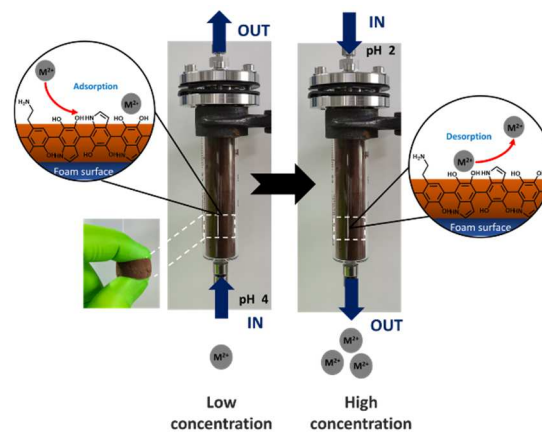
Highlights

- Ultrarapid PDA deposition based on the compression-decompression of melamine foam.
- The resulting **me@PDA** is a low-cost, robust and flexible adsorbent.
- **me@PDA** adsorbs ppm/ppb of Pb(II) in a continuous process with a low pressure drop.
- Adsorption/desorption cycles were realized without loss of the **me@PDA** efficiency.
- Compression allows higher specific surface in a given volume increasing adsorption.

Abstract

Given the limited resources and the growing demand for critical metals as well as the strict environmental regulations, it is essential to develop new metals recovery technologies (more efficient, less expensive and environmentally friendly) especially concerning the treatment of high volume of diluted wastes. In this sense, continuous flow processes appear as the best alternative. But this approach requires suitable adsorbents in term of low pressure drop and ability to adsorb ppm or even ppb traces of metal which are *sine qua non* key-features. Herein, we have modified the surface of a commercially available open cell melamine foam using the mussel inspired chemistry through an original and ultrafast process. This non-toxic bioinspired coating is based on the polymerization of polyphenols such as dopamine leading to a commonly called polydopamine (PDA) layer resulting to **me@PDA** adsorbent. Using Pb(II) as model, we have demonstrated its efficient adsorption even from ppb level, leading to a capacity of 1.2 mmol.g⁻¹ determined from a continuous process. By increasing the path passing through **me@PDA**, it is observed an increase of the Pb(II) loading capacity concomitantly with the PDA mass. Since **me@PDA** is an elastic adsorbent, its compression in the filtration column to insert more foam results in an increase of Pb(II) adsorbed without significant increase of the pressure drop. Furthermore, desorption is obtained using a flow of acid solution. Finally, the similarity of three successive cycles of adsorption-desorption of Pb(II) highlights the repeatability of the process and the chemical robustness of the adsorbent **me@PDA** as designed.

Graphical abstract



Keywords

Polydopamine, open-cell polymer foam, continuous process, recyclability, flexible adsorbent.

1. Introduction

Nowadays, heavy metals pollution is one of the most important environmental problems even threatening human life. Many industries produce and discharge wastewater containing various kinds of metals into the environment, such as mining and smelting of metalliferous ores, surface finishing industry, energy and fuel production, fertilizer and pesticide industry, metallurgy, electroplating, electrolysis, electro-osmosis, etc. [1]. The technologies currently used for the wastewater treatment by industries such as chemical precipitation, membrane filtration, ion exchange, flocculation and coagulation have two major limitations [2]: first, they lead to the formation of solid wastes that must be treated in a second step or be stocked in landfill sites; second, the treated effluents still contain toxic metals in concentration of traces. Even if they are released into the environment in trace amounts respecting the legal thresholds, it has been shown that they accumulate locally in living organisms (plants, bugs, fish, algae, etc.) and then exceed the toxicity thresholds leading to an entire contamination of the food chain. In addition, since the level of metal accepted by the international communities is becoming more and more restrictive through regular changes of standards, the future of these technologies is compromised. Among the alternative approaches developed so far, adsorption process is considered as one of the most promising technologies for metal removal in wastewater due to its flexibility in design and operation, sludge free operation, possibility to concentrate the diluted effluents and potential for regeneration of sorbents (recycling), e.g. by desorption [3]. Several materials have been reported to adsorb metals present in wastewater, such as activated carbon, [4] polymer resins, [5] and nanomaterials [6]. Despite their effectiveness in fixing heavy metals, their uses can cause high pressure drops and require to filter or centrifuge the decontaminated water, which induces additional treatment steps. Furthermore, the preparation of these materials and their further treatment are expensive. Last but not least, these approaches are difficult to transpose for large-scale applications. Thus, the design of a suitable adsorbent allowing the adsorption and desorption of metallic ions in a continuous process would be of high interest.

Mussel-inspired coating is a biomimetic and universal approach to coat efficiently all kinds of material with a robust polyphenolic film whatever the nature and the shape of the substrate [7]. By using oxidizing conditions in water and at room temperature, phenolic derivatives start to polymerize leading to a robust film strongly anchored on the surface of the material dipped in this aqueous

solution [8]. This polyphenolic layer exhibits phenol groups providing thus the following new features to the material [9]: UV protection (oxidized polyphenols-based films absorb in the visible and the UV spectral window), radical scavengers (polyphenols derivatives are excellent reductive agents and thus entrap radicals) and flame-retardant properties, for instance. Since phenols are reactive chemical groups that can be easily transformed, the introduction of additional components all along the polyphenolic layer is possible through a covalent grafting for catalysis or biomedical applications [10-12]. Finally, catechol moieties (*i.e.* 1,2-dihydroxyphenol) in polyphenolic structures are excellent chemical ligand for many metal ions through coordination [13]. This supramolecular interaction can be displaced in acidic conditions and is thus reversible by definition. In the last decade, functionalization of materials with an oxidized polyphenol film for metal removal processes has been reported. Among the polyphenols commercially available, dopamine is the most used one, leading to polydopamine (PDA) layer. The decoration of magnetic nanoparticles with PDA was described in 2014 to get high specific surface in order to adsorb a maximum of metal ions [14]. These nanoparticles can be easily removed from the batch by using a strong magnet. Tannic acid derived coating on silica nanoparticles was also shown to be efficient to remove copper salts from contaminated water [15]. A quite similar approach has been investigated to modify the surface of zeolites for the same purpose [16]. In addition to inorganic support, polymer-based materials were also investigated, in particular non-woven polymer fibers. In 2020, it was shown that non-woven poly(propylene) can be first modified by PDA and by salicylic acid in a second step to increase the adsorption capacity of the so-prepared adsorbent toward Cu(II), Cd(II) and Pb(II) [17]. So far, all these investigations have highlighted the ability to support polyphenolic film and then get a powerful material to remove metal ions. But none of them can be used, and reused, in an efficient continuous process. Very recently, polymer foams coated by polyphenolic films were described. Indeed, in 2019 Turco *et al.* [18] have reported the PDA modification of poly(dimethylsiloxane) foam as an adsorbent of Cu(II) in batch conditions. Optimization of the capacity of adsorption was done through the successive addition of PDA layers. Acidic solutions were used to remove the copper ions but no re-usability of the adsorbent has been mentioned. As far as we know, open-cell polymer foams coated with an oxidized polyphenolic layer has never been reported for continuous adsorption/desorption cycles of metal ions. Herein, we demonstrate the possibility of coating melamine foams in an ultra-fast way by using compression/relaxation of the elastic material which increases the exchanges between the interior of the foam and the exterior of the foam. We will demonstrate the possibility of using this material as an adsorbent of metal ions in plug-flow reactors for the reversible capture of metals in water. Using the elastic property of an adsorbent is a paradigm shift in the field of waste water filtration, paving the way toward to the design of new kind of filtration devices.

2. Experimental methods

Details regarding the materials and chemicals (Section A1), the preparation and characterization of **me@PDA** (Section A2), the description of batch adsorption and desorption experiments (Section A3), the PDA surface study by infrared spectroscopy (Section A4), the dynamic adsorption/desorption experiments (Section A5) and the additional Figures A1-A9 were provided in the Appendix.

3. Results and discussion

3.1. Preparation and characterization of the adsorbent me@PDA

The adsorbent material used is a surface-modified melamine foam with a mussel-inspired chemistry, *i.e.* a polydopamine coating [7]. It is prepared through a single step from commercially available open-cell melamine foam, a porous and cheap polymer material. This starting material is lightweight (density: $9.5 \times 10^{-6} \text{ g}\cdot\text{mm}^{-3}$) and displays a specific surface of $6 \times 10^5 \text{ mm}^2$ according to X-ray tomography analyses (Fig. 1a and A1). The average cell diameter is roughly 200 μm . Dipping processes are largely described in the literature to get PDA films from dopamine and sodium periodate aqueous solution [16-18]. Despite its simplicity, this approach requires several days to coat polymer foam samples with PDA (including the drying steps) and this duration is not suitable for its transfer to industry and thus for large-scale applications [19,20]. To circumvent this aspect, the group of Haeshin Lee has developed an ultrafast process based on spraying [21]. This method has achieved successes on planar substrates resulting in PDA coating in few minutes [22]. However, the spraying method is not adequate for the PDA coating of a 3D porous material, especially when the functionalization of the whole surface within the foam is required. Melamine foam is a visco-elastic material and this feature was used to design an original process to get a PDA coating on the melamine foam in less than 30 min: simple repeated cycles of compression/release of the melamine foam in contact with a solution of dopamine and sodium periodate, followed by a drying step (1h), lead to the whole deposition of PDA on the foam surface (Fig. A2). Starting from a white cylinder model sample of melamine foam (diameter 2 cm; height 2 cm; 46.4 mg), called **me@ref**, our PDA coating process leads to fully black-colored sample of **me@PDA**, both outside and inside the foam (Fig. 1b and c). A $8.8 \pm 1.7 \text{ wt}\%$ ($4.6 \pm 1.0 \text{ mg}$, Fig. A3) increase is measured for **me@PDA** compared to **me@ref** and the scanning electron microscopy (SEM) images show a similar rough PDA coating everywhere on the edges of the foam, as expected for PDA (Fig. 1d, e and SEM magnifications in Fig. A4). In addition, the chemical analysis of this PDA layer displays the same X-ray photoelectron spectroscopy (XPS) and IR spectra (Fig. A5 and A8) than those reported with PDA obtained through a dipping process [23,24]. Finally, the Young modulus of **me@ref** and **me@PDA** are roughly equivalent around 0.4 kPa showing that the polyphenolic coating does not change the rigidity of the foam (Fig. A6).

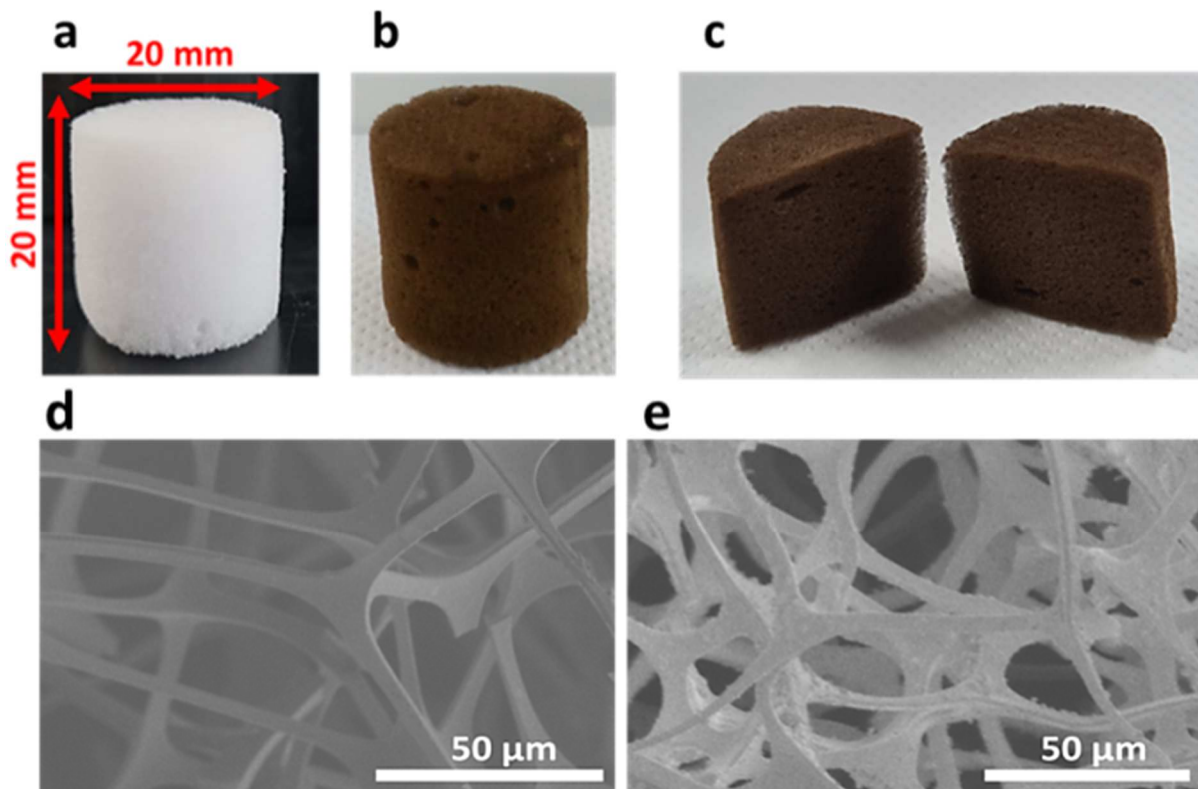


Fig. 1. (a) commercially available melamine foam **me@ref**, (b) a model sample of **me@PDA**, (c) cut vertically in two pieces. SEM images of (d) **me@ref** and (e) **me@PDA**.

3.2 Batch adsorption studies

3.2.1. **me@PDA** performance in the heavy metal's adsorption

To evaluate the ability of **me@PDA** to adsorb metal ions, one sample of **me@PDA** was dipped in 20 mL 0.1M NaNO₃ solution at pH 4 containing five different species at the same molar concentration, *i.e.* 0.2 mM (Fig. 2a). The presence of NaNO₃ fixes the ionic strength of solution. The metal ions used to prepare the test solution are nitrate salts of Pb(II), Cu(II), Ni(II), Zn(II) and Cd(II). A strong selectivity for Cu(II) and Pb(II) was observed since 26.4 and 50.5% of Pb(II) and Cu(II) respectively were adsorbed when less than 2% for the three other metals (Fig. 2b). This preference for these two metals is in agreement with reported results in the literature [13]. Cd(II) can also be adsorbed on **me@PDA** when this metal is solely present in the solution (0.2 mM, NaNO₃ 0.1M, pH 4) leading to 90% of adsorption and showing the competition between the different ions when simultaneously presents. When **me@ref** is used instead of **me@PDA**, no adsorption is measured 24h after the dipping of the foam. Despite the stronger adsorption of Cu(II), Pb(II) was chosen as metal model for the kinetic, equilibrium and reusability studies of **me@PDA** because lead is one of the most toxic heavy metals, with mutagenic and carcinogenic potential. Besides, Pb(II) is a widespread contaminant since it is used in many industries including electroplating, battery, pesticides [25].

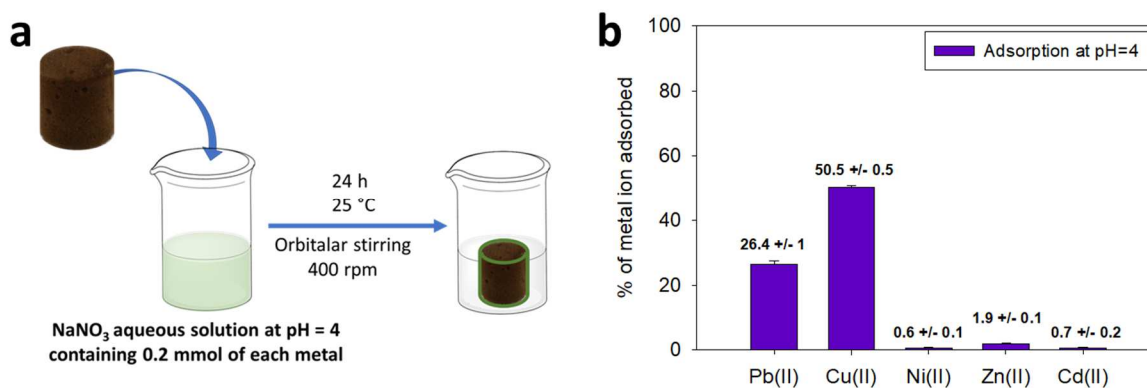


Fig. 2. (a) Schematic of the batch adsorption experiment and conditions used. (b) % mass of metal ions adsorbed on one sample of **me@PDA** 24h after its dipping. Mean values and standard deviations were calculated from three independent measurements.

3.2.2 Kinetic, equilibrium and desorption of Pb(II) in batch conditions

When one sample of **me@PDA** is dipped in 20 mL of $C_0 = 100$ ppm of Pb(II), we observed that 24% of the metal is adsorbed in less than 30 minutes (Fig. 3a) which is remarkable for a non-powder material. The equilibrium concentration (C_{eq}) is reached in less than 1200 minutes with a plateau corresponding to 52 % of the Pb(II) for the specific experimental conditions used. The determination of the maximum adsorption capacity of **me@PDA** is another essential feature for further design of metals recovery treatments. Thus, we established the adsorption isotherm of Pb(II) from one sample of **me@PDA** after 24h of contact (Fig. 3b). Overall, an increase of adsorption capacities was observed as the equilibrium concentration increases. However, the isotherm shape was slightly different from *H*- or *L*-shaped isotherms most commonly encountered. This isotherm was a double S-shaped isotherm with two inflection points and an almost vertical first slope at very low concentration of Pb(II) [26]. This type of isotherm has two possible origins. They have been firstly described as isotherms found for adsorption processes in which the energy of activation for the removal of solute is concentration dependent. It is sometimes found under the name “cooperative adsorption”, the adsorption being easier as concentration rises [26,27]. The first S-shape (until $C_{eq} = 1.2$ mmol.L⁻¹) is attributed to adsorption on the adsorption sites and the second to the formation of adsorption clusters. Another potential cause of the obtainment of S-shaped isotherms is the presence of competing reactions within the solution, which has also been discussed by Giles *et al.* and was illustrated by Limousin *et al.* [26,27]. The latter stated that S-shaped isotherms originate from the presence of at least two mechanisms, one at low metal concentrations and one at higher metal concentrations. The inflection point near $C_{eq} = 2$ mmol.L⁻¹ corresponds to a change of selectivity, which can be caused by the involvement of several types of binding sites [28]. This is consistent with the **me@PDA** adsorbent nature since catechol groups and nitrogen heteroatoms from PDA’s structure are two different kinds of ligand having both a strong propensity to interact with positively charged metal ion species [29]. The maximum experimental capacity was 1.2 mmol of Pb(II).g PDA⁻¹. This adsorption amount of Pb(II) is superior to similar technologies reported [30,31,32,33]. A comparison between **me@PDA** and some previously reported adsorbents are summarized in Table A1.

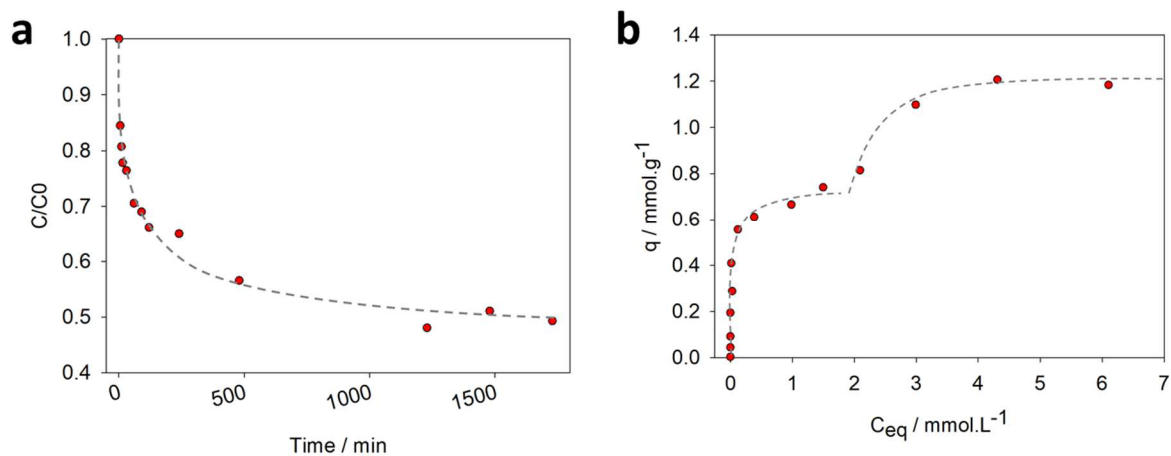


Fig. 3. (a) Adsorption kinetic of Pb(II) ($C_0 = 100$ ppm) in presence of one sample of **me@PDA**. (b) Adsorption isotherm of **me@PDA** $C_0 = 1 - 200$ ppm Pb(II). For (a) and (b), media: 0.1 M NaNO₃; 25°C ± 1; pH₀ = 4. The curved dotted line represents an eye guide.

Regeneration and reusability of the adsorbent are criteria that directly influence the cost-effectiveness of the sorption process [34]. The potential of reusability of **me@PDA** was estimated in batch conditions using an aqueous solution at pH 2 (0.1 M NaNO₃). At this pH value, the protonation of catechol and the amine groups leads to the desorption of all metal ion considered. In our case, when 1.2 mmol.g⁻¹ of PDA is adsorbed on **me@PDA**, we observed 94.7 % of desorption 24 hours after a dipping step at pH 2. PDA structure analysis before Pb(II) absorption and after the acidic desorption was realized by infrared spectroscopy showing no structural changes of the polyphenolic layer (Fig. A7 and A8). This is in agreement with a second cycle of adsorption and desorption resulting in an equivalent proportion of Pb(II) desorbed (98.2%). Finally, 650 ppb effluent concentration of Pb(II) can be also quasi-entirely filtrated (2.9 ppb) using **me@PDA** demonstrating the ability of **me@PDA** for traces decontamination of waste water. These performances in batch conditions encourage to apply it as adsorbent in a continuous process.

3.3. me@PDA applied in a continuous process

Because of its polymer nature, **me@PDA** is a lightweight material that can be easily cut up and implemented in a tubular column for continuous developments. Thus, we have designed a continuous filtration device equipped with a 11 cm height glass tube that can be filled with five pieces of **me@PDA** (Fig. 4a and A9). Two pressure sensors on the filtration column inlet and outlet, an adequate pump and a fraction collector complete this system. We have studied the ability of **me@PDA** to adsorb Pb(II) from a 10 ppm concentration (pH 4, NaNO₃ 0.1 M, 25°C) at a 0.5 mL.min⁻¹ of flow rate. The desorption was realized with a more acidic solution (pH 2, NaNO₃ 0.1 M, 25°C) at the same flow rate. A first set of three cycles of adsorption (ADS1, ADS2 and ADS3) and desorption (DES1, DES2 and DES3) was studied using three **me@PDA** packed in the filtration column.

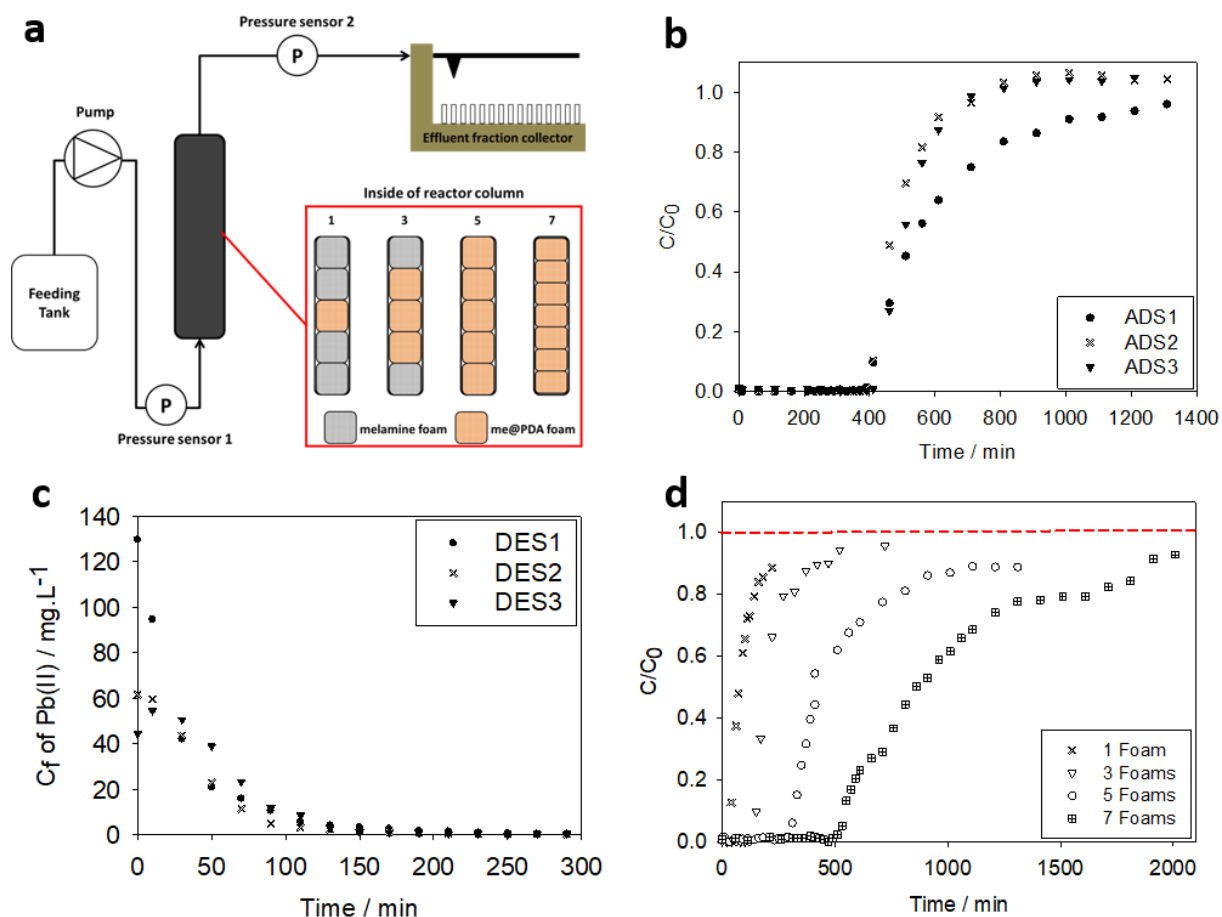


Fig. 4. (a) Setup used for the evaluation of *me@PDA* as Pb(II) adsorbent in a continuous process. (b) Three successive dynamic (b) adsorption (ADS1, ADS2 and ADS3, $C_0 = 10$ ppm Pb(II)) and (c) desorption (DES1, DES2 and DES3) cycles (flow rate = $0.5 \text{ mL}\cdot\text{min}^{-1}$) when five *me@PDA* are filling the column. (d) Comparison of the adsorption capacity of one, three, five and seven *me@PDA* filling the filtration column. A test with seven *me@PDA*, squeezed in the column, was realized as well.

Fig. 4b reveals breakthrough curves with a quick increase in Pb(II) concentration after the breakthrough time was reached at column outlet. This behaviour suggests a smaller mass transfer zone close to a step function which is the type of curve with ideal behaviour [35]. Fig 4b and 4c show a satisfactory adsorption and regeneration potential of the adsorbent in continuous flow, removing Pb(II) appropriately over three cycles at least. The adsorption curve ADS1 of the first run is slightly different than the two others, *i.e.* ADS2 and ADS3. This could be linked to a wettability effect since the *me@PDA* are dried at the first run and are wet at the second and third run. The complete desorption of Pb(II) from *me@PDA* is in accordance with the disappearance of the Pb signals in the XPS spectrum after desorption (Fig. A5). The breakthrough time remained considerably stable in the three cycles, with 370, 390 and 410 min, respectively when five *me@PDA* filled the column. It is also observed that breakthrough curves and capacities ($q_b / \text{mmol}\cdot\text{L}^{-1}$ run 1: 0.27; run 2: 0.29 and run 3: 0.31) during three cycles are quasi-similar confirming the potential of *me@PDA* as an efficient reusable adsorbent of metal ions through a continuous flow process. Furthermore, thanks to its elastic feature, the compression of polymer foam within a given volume should increase the global specific surface available to adsorb more metallic ions and thus increase the competitiveness of the proposed system

(Fig. 4d). The breakthrough time and adsorption capacities increase with the number of foams: 1, 3, 5 and 7 foams correspond to breakthrough capacities of 49.7, 60.0, 70.4 and 82.8 mg of Pb.g PDA⁻¹, respectively. This result shows an increasing adsorption capacity when the number of **me@PDA** are packed and even squeezed. A linear relation with the amount of PDA and the adsorption capacity of Pb(II) is observed (Fig. A10). In addition, thanks to the large pore of the adsorbent, a pressure drop difference value below 0.1 bar is measured for both the non-compressed (one, three and five **me@PDA**) and the compressed system (seven **me@PDA**) when the filtration process is in operation.

4. Conclusions

me@PDA is an available and cost-effective material used to recover ppm or ppb level of Pb(II) from effluents. Compared to other kinds of adsorbents, such as powder, (nano)particles or woven polymer fibres, polydopamine-modified foams are effective adsorbents resulting in 1.2 mmol Pb(II).g⁻¹ PDA. This adsorption amount of Pb(II) is superior compared to similar technologies. Furthermore, such adsorbents are cheap, safe, easy to prepare and easy to use material. Based on its porous structure, open-cell foam is a lightweight support and can be used in continuous process with reduced pressure drop. Last but not least, we have shown that polydopamine-modified foams can be squeezed, keeping its adsorbent properties. This unique property paves the way toward the design of original filtration devices. The performance achieved in the repeatability of the successive adsorption and desorption steps enables us to develop a filtration device suitable for real effluent filtration. But first, optimization of operational conditions in flow are necessary to maximize the metal ions adsorption and minimise the mass transfer resistances. These investigations are currently in progress in our groups. Then, for potential industrialization, large-scale production of modified foams and hydrodynamic problems such as the suppression of preferential flow paths through the foams are expected problems to address.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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