

Combined Approach To Remove and Fast Detect Heavy Metals in Water Based on PES–TiO₂ Electrospun Mats and Porphyrin Chemosensors

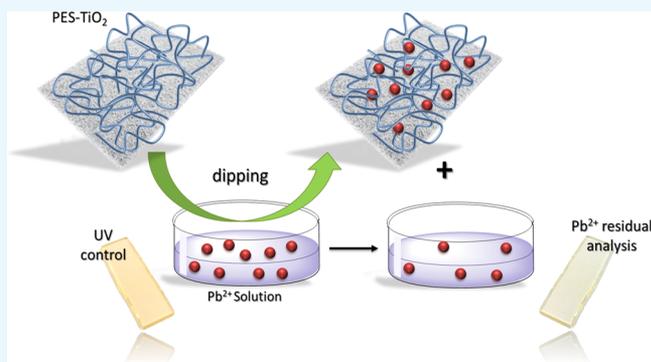
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Supporting Information

ABSTRACT: Hybrid poly(ether sulfones) (PES)–TiO₂ electrospun mats are used as selective filters to remove lead and zinc ions from water. Presence of TiO₂ is functional to trigger fiber’s surface charge that allows for better performances in terms of ionic adsorption with respect to bare PES mats. Temperature increase promotes a speed up of ion removal. Ability of electrospun mats to retain adsorbed ions is proven by washing procedures, which confirm the lack of released Pb²⁺ in solution, even after sonication. To detect presence of metal ions in aqueous solutions, water-soluble porphyrins are used as chemosensors, which are able to provide fast, in-field, and real-time analysis. In particular, cationic H2T4 metalation, occurring both in solution or at transparent glass surface, allows for a straightforward spectrophotometric (UV–vis) detection of metal ions in solution.



INTRODUCTION

Water shortening is a global problem threatening modern society, and, consequently, there is a worldwide urgency to provide solutions allowing for treatment and reuse of the reclaimed wastewater. Heavy metals, such as Pb, Cd, Cr, Cu, Ni, As, and Zn, are environmental pollutants extensively existing in water; they can be discharged into the water sources from various human activities, especially from industrial one. Even at trace levels, they are poisonous to human health because of their nonbiodegradability and bioaccumulation in the human body and therefore causing various diseases and disorders.¹ In particular, lead, in both its forms Pb²⁺ and Pb⁴⁺, is one of the extremely toxic heavy metals, even at low concentrations.^{2,3} Hence, it seems a priority to treat lead contaminated wastewaters before releasing them into the environment. Removal of lead is achieved by one or more of the methods like chemical precipitation, adsorption, ion exchange, ultrafiltration, reverse osmosis, electrodeposition, solvent extraction, foam floatation, complexation/sequestration, filtration, and evaporation.⁴ Among all these techniques, adsorption is considered a very effective and economical process for metal ions removal from wastewaters due to availability of several low-cost, easily accessible and more important there is no release or use of secondary pollutants.

Fibrous electrospun mats represent an innovative solution to face out water pollution:^{5,6} in fact, electrospinning is an easy and highly versatile technique, which allows for fabrication of one-

dimensional micro/nanofibers characterized by very high surface area, porosity, and tailored mechanical properties.⁷ Use of fibrous mats to eliminate metal ions from water have been recently proposed,^{5,8} and potentialities of electrospun mats as sorbent materials to be used for water treatment purpose have been discussed in many papers,⁹ especially by considering the versatility of electrospinning technique in fabrication of polymeric and ceramic materials in nanofibrous form.⁵ Moreover, electrospun mats can be obtained as self-supporting veils, which can be additively manufactured to conventional membranes and filters to provide them additional functionalities. Different polymers are under investigation, and contaminants removal is achieved by exploiting the ability of these polymer-based materials to interact with polluting species by dispersive forces, electrostatic or chemical interactions, depending on the nature of used polymers and/or presence of functional molecules attached onto fibers surface.⁸ To our knowledge, few papers report about use of poly(ether sulfone) (PES) electrospun nanofibers for water contaminants removal, whereas most of the literature data refer to copolymer electrospun mats based on, for example, poly(acrylic acid) (PAA)/poly(vinyl alcohol) (PVA)¹⁰ or nylon-6 and polycaprolactone.¹¹ Poly(acrylic acid) (PAA)

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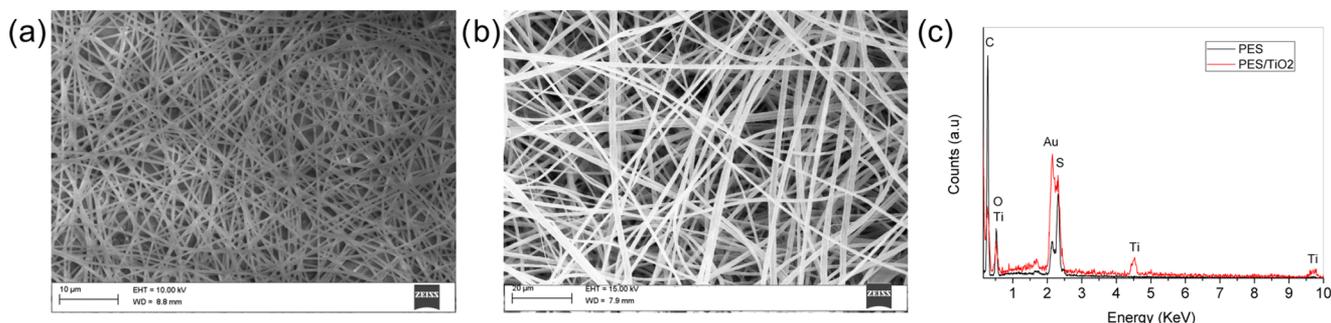


Figure 1. SEM images of PES (a) and PES–TiO₂ (b) polymeric fibers; (c) energy-dispersive spectroscopy (EDS) analysis of PES–TiO₂ mats (Au signal is due to surface metallization).

thermally cross-linked with poly(vinyl alcohol) (PVA) fibrous mats has been tested for removal of copper(II) ions in water;¹² poly(vinyl chloride) fibers are used to remove Cu(II), Cd(II), and Pb(II);¹³ aminated polyacrylonitrile nanofiber mat's ability to remove Ag(I), Cu(II), Pb(II), and Fe(II) from aqueous solution was studied.¹⁴ Many other polymeric mats have been studied for water treatment applications,¹⁵ but poly(ether sulfone) is particularly appealing since it is conventionally employed as material in water filter fabrication.^{16,17} As to the use of these mats for water treatments, recent work reported about their use to remove and/or degrade organic dyes¹⁸ by combination of electrospinning techniques with physical vapor deposition¹⁹ or chemical bath deposition.⁶ Semiconducting oxides are generally coupled to polymeric fibers: electrospinning is often combined with nanostructures deposition techniques or oxide nanoparticles are dispersed into micro–nanofibers.

In this work, hybrid poly(ether sulfone)–TiO₂ (PES–TiO₂) electrospun mats are tested as sorbent filter to remove lead and zinc from water. The role of TiO₂ to improve sorption performance has been demonstrated as well as the ability of fibrous mats to retain metal ions.

Another important result is also represented by the possibility to perform a fast and real-time determination of residual lead (or zinc) in solutions to estimate mats removal performances by using cationic porphyrins as molecular probes.²⁰ Porphyrins represent a multitopic class of organic compounds, which can be promptly exploited in sensing;²¹ as for heavy metal detection in water, metal ions can be coordinated by pyrrolic nitrogens of porphyrin core by forming a metallated derivative,²² whose presence in solution induces significant spectral modifications in the wavelength region between 350 and 700 nm, allowing for detection of metal ions at concentration below parts per million (ppm).²³ Herein, porphyrins are used both in solution or immobilized on transparent glass;²⁴ the latter approach benefits any detrimental effect deriving from dispersion of molecular probe (even if in micromolar concentration) in water.

Noteworthy, most of the reported approaches to estimate the adsorption efficiency make use of inductively coupled plasma spectrometry (ICP), which is a conventional procedure to determine mat's uptake capability. Accordingly, the possibility to use UV–vis spectroscopy for indirect determination of metal ion concentration after treatment paves the way to alternative strategies for in-field and real-time water analysis.

RESULTS

PES and PES–TiO₂ Electrospun Mats. Self-supporting veils of PES-based electrospun mats are tested as filters to remove lead from water. Figure 1a shows a typical scanning electron

microscope (SEM) image of PES polymeric fibers, which are dimensionally uniform (mean diameter 500 nm) and bead-free.

PES–TiO₂ mats are obtained by adding Ti-isopropoxide (TIIP) to PES dissolved in dimethylformamide (DMF)/toluene solutions (Figure 1b); presence of titanium precursor in the mats is confirmed by EDS analysis (Figure 1c).

Amorphous hydrous oxide precipitate (TiO₂·*n*H₂O) formation inside fibrous mats is promoted by hydrolysis and condensation of TIIP²⁵ due to water presence in the environment and solvent solution. Thermal treatments of mats at 100 °C (overnight) induce a partial loss of water but cannot lead to crystallization. Figure 2 shows UV–vis spectra of electrospun solution characterized by a strong absorption at $\lambda \approx 350$ nm, attributed to TiO₂ band–band transition.²⁶

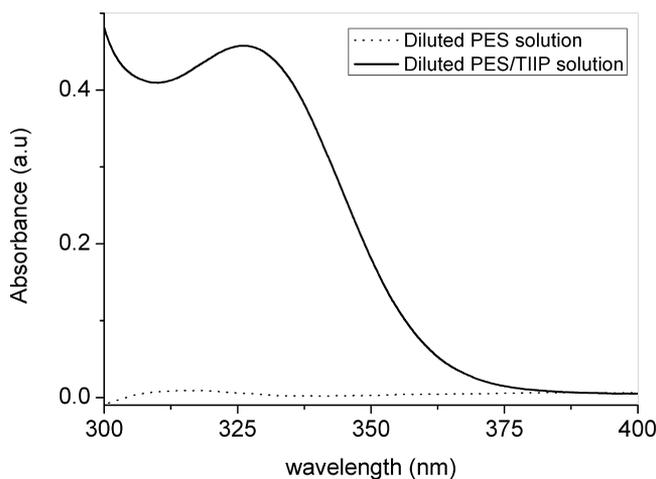


Figure 2. UV–vis absorption spectra of diluted PES (dot line) and PES/TIIP (solid line) in toluene/DMF.

Pb²⁺ Removal Using PES and PES–TiO₂ Fibrous Mats.

Residual Pb²⁺ ion concentration in aqueous solutions treated with bare PES mats is measured in real time by UV–vis spectroscopy after addition of H₂T₄ (1 μM). Experiments were conducted by placing 20 cm² fibrous mats in a beaker and by pouring 20 mL of Pb²⁺ containing aqueous solution at pH = 7.

Presence of Pb²⁺ metal ions in solution promotes H₂T₄ metalation and related formation of the metal derivative (PbT₄), as clearly indicated by Soret band splitting in two components, at $\lambda_1 = 423$ nm and $\lambda_2 = 476$ nm, respectively. By studying metalation kinetic of H₂T₄ by varying the metal ions concentration in water, it is possible to estimate the residual ions concentration after spontaneous adsorption into the fibrous

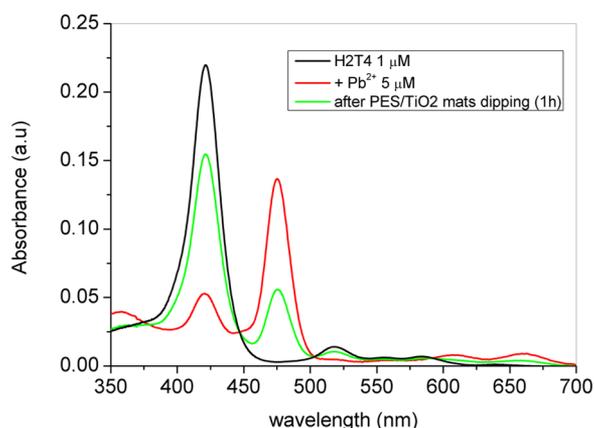


Figure 5. UV-vis absorption spectra of $[H2T4] = 1 \mu M$ (black curve) after addition of $[Pb^{2+}] = 5 \mu M$ (red curve) and after 1 h PES-TiO₂ mats dipping (green curve) at $T = 20 \text{ }^\circ C$.

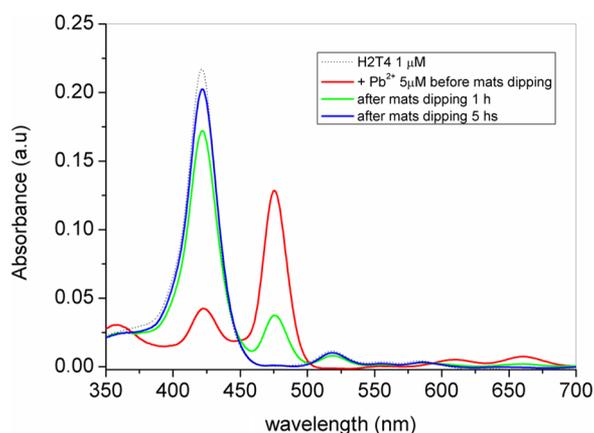


Figure 6. UV-vis absorption spectra of $[H2T4] = 1 \mu M$ (gray dotted line) after addition of $[Pb^{2+}] = 5 \mu M$ (red line) and after 1 h (green line) and 5 h (blue line) mats dipping at $T = 35 \text{ }^\circ C$.

To demonstrate the ability of the fibrous mats to retain adsorbed lead, they are washed/sonicated with water after Pb^{2+} adsorption. To determine presence of Pb^{2+} in washing solution, H2T4 $1 \mu M$ is added as chemosensor (Figure 7).

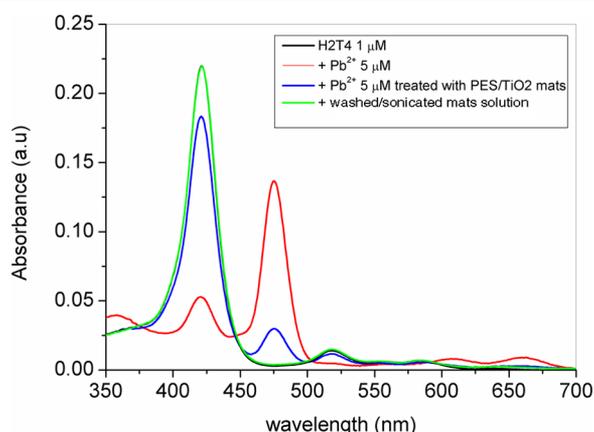


Figure 7. UV-vis absorption spectra of $[H2T4] = 1 \mu M$ (black line) at $T = 20 \text{ }^\circ C$: after addition of $[Pb^{2+}] = 5 \mu M$ (red line), after treatment with PES-TiO₂ mats (blue line), and after addition to washing solution of Pb^{2+} adsorbed mats (green line).

UV-vis spectra confirm the decrease of lead concentration after mats dipping in $[Pb^{2+}] = 5 \mu M$ solution (blue line). H2T4 addition to fibers washing solution (green line), resulting from 3 h sonication, does not reveal presence of any appreciable trace of Pb^{2+} ions as pointed by the shape of Soret band, perfectly superimposable to the signal of free porphyrin reference (black line).

Zn²⁺ Removal Using PES and PES-TiO₂ Fibrous Mats.

H2T4 solutions cannot be used to detect Zn^{2+} presence in sub-millimolar concentration (Figure S3, Supporting Information) due to an unfavorable metalation kinetic.³² However, we can demonstrate the capability of H2T4 layers, deposited on glass slides, to detect zinc presence by exploiting the fast metal insertion into the cavity of distorted porphyrin immobilized on glass surface (Figure S4, Supporting Information). Dipping of H2T4-treated glass in a zinc nitrate control solution ($5 \mu M$) causes modification of the Soret band of deposited H2T4, which appears red shifted, broader, and less intense than that observed for reference glasses.^{33,34} In presence of Zn^{2+} ions, the band centered at $\lambda = 433 \text{ nm}$ (attributed to free porphyrin immobilized on surface) shows a new component at $\lambda = 446 \text{ nm}$ due to formation of ZnT4 and modification of Q-band (inset) region, where a new band at $\lambda = 575 \text{ nm}$ appears (red line).

The same control is performed on same solution after treatment with PES-TiO₂ mats: the lack of significant spectral modification suggests a scarce ability of mats to retain Zn^{2+} ions, even after long treatment times. In fact, $[Zn^{2+}]$ concentration in solution does not seem significantly changed even after 24 to 48 h of mats dipping (Figure 8a, green and blue line, respectively).

On the contrary, if mats treatment is executed at $35 \text{ }^\circ C$, Zn^{2+} ions are almost totally removed from solution after 5 h (Figure 8b). By observing porphyrin Soret band evolution, before and after fibers dipping, an evident shift of Soret maximum as well as modification of Q-bands (inset) is now observable. After 1 h treatment, Zn^{2+} concentration in solution is still slightly decreased (green line), but after 5 h, zinc is almost completely removed, as indicated by the position of Soret and Q-bands pattern (blue line), similar to that associated to free base on glass.

Similar results are obtained when same approach is used to detect Pb^{2+} adsorption on fibers (Figure 9), performed by operating both at $20 \text{ }^\circ C$ (Figure 9a) and $35 \text{ }^\circ C$ (Figure 9b).

At $20 \text{ }^\circ C$, Pb^{2+} concentration is completely removed in about 48 h, whereas at $35 \text{ }^\circ C$, the same results are achieved in about 5 h. Noteworthy, treated glass response agrees well with that provided by the use of H2T4 $1 \mu M$ solution as Pb^{2+} ion sensor.

Selective Removal of Zn²⁺ and Pb²⁺ in Solution Using PES and PES-TiO₂ Fibrous Mats. H2T4 ($1 \mu M$) Soret band modification after addition to aqueous solutions containing both $Pb^{2+} 5 \mu M / Zn^{2+} 5 \mu M$ in which PES-TiO₂ mats were dipped for 24–48 h is reported in Figure 10a. Noteworthy, broadening of band component centered at $\lambda = 423 \text{ nm}$ indicates formation of both ZnT4 and PbT4. In fact, Pb^{2+} presence promotes Pb^{2+} to Zn^{2+} transmetalation, leading to formation of ZnT4 (not formed in absence of Pb^{2+}). Band narrowing (observed after 48 h) indicates a concentration decrease of both Zn^{2+} and Pb^{2+} ions.

Using H2T4 deposited on glass to monitor the ionic residual concentration, we can confirm the partial removal of both ions as indicated by increased intensity and narrowing of component at $\lambda = 433 \text{ nm}$ and presence of component at $\lambda = 500$ and 575 nm attributable to PbT4 and ZnT4 species, respectively (Figure 10b). These results point to a decreased selectivity, at $T = 20 \text{ }^\circ C$, of PES-TiO₂ mats toward adsorption of Zn^{2+} and Pb^{2+} when both species are present in solution.

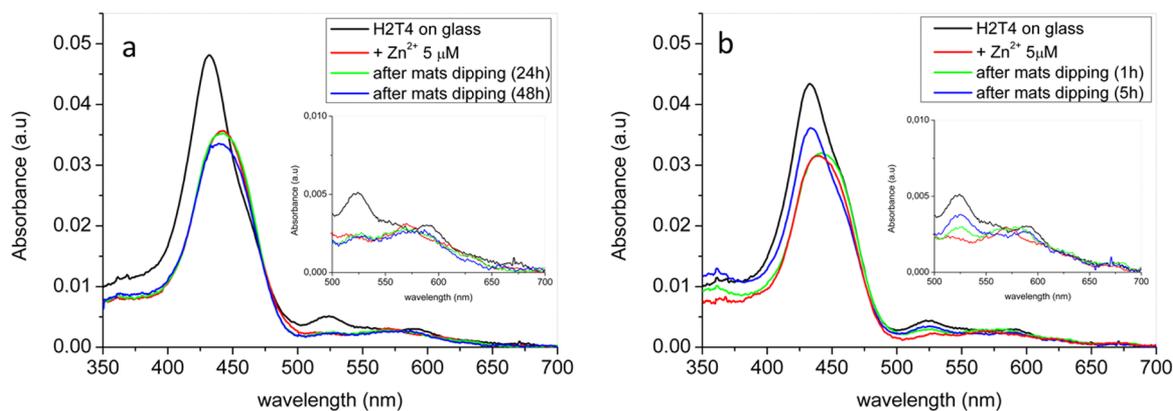


Figure 8. (a) UV–vis absorption spectra of H2T4 on glass (black line): after dipping in Zn^{2+} solution [$5 \mu\text{M}$] (red line) and after dipping in the solution of Zn^{2+} treated with mats for 24 h (green line) and for 48 h (blue line) at $T = 20^\circ\text{C}$. (b) UV–vis absorption spectra of H2T4 on glass (black line): after dipping in Zn^{2+} solution ($5 \mu\text{M}$) (red line) and after dipping in the solution of Zn^{2+} treated with mats for 1 h (green line) and for 5 h (blue line) at $T = 35^\circ\text{C}$. Q-bands region is shown in the insets.

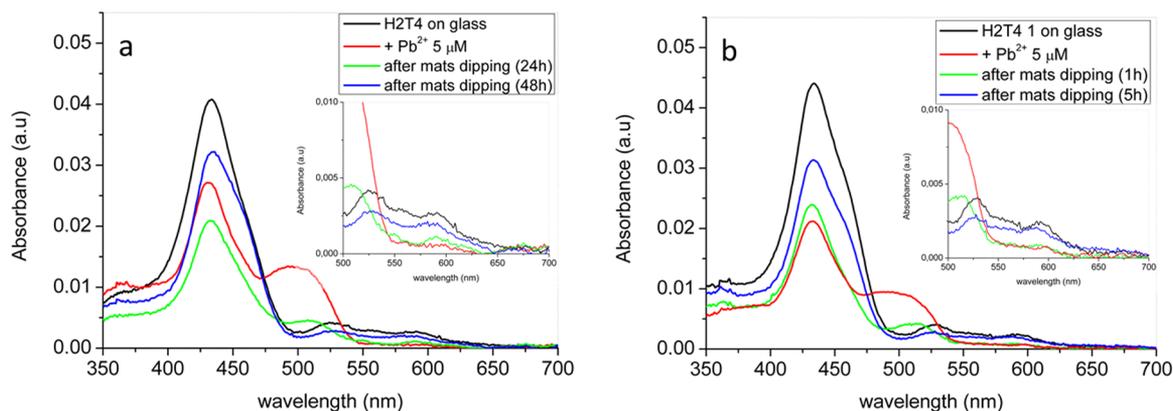


Figure 9. (a) UV–vis absorption spectra of H2T4 on glass (black line): after dipping in Pb^{2+} ($5 \mu\text{M}$) solution (red line) and after dipping in the solution of Pb^{2+} treated with mats for 24 h (green line) and for 48 h (blue line) at $T = 20^\circ\text{C}$. (b) UV–vis absorption spectra of H2T4 on glass (black line): after dipping in Pb^{2+} ($5 \mu\text{M}$) solution (red line) and after dipping in the solution of Pb^{2+} treated with mats for 1 h (green line) and for 5 h (blue line) at $T = 35^\circ\text{C}$. Q-bands region is shown in the inset.

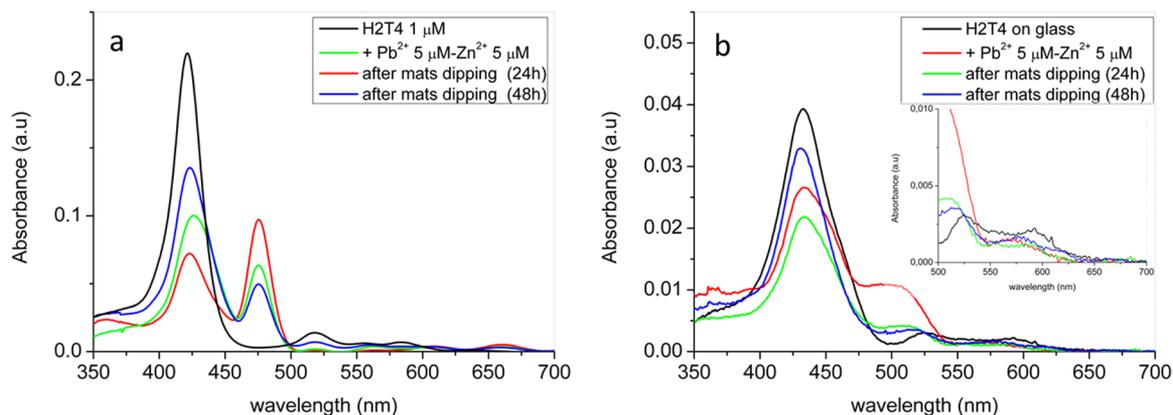


Figure 10. (a) UV–vis absorption spectra of $[\text{H2T4}] = 1 \mu\text{M}$ solution (black line) at $T = 20^\circ\text{C}$: after addition to Pb^{2+} ($5 \mu\text{M}$)/ Zn^{2+} ($5 \mu\text{M}$) solution (red line) and after addition to Pb^{2+} / Zn^{2+} solution treated with mats for 24 h (green line) and for 48 h (blue line). (b) UV–vis absorption spectra of H2T4 on glass (black line) at $T = 20^\circ\text{C}$: after dipping in Pb^{2+} ($5 \mu\text{M}$)/ Zn^{2+} ($5 \mu\text{M}$) solution (red line) and after dipping in Pb^{2+} / Zn^{2+} solution treated with mats for 24 h (green line) and for 48 h (blue line). Q-bands region is shown in the inset.

Different adsorption performances are achieved if temperature is increased to $T = 35^\circ\text{C}$, as shown in Figure 11.

Figure 11a shows H2T4 ($1 \mu\text{M}$) Soret band modification behavior after addition in Zn^{2+} / Pb^{2+} solution, before and after treatment with PES– TiO_2 mats. It is clear how high temperature

promotes ZnT4 formation via Pb^{2+} – Zn^{2+} transmetalation; in fact, a clear red shift of H2T4 Soret band associated with metalated derivative is well evident (red line). After 1 h dipping of PES– TiO_2 mats, a remarkable decrease of the component at $\lambda = 476 \text{ nm}$ is due to a faster adsorption of Pb^{2+} with respect to

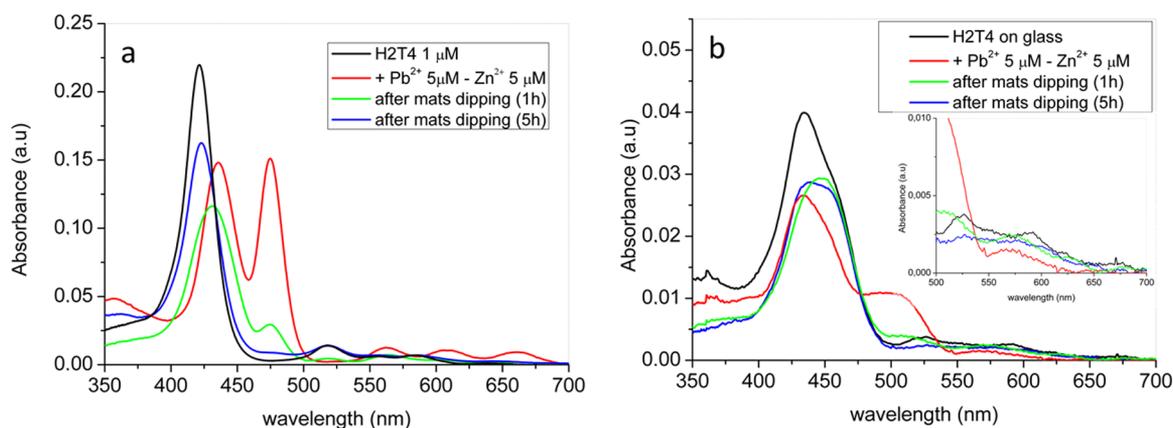
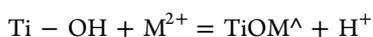


Figure 11. a) UV-vis absorption spectra of H2T4 (1 μM) solution (black line) at $T = 35\text{ }^\circ\text{C}$: after dipping in Pb^{2+} (5 μM)/ Zn^{2+} (5 μM) (red line) and after dipping in Pb^{2+} / Zn^{2+} solution treated with PES-TiO₂ mats for 1 h (green line) and for 5 h (blue line). (b) UV-vis absorption spectra of H2T4 on glass (black line) at $T = 35\text{ }^\circ\text{C}$: after dipping in Pb^{2+} (5 μM)/ Zn^{2+} (5 μM) (red line) and after dipping in Pb^{2+} / Zn^{2+} solution treated with PES-TiO₂ mats for 1 h (green line) and for 5 h (blue line). Q-bands region is shown in the inset.

Zn^{2+} (green line), while the other component remains still red shifted with respect to free base reference. After 5 h, Pb^{2+} is almost totally removed and, for this reason, transmetalation is slowed down. However, presence of low concentration of PbT4 is indicated by a Soret band intensity (now centered at $\lambda = 423\text{ nm}$) lower than that referred to porphyrin-free base (black line). Validation of hypothesis of a reduced adsorption of Zn^{2+} with respect to Pb^{2+} is provided by spectral analysis of H2T4 deposited on glass (Figure 11b). In this case, an evident modification of the Soret band shape, after 1 h mats dipping, clearly indicates the presence in solution of $[\text{Zn}^{2+}] = 5\text{ } \mu\text{M}$ (see Figure 8 for comparison), whereas Pb^{2+} concentration is dramatically reduced and estimated close to $\sim 1\text{ } \mu\text{M}$. By prolonging dipping time, $[\text{Zn}^{2+}]$ slightly decreases by formation of a well discernible component at $\lambda = 432\text{ nm}$ having same intensity as that at $\lambda = 450\text{ nm}$ associated to ZnT4 . Spectral changes in Q-bands region confirm the invariance of $[\text{Zn}^{2+}]$ as indicated by predominance of component at $\lambda = 575\text{ nm}$ (green line) whose intensity slightly decreases after 5 h (blue line).

DISCUSSION

Lead selective adsorption provided by the investigated polymeric mats is significantly higher on PES-TiO₂ fibers (Figure 5) than on PES ones (Figure 3). Modulation of PES-TiO₂ surface charge by varying pH (from 5.5 to 8) is verified by adsorption performances toward cationic H2T4 (Figure 4). In fact, TiO₂ IEP (~ 6) triggers surface charge from positive (below IEP) to negative (above IEP).²⁵ Hydroxylated bridging groups and terminal groups on oxide surface, which can be positively charged ($-\text{OH}-\text{H}^+$) or negatively charged ($-\text{O}^-$), are progressively deprotonated upon increasing pH, forming negative surface charge. These functional groups are responsible for coordinative interactions with metal ions that “interfere” with protonation equilibrium



At neutral pH, ion complexation is responsible for both physisorption and chemisorption on PES-TiO₂ fibers.³⁵ The overall surface charge of fibers, at neutral pH, favors binding of metal ions to hydrous amorphous oxide through interaction at the solid surface-solution interface. Accordingly, these processes are triggered by many factors that influence the resulting surface complexing constant. In particular, stability of aqua ions and their

acidity need to be accounted for. In fact, divalent metal ions undergo hydrolysis in water; thus, this equilibrium in homogeneous solution can compete with formation of hydroxo complexes at solid surface.³⁶

Noteworthy, working at room temperature ($\approx 20\text{ }^\circ\text{C}$), PES-TiO₂ fibers show a high selectivity toward Pb^{2+} rather than Zn^{2+} ; no significant decrease of Zn^{2+} concentration in solution is observed even if dipping time of PES-TiO₂ mats is prolonged up to 48 h. Zn^{2+} ions are hydrolyzed at pH higher than Pb^{2+} , and this condition can explain their lower affinity toward amorphous TiO₂ surface.^{37,38} Upon increasing temperature, Zn^{2+} adsorption is increased due to the endothermic nature hydrolysis and surface adsorption onto TiO₂ surface; thus, this evidence supports the role of chemisorption process in both Pb^{2+} and Zn^{2+} ions adsorption on PES-TiO₂ mats surface, since generally physisorption should decrease upon increasing temperatures. In fact, adsorption at surface hydroxyl sites can be discussed in terms of formation of coordination bond, resulting from an electron lone pair donation of surface oxide ion to metal ions. Of course, electrostatic nature of adsorption process is supported by considerations about hydration energy and stability of an aqua ion in solution (proportional to Z/r ratio), which can be invoked to explain Zn^{2+} reduced adsorption³⁶ on TiO₂ surface. In particular, it has to be remarked how chemical reactivity of the aqua ions is connected with stability of the intermediate products formed during ion coordination of water molecules exchange with ligands (i.e., $\text{M}(\text{H}_2\text{O})_5^{2+}$); in the present case, Zn^{2+} penta-coordination tendency can explain its inertia.

CONCLUSIONS

A combined adsorption-detection approach to treat heavy metal ions dispersed in water has been proposed. The presented results have been shown in the preliminary study aimed to demonstrate ability of PES-TiO₂-based mats to work as heavy-ion sorbent. The approach proposed to monitor Pb^{2+} and Zn^{2+} removal is based on the use of porphyrins as molecular probes, which are able to reveal ion concentration below ppm. The presented approach allows for a real-time detection and removal of trace lead in wastewater without the requirement of expensive and complex instrumentation, such as atomic absorption spectroscopy or inductively coupled plasma (ICP) spectroscopy.

Electrospun PES-based fibrous mats are validated as effective sorbent material to be used in water without any drawback

related to their dispersion and contamination in solution. After treatment, in fact, they can be easily removed out from solution, and any filtration or purification procedure is further required. Addition of titanium isopropoxide to PES electrospun solution leads to hybrid PES–TiO₂ mats, whose negative surface charge, easily modulated by pH, promotes an enhanced adsorption of metal ions with respect to bare PES. A remarkable difference in term of affinity toward Zn²⁺ and Pb²⁺ ions is observable at room temperature (*T* = 20 °C). In particular, PES–TiO₂ mats are able to drop Pb²⁺ concentration without interference of Zn²⁺ ions. On the contrary, upon increasing temperature (*T* = 35 °C), both species are readily removed out from water. In particular, ion removal is almost complete (>90%) at 35 °C, after 5 h dipping (corresponding to a removal of ~1.3 mg/g for Pb²⁺ and 0.5 mg/g for Zn²⁺).³⁹

This behavior remarks the importance of aqua ion's coordination chemistry to rationalize selective adsorption of metal ions on hydroxylated surface, thus pointing to a more complex phenomena description rather than mere system electrostatics.

Noteworthy, ability of PES–TiO₂-based electrospun fibrous mats to absorb lead and zinc ions present in water has been investigated using cationic H2T4 as metal ion chemosensor. Homogeneous (in 1 μM aqueous solution) and heterogeneous (onto glass surface) H2T4 core metalation both provide clear spectroscopic evidences to sense metal ions presence in water (at sub-micromolar concentration). For this reason, very low metal ion (Pb²⁺ and Zn²⁺) initial concentrations (~1 ppm) are used to confirm the ability of H2T4 probes used both as diluted solution and deposited monolayers on glass, to detect residual ion concentration at sub ppm level. Such values are much lower than those conventionally used (>100 ppm) to calculate sorption capability and, in this regard, it is also important to remark that sorption capability depends on initial metal ion concentration. In fact, it has been demonstrated that an increase in the initial metal ion contributes to overcome mass transfer resistance between solid/solution interfaces.^{40,41}

The fabricated mats are extremely stable in water, easy to handle, and robust, thus allowing for a prolonged use (up to complete removal of ionic species) without any release of both fibrous material as well as adsorbed species.

In this perspective, we believe that the proposed hybrid PES–TiO₂ mats represent scalable and versatile solutions for application in water remediation. Their ability to adsorb heavy metal ions represents a specific functionality that can be combined also to photocatalytic properties of the material to obtain active membranes for wastewater treatment.

■ EXPERIMENTAL SECTION

Materials. Commercial poly(ether sulfone) (PES) with a molecular mass of about 20 000 Da was chosen for membrane production. Dimethylformamide (DMF), toluene, titanium isopropoxide (TIIP), and acetylacetone were purchased from Sigma-Aldrich.

Tetrakis(*N*-methyl-4-pyridyl)porphyrin (H2T4), Pb(NO₃)₂, and Zn(NO₃)₂ were used without further purification. All stock solutions were prepared by dissolving the solid in ultrapure water obtained from the Elga Purelab Flex system by Veolia.

H2T4 stock solution (1 × 10⁻⁴ M) was prepared by dissolving the solid in ultrapure water at pH 7. H2T4 1 μM solutions ($\epsilon_{422} = 2.34 \times 10^5$) were prepared directly in cuvettes by adding microliter aliquots of the stock solution to 2.5 mL of water (pH = 7).

Pb(NO₃)₂ and Zn(NO₃)₂ stock solutions (1 × 10⁻³ M) were prepared in ultrapure water at pH = 7 directly from the solid.

Fibrous Mats Preparation. PES solutions were obtained by dissolving 2.5 g of polymer in a DMF/toluene (1:1) solution: the mixture was stirred continuously for 3 h at 40 °C. A second solution was prepared by mixing 2.5 mL of toluene, 1.5 mL of TIIP, and 1 mL of acetylacetone and stirring for 3 h under nitrogen flow. This latter solution was slowly added to former polymer solution and stirred overnight under nitrogen flow. Then, it was loaded into a 10 mL syringe mounted on a peristaltic pump (flow rate 20 μL/min) and electrospun: distance between the needle tip and collector was kept at 15 cm and voltages were set at +18 and -3 kV, respectively.

Metals Adsorption. Lead nitrate (Pb(NO₃)₂) and zinc nitrate (Zn(NO₃)₂) were dissolved in deionized water at room temperature. Electrospun fibers (20 cm², weight ≈ 40 mg) were dipped in 20 mL of resulting solutions (pH = 7) where initial concentration of Pb²⁺ and/or Zn²⁺ ions was set at 5 μM. Dipping time is varied from 1 h up to 48 h and temperature from 20 to 35 °C.

After dipping, 2.5 mL aliquots of treated solutions were analyzed by adding 25 μL of H2T4 stock solution to estimate residual metal concentration. No filtration is required for any solution withdrawals.

Spectrophotometric Metal Ion Detection in Water Using H2T4 in Solution or Immobilized on Glass. H2T4-treated glass was used to directly monitor metal residual concentration in treated solution, thus avoiding porphyrin dispersion in water. Microscopic glass slides (Forlabs; Carlo Erba, cut into 2.5 cm² pieces) were sonicated in water, isopropyl alcohol, and ultrapure water before use.

H2T4 deposition is achieved by dipping glass slides into H2T4 solutions (10 μM) at pH 5.5 for 45 min: afterward glass slides were rinsed with water to remove the excess of porphyrin. The amount of H2T4 deposited on glass has been spectroscopically calculated by desorption experiments (in sodium dodecyl sulfate solution at 10%_w) and estimated to be ~3 × 10⁻⁷ M.

UV–visible spectra were obtained on a JASCO V-560 UV–vis spectrophotometer. All of the measurements were performed at room temperature and under an atmospheric pressure. UV–vis spectra of H2T4 deposited on glass were recorded from λ = 700 to 350 nm (data pitch 0.5 nm; band width 2.0 nm; scanning speed 100 nm/min) before and after dipping (time ranging from 1 to 48 h) in the water containing the residual Pb²⁺ and/or Zn²⁺ after fibers PES–TiO₂ treatment.

SEM analysis was performed using a Field Emission Supra ZEISS VP 55 microscope equipped with an Oxford 10 mm² SDD Detector for energy-dispersive spectroscopy (EDS).

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00284.

Plot of UV–vis absorption peak intensity ratio at λ = 476 and 423 nm (I_{476}/I_{423}) vs Pb²⁺ concentration in water, UV–vis spectra of H2T4 aqueous solution (1 μM) recorded in presence of increasing concentration of Pb²⁺ ions before and after mat dipping (24 and 48 h), UV–vis absorption spectra of H2T4 aqueous solution (1 μM) in presence of Zn²⁺ ions having concentrations of 500 μM and 5 mM, UV–vis absorption spectra of H2T4 deposited

on glass before and after dipping in aqueous solutions containing $[Zn^{2+}] = 1 \mu M$ and $[Zn^{2+}] = 5 \mu M$ (PDF)

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G.O. and C.M.A.G. equally participated in the whole experiment and in manuscript preparation. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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