

# Elastomeric Nanocomposite Foams for the Removal of Heavy Metal Ions from Water

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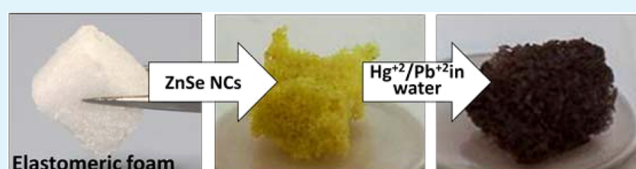
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## S Supporting Information

**ABSTRACT:** We report the fabrication and utilization of elastomeric polymer nanocomposite foams for the efficient removal of  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  heavy metal ions from polluted water. The polydimethylsiloxane (PDMS) foams are properly modified in order to become hydrophilic and allow the polluted water to penetrate in their volume. The ZnSe colloidal nanocrystals (NCs) that decorate the surface of the foams, act as active components able to entrap the metal ions. In this way, after the dipping of the nanocomposite foams in water polluted with  $\text{Pb}^{2+}$  or  $\text{Hg}^{2+}$ , a cation exchange reaction takes place, and the heavy metal ions are successfully removed. The removal capacity for the  $\text{Pb}^{2+}$  ions exceeds 98% and the removal of  $\text{Hg}^{2+}$  ions approaches almost 100% in the studied concentrations region of 20–40 ppm. The reaction is concluded after 24 h, but it should be noticed that after the first hour, more than 95% of both the metal ions is removed. The color of the foams changes upon heavy metal ions entrapment, providing thus the opportunity of an easy detection of the presence of the ions in water. Taking into account that the fabricated foams provide good elastic properties and resistance to heat, they can be used in different conditions of water remediation.

**KEYWORDS:** polydimethylsiloxane, ZnSe nanocrystals, surface properties, cation exchange, water remediation



## INTRODUCTION

Industries such as agro-processors, textile dyeing, abattoirs and tanneries can introduce toxic pollutants in local water resources. On top of that, agricultural or urban wastes introduce a significant number of water pollutants, such as organic chemicals, pesticides, nitrates, heavy metals and water-borne pathogens.<sup>1,2</sup> Such pollutants can easily pass to the food chain if the polluted water or untreated wastewater from industries is used for agriculture, food processing or even drinking, mostly in zones where wastewater treatment infrastructures are inadequate.<sup>3</sup> The presence of heavy metal ions like lead ( $\text{Pb}^{2+}$ ) or mercury ( $\text{Hg}^{2+}$ ), can cause various and serious health problems, such as gastrointestinal diseases, liver problems, and nervous system damage.<sup>4</sup> Therefore, according to the World Health Organization (WHO), the concentration limit for  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  in drinking water should be below 0.01 and 0.001 ppm, respectively.<sup>5</sup>

To remove heavy metal ions from water, various materials have been tested so far, based on mechanisms like chemical precipitation, adsorption, membrane filtration, or photocatalytic degradation.<sup>6,7</sup> However, in some cases, low adsorption capacities, and relatively weak interactions with the metallic ions<sup>8</sup> were obtained, due to various factors such as low chemical affinity or environmental conditions. Moreover, in different cases, solid residuals are formed that need to be removed with further processes, pretreatment of the polluted water is

necessary, or specific conditions such as high pressures are required.<sup>8</sup> A way to increase the performance of such systems is the utilization of 3D polymeric structures, due to their unique properties like nano- and microporosity, high surface area, damping properties and possibility of increased strength by addition of nanofillers.<sup>9–11</sup> Indeed, diverse studies have been conducted on the utilization of polymer composite foams, such as polyurethane mixed with organic or inorganic natural systems,<sup>12,13</sup> for the removal of heavy metal ions like  $\text{Pb}^{2+}$  from aqueous solutions. However, the difficulties faced in the dispersion of high concentrations of the fillers demonstrate some of the limitations of such systems.

Ion exchange between the polluted water and the surface of the developed systems is a reliable method for the selective heavy metal ions removal from water solutions.<sup>14</sup> Sulfide based materials are considered promising candidates for this application, and in some cases are immobilized onto porous structures allowing higher metal ions removal capacities compared to the bulk materials, due to the high surface area able to react with the pollutants. In fact, recently ZnS NCs aerogels/xerogels have been utilized for the removal of  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  metal ions from water,<sup>15</sup> with more than 95% of  $\text{Pb}^{2+}$

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ions removed from 20 to 200 ppm  $\text{Pb}^{2+}$  solutions. However, the aerogels preparation method is quite lengthy, whereas their drying process requires specific conditions like supercritical environment, as normal drying at ambient conditions causes the collapse of the network into dust. In addition, for the characterization of the metal ions uptake a centrifugation step should be followed in order to separate possible solid residuals, whereas the destruction of the aerogel network and the damage of the initial porosity of the system are highly possible. In another recent study, ZnS quantum dots impregnated in chitosan hydrogel films were used for the detection and removal of  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  ions.<sup>16</sup> Although the proposed nanocomposite is simpler in terms of fabrication and utilization, the low removal capacity, e.g., 24% of  $\text{Pb}^{2+}$  ions from a 20 ppm  $\text{Pb}^{2+}$  aqueous solution within 2 h, and 50% of  $\text{Hg}^{2+}$  ions from 20 ppm of  $\text{Hg}^{2+}$  aqueous solution within 1 h, can be a serious limitation for its utilization. Therefore, a need is emerging to explore new systems that offer high removal capacity, and above all can be easily fabricated and utilized for water remediation through the ion exchange mechanism.

Herein, we present the fabrication of ZnSe loaded PDMS nanocomposite foams and we investigate their ability to purify polluted aqueous media by collecting and entrapping dispersed heavy metal ions. Although, so far, ZnSe NCs were mainly utilized in optoelectronic and photoelectrochemical applications,<sup>17–19</sup> their potential use in water remediation is an interesting alternative due to their cation exchange capability.<sup>19,20</sup> In fact, because the ZnSe NCs display relatively weaker chemical bonding compared to ZnS,<sup>21</sup> it is expected that the exchange reaction process can be facilitated. At first, the polymeric foams are fabricated by using the leaching technique while the modification of their surface properties is carried out by introducing an appropriate amphiphilic copolymer that makes the foams water absorbing. Because of their elastomeric nature, the foams present elastic and shape memory properties, and can be used in different stress conditions without losing their pristine mechanical characteristics. Subsequently, a simple dip adsorption procedure is applied, in order to introduce an appropriate amount of ZnSe functional NCs on their porous surface throughout the foams volume that enables the ion exchange process and the entrapping of the ions in the whole material. The prepared porous systems can remove  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ions from water with capacity of above 98% for both concentrations studied, i.e., 20 and 40 ppm, at ambient conditions. Importantly, the heavy metal ions are entrapped into the foams, collected and safely disposed, whereas the color change of the foams after the removal can be an accurate indicator of the presence of such pollutants.

## ■ EXPERIMENTAL SECTION

**Materials.** Polydimethylsiloxane (PDMS) (Sylgard184 Silicone Elastomer) consisting of two components, the base and the curing agent, was purchased from Dow Corning Corporation. Poly(ethylene oxide)-*co*-polydimethylsiloxane (PEO-*b*-PDMS) was purchased from Polysciences Inc.; toluene and lead nitrate from Sigma-Aldrich. Sugar cubes were purchased from the local market. Mercury bromide was purchased from Strem chemicals. All the above chemicals were used without any further purification. For the synthesis of the ZnSe NCs, Zinc stearate (technical grade), octadecylamine (99%), 1-octadecene (90%), oleylamine (70%) were purchased from Sigma-Aldrich; squalane (98%) was purchased from Alfa Aesar; selenium powder (99.99%) from Strem Chemicals; toluene and methanol used for the

washing of NCs were purchased from Carlo Erba and used without further purification.

**ZnSe Nanocrystals.** According to previous studies, the characteristics of the pristine NCs play a critical role to suppress or stimulate the cation exchange reaction.<sup>22</sup> To test this, two different syntheses of ZnSe NCs were followed for the water purification experiment, as reported.<sup>19,23</sup> First method: The ZnSe NCs were prepared by exchanging  $\text{Cu}^{2+}$  ions with  $\text{Zn}^{2+}$  in  $\text{Cu}_{2-x}\text{Se}$  NCs. The parent  $\text{Cu}_{2-x}\text{Se}$  NCs were synthesized by using our previously reported methods.<sup>24</sup> Specifically, a stock solution of  $\text{Zn}^{2+}$  cations was prepared by dissolving 1 mmol  $\text{ZnCl}_2$  in a solution of 3 mL of degassed 1-octadecene (ODE) and 2 mL of degassed Oleylamine (OLAM) at 250 °C under  $\text{N}_2$  flow.  $\text{Cu}_{2-x}\text{Se}$  NCs<sup>24</sup> (0.2 mmol  $\text{Cu}^{2+}$ ) dispersed in trioctylphosphine (TOP) were injected into the Zn solution (atomic ratio Zn:Cu = 5) and kept in the hot solution for 5 min to complete the cation exchange reaction. After the synthesis, the ZnSe NCs were precipitated with ethanol; they were subsequently washed by repeated redissolution in toluene and precipitation with the addition of methanol, and finally dispersed in toluene. With this method, the spherical ZnSe NCs with diameter of  $14.368 \pm 1.959$  nm were formed (see Supporting Information Figure S1a). Second method: Zn stearate (0.0632 g), octadecylamine (0.054 g), squalane (3.125 mL) and 2.5 mL of octadecene were mixed under vacuum at 120 °C for 1 h. After that, under argon flow, the temperature was increased to 330 °C and then 3 mL of a solution of Se powder in oleylamine (13 mg of Se/mL) was injected into the solution. After 20 min, the ZnSe NCs were grown. The mixture was quenched and transferred into a mixture of toluene and methanol solution, causing the precipitation of the NCs. Finally, the mixture was centrifuged, washed and the NCs were suspended into 2–3 mL of toluene. In this way, ZnSe NCs with diameter of  $6.60 \pm 0.98$  nm were formed (see Supporting Information Figure S1b).

**Fabrication of Nanocomposite Foams.** The hydrophilic PDMS foams (porosity  $\approx$  70–80%) were fabricated using a simple leaching technique.<sup>25</sup> In particular, the PEO-*b*-PDMS surfactant additive<sup>26</sup> was first mixed with the PDMS polymer base under stirring at room temperature and subsequently the curing agent was introduced (weight ratio 0.1:10:1, respectively). After that, the mixture was poured in a Petri dish and sugar cubes were placed into it. Upon low vacuum for 2 h, the solution penetrates in the pores of the sugar cubes, filling thus the void spaces, due to capillary forces. The system was then placed in oven at 80 °C for 24 h to complete the curing of the prepolymer. Finally, sugar was dissolved by using hot water and ultrasonication for 2 h, resulting in the porous hydrophilic PDMS foam with pore size in the range of few hundreds of micrometers (Supporting Information Figure S2).

The prepared foam was loaded with ZnSe NCs using the dip adsorption procedure.<sup>27</sup> In particular, the foam was placed into a ZnSe NCs toluene solution and kept for 24 h at room temperature followed by drying under nitrogen atmosphere where the foam recovers its initial dimensions. Depending on the initial concentration of the ZnSe solution, a specific quantity of ZnSe NCs is adsorbed in the foams, which in our case, corresponds to 1 and 3 wt % as calculated by the ICP study discussed below.

**Ion Exchange Process.** For the ion exchange study, 100 mL aqueous solutions of 20 and 40 ppm of  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  were prepared. Test experiments showed that there is no evident difference in the efficiency of the ion removal by the utilization of NCs developed with the two different synthetic approaches. Therefore, we present the ion exchange study of  $\text{Pb}^{2+}$  (20 and 40 ppm) metal ion solutions using the ZnSe NCs synthesized by the first method after their loading in the PDMS foams (3 wt %), whereas for the study of the ion exchange process of  $\text{Hg}^{2+}$  (20 and 40 ppm) metal ion solution, the ZnSe NCs obtained with the simpler synthetic method (second method) (1 wt % in the PDMS foams). The ZnSe loaded PDMS foams with weight of  $\sim$ 200 mg (1 and 3 wt %) were placed in 10 mL of each metal ions solution under stirring at room temperature. The samples were removed from the solution at specific time intervals in order to be further analyzed as will be discussed below.

After the exchange reaction, the used foams were immersed in aqua regia solution (1HNO<sub>3</sub>:3HCl) overnight and then washed three times with water. In this way, the NCs were removed and after drying, the color and physical appearance was the same as the pristine PDMS foams. Therefore, these foams could be reused as new substrates for further functionalization.

**Characterization.** The surface properties of the fabricated foams were characterized by using an OCAH 200 video based optical contact angle measuring instrument (DataPhysics, Germany). Water drops of 5  $\mu$ L were placed on the surface of the foams and the change of the drop volume during time was recorded and analyzed. The mechanical properties of the PDMS foams were investigated using a dynamic mechanical analyzer (DMA) (Q800, TA Instruments, USA). The compression tests were carried out at room temperature and at 150 °C under preload of 0.1 N with 50% compression and rest time 2 min followed by unloading. We have carried out five cycles and stress measurements under the specific conditions. XRD patterns were recorded using a Smart lab 9 kW Rigaku diffractometer equipped with a copper rotating anode. The X-ray source was operated at 40 kV and 150 mA. A Göbel mirror was used to obtain a parallel beam and to suppress Cu  $K\beta$  radiation (1.392 Å). The  $2\theta/\omega$  scan was performed with two radiations, Cu  $K\alpha_1$  (1.544 Å) and Cu  $K\alpha_2$  (1.541 Å), with a step of 0.05° ( $2\theta$ ) and with a scan speed of 0.08°/min. SEM images were acquired using a JEOL JSM-6490LA (JEOL, Tokyo, Japan) equipped with a tungsten (W) thermionic electron source working in low vacuum with a pressure of around 50–60 Pa, to avoid charging effect. High-resolution SEM images were obtained using a JEOL JSM-7500F (JEOL, Tokyo, Japan) equipped with a cold FEG, operating at 10 kV acceleration voltage. Compositional contrast was achieved using a retractable backscattered electron imaging (RBEI) detector. When needed, samples were coated with a 10 nm thick carbon film using an Emitech K950X high vacuum turbo system (Quorum Technologies Ltd., East Sussex, UK). Energy dispersive X-ray spectroscopy was performed using an Oxford X-Max 80 system with a silicon drift detector (80 mm<sup>2</sup> effective area of detecting device).

The concentration of ions was determined by elemental analysis using an ICP-AES (inductive coupled plasma-atomic emission) spectrometer (iCAP 6500, Thermo). The collected solutions during the ion exchange experiments were digested in aqua regia. Specifically, 250  $\mu$ L of the collected liquid sample was mixed with 2.5 mL of aqua regia and left overnight for the complete digestion of metal ions. Then the solution was further diluted with Milli-Q water up to 25 mL and filtered through 0.45  $\mu$ m PTFE filters prior to elemental analysis. The removal percentage of ions over time, is calculated by eq 1,

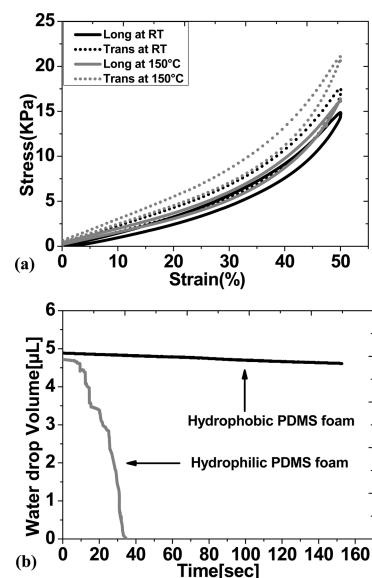
$$\text{removal of ions (\%)} = [(C_0 - C_t)/C_0] \times 100 \quad (1)$$

Where,  $C_0$  is the initial concentration of ions (in ppm), and  $C_t$  is their concentration at a given time,  $t$  (h), (in ppm).

## RESULTS AND DISCUSSION

The mechanical and wetting properties of the prepared elastomeric foams are presented in Figure 1. In particular, Figure 1a shows the mechanical properties of the foams at two different temperatures. In both cases, an anisotropic behavior was observed during compression, because the compressive strength at the transversal direction, i.e., in the direction of the foams growth, is higher than at the longitudinal one. Most importantly, independently from the temperature conditions, a full strain recovery was observed. The same behavior was observed for the subsequent four compression cycles proving that the fabricated foams have shape memory properties (Supporting Information Figure S3), making thus possible their use in different stress conditions without losing their pristine mechanical characteristics.

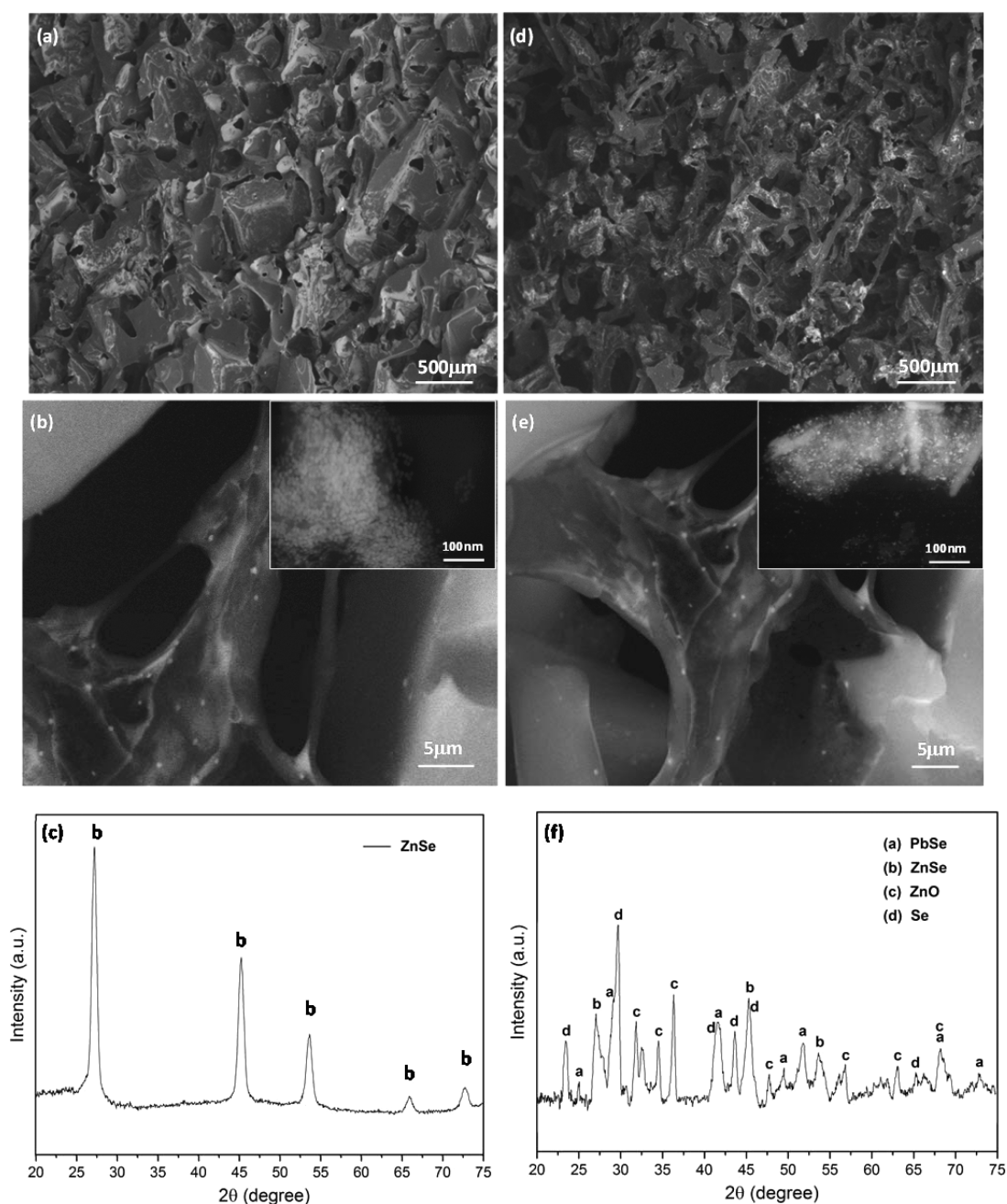
Concerning the wetting properties, the pristine PDMS foams have a waterproof hydrophobic nature with water contact angles (WCA) of  $114^\circ \pm 2^\circ$ , due to the hydrophobic properties



**Figure 1.** (a) DMA at RT and 150 °C. Mean stress values at 50% of compression after five cycles of longitudinally compressed foams are  $14.50 \pm 0.82$  KPa and  $18.40 \pm 1.07$  KPa at RT and 150 °C, respectively. For transversally compressed foams,  $17.60 \pm 1.06$  KPa at RT and  $23.56 \pm 1.41$  KPa at 150 °C. (b) Water drop volume measurements on hydrophobic and hydrophilic PDMS foams.

of the bare elastomer (WCA of PDMS films =  $116^\circ \pm 2^\circ$ ), as shown in Figure 1b. In particular, the volume of water drops placed on the surface of the foams was stable during time. However, during the ion exchange process the foams should be dipped into the ion–water solution and stay immersed during the whole exchange process, to allow the water to interact with their porous surface. Therefore, it is necessary to change their wetting properties turning them into hydrophilic. To do so, the PEO-*b*-PDMS hydrophilic component was introduced in the prepolymer gel, and after following the same steps of the foams fabrication, they became hydrophilic, allowing water to penetrate into their internal pores within 35 s.

The hydrophilic PDMS foams were then functionalized with ZnSe NCs by a simple dip adsorption method. In fact, when the PDMS is dipped in the toluene solution, it swells,<sup>28</sup> facilitating the homogeneous entrapment of a defined amount of ZnSe NCs in the pores of the foams throughout their volume. This amount depends on the initial concentration of the ZnSe in the toluene solution and on the dimensions of the dipped foam. ZnSe–PDMS foams (3 wt %) were prepared by dipping of 194 mg of foam ( $1.1 \times 1.0 \times 0.8$  cm<sup>3</sup>) into 5.4 mL of ZnSe NCs/toluene solution (the solution consists of 1.2 mL of a 7.5 mg/mL ZnSe NCs solution, and 4.2 mL of pure toluene) overnight at room temperature. The NCs are fixed on the 3D surface of the PDMS foams via weak attractive surface forces, which are able to keep the NCs bonded to the foam during the exchange reaction. Indeed, as it will be described later on, dipping of the functionalized foams in pure water solution results in a negligible release of Zn<sup>2+</sup> and Se<sup>2-</sup> in the liquid medium confirming the stability of the above-mentioned process. As shown in the SEM images of Figure 2a,b, aggregates of ZnSe NCs decorate the surface of the pores of the foam (see also Supporting Information Figure S4a). Their presence, as exposed features of the foam's surface, results in the maximization of their reactivity with external agents. Indeed, when the ZnSe NCs were mixed with the prepolymer solution



**Figure 2.** (a, b) SEM images and (c) XRD pattern of for ZnSe–PDMS foam before exchange. (d, e) SEM images and (f) XRD pattern of ZnSe–PDMS foam after exchange. The insets are magnified images of panels b and e, respectively.

to form the foams, their surface was covered by the polymer resulting in minimal performances (data not shown). The XRD data for the functionalized foams confirm the presence of the ZnSe NCs, as shown in the pattern reported in Figure 2c, which displays the characteristic diffraction peaks, i.e., panel b, at  $2\theta$  values of  $27.14^\circ$ ,  $45.05^\circ$ ,  $53.39^\circ$ ,  $65.61^\circ$  and  $72.37^\circ$  corresponding to reflections from the (111), (220), (311), (400) and (331) planes of cubic sphalerite ZnSe (PDF #00-037-1463 of ICDD database).

The surface morphology of the ZnSe–PDMS foam after dipping in the  $\text{Pb}^{2+}$  solution, is not altered as shown in Figure 2d,e, and the presence of NCs on the surface of the pores is still evident. Although the foam remains morphologically unaltered in low magnification, its surface chemistry is clearly modified by the presence of  $\text{Pb}^{2+}$  as confirmed by the EDS analysis (see

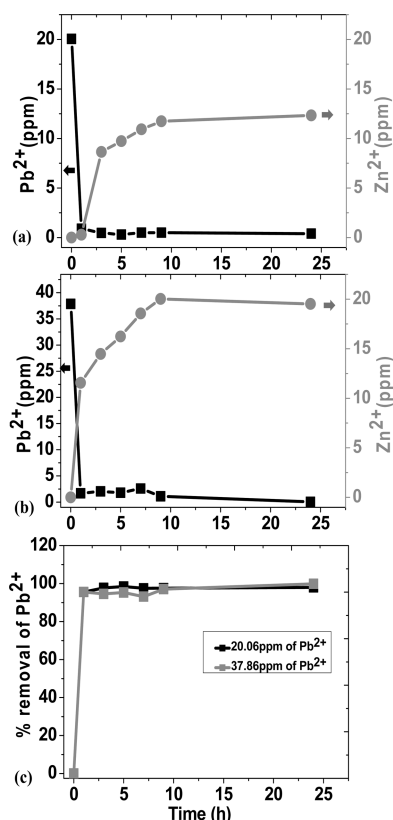
Supporting Information Figure S4b). Furthermore, the XRD data presented in Figure 2f, confirm the presence of PbSe NCs, with peaks at  $2\theta$  values of  $29.14^\circ$ ,  $41.68^\circ$ ,  $51.66^\circ$ ,  $68.2^\circ$  and  $76.2^\circ$  corresponding to reflections from the (200), (220), (222), (420) and (422) planes of clausthalite PbSe (PDF #01-077-0245). The concomitant presence of ZnSe peaks indicates that the ions present in solution were not enough to fully cation exchange the NCs entrapped in the foam. Additionally, some side products were present, such as ZnO (PDF #01-074-9940), due to the possible interaction of released  $\text{Zn}^{2+}$  ions with oxygen agents from water or the polymer, and additionally Se (PDF #00-006-0362), which are likely due to a partial oxidation of the NCs. The presence of such species is also confirmed by EDS analysis (see Supporting Information Figure S4b). Macroscopically, a remarkable color change of the foams was

observed after  $\sim 30$  min, from yellow to brownish, while after 24 h, the foams became dark brown, as shown in Figure 3.



**Figure 3.** Photographs of the elastomeric foam before (white), after the ZnSe loading (yellow) and after the removal of  $\text{Pb}^{2+}$  ions from water (dark brown).

To investigate further the ion exchange reaction between  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  ions, and to confirm the  $\text{Pb}^{2+}$  removal from polluted water, the presence of both ions and the variation of their concentration during the ZnSe–PDMS foams immersion in  $\text{Pb}^{2+}$  ion water solution were studied. Specifically, 3 wt % ZnSe–PDMS foams were dipped in two different water solutions with  $\text{Pb}^{2+}$  ions concentrations of 20.06 and 37.86 ppm. As shown in Figure 4a,b, in both cases, there was a



**Figure 4.** Kinetics of ion removal (a) 20.06 ppm of  $\text{Pb}^{2+}$  and (b) 37.86 ppm of  $\text{Pb}^{2+}$  ion concentration. (c) Removal percentage of  $\text{Pb}^{2+}$  ions during time for both concentrations. (For both the cases, 3 wt % of ZnSe–PDMS foam was used).

sudden decrease in  $\text{Pb}^{2+}$  ions concentration in the first hour with 95.6% of the  $\text{Pb}^{2+}$  ions removed (Figure 4c) and a simultaneous increase of the  $\text{Zn}^{2+}$  ion concentration. After this critical time, the ion exchange reaction continued, albeit with a slower rate, and final percentage removals of 98.0% and 99.9% were observed in the low and highly concentrated  $\text{Pb}^{2+}$  ions solutions respectively, after 24 h. These results indicate that the kinetics of ions removal is independent from the initial ion concentration in the range studied herein, while the maximum amount of  $\text{Pb}^{2+}$  ions was removed in the first hour in both cases. At the specific time, e.g., after 1 h of reaction, the corresponding release of  $\text{Zn}^{2+}$  is far below the acceptable limit, i.e., 5 ppm as defined by the EPA,<sup>29</sup> for the  $\text{Pb}^{2+}$  concentration of 20.06 ppm (0.29 ppm), whereas for 37.86 ppm, is higher but still in the same range.

The affinity of the ZnSe to the  $\text{Pb}^{2+}$  metal ions can be estimated by the distribution coefficient,  $K_d$  (eq 2).

$$K_d = (V/m) \left[ \frac{(C_0 - C_f)}{C_f} \right] \quad (2)$$

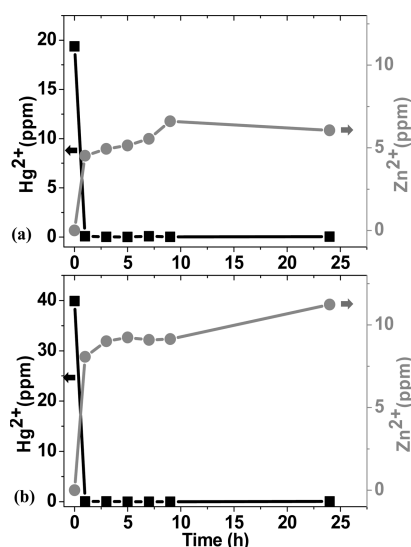
where  $C_0$  and  $C_f$  the initial and final metal ion concentrations (ppm) in the water,  $V$  the testing solution volume (mL) and  $m$  the amount of solid exchanger (g) used in the experiment.<sup>15</sup> The higher the  $K_d$  value, the higher the affinity of the exchanger with the heavy metal ions and the more efficient their removal. It is generally accepted that if the value of  $K_d$  is larger than 500 mL/g then the interaction with the metal ions is considered acceptable, above 5000 mL/g very good, and above 50 000 mL/g outstanding.<sup>30</sup> In our case, when 20.06 ppm of  $\text{Pb}^{2+}$  ions were present in water, the interaction of the ions with the ZnSe–PDMS foam is considered acceptable ( $K_d$ : 2102.46 mL/g) and for 37.86 ppm of  $\text{Pb}^{2+}$  ions it is very close to outstanding, with a  $K_d$  value of 42 371.34 mL/g, proving the efficiency of the method.

Compared to other studies in which ZnS NCs were used for the removal of similar quantity of  $\text{Pb}^{2+}$  metal ions from water following the ion exchange procedure, the presented system shows improved performance in terms of capacity and kinetics.<sup>15,16</sup> Specifically, ZnS Q-dots–chitosan films showed a removal percentage of ca. 24.9% after 2 h,<sup>16</sup> whereas ZnS aerogels show a maximum 98.6% removal after 24 h of reaction time.<sup>15</sup> In our case, the removal of the  $\text{Pb}^{2+}$  ions is faster and the percentage removal is higher, i.e., 95.6% within 1 h, and maximum of 99.9% after 24 h. Additionally, the foams presented in this work are fabricated with a simpler and faster method compared to previous studies, they are mechanically stable and can be recycled. In fact, after the exchange reaction, the pristine foams can be regenerated by treating with aqua regia or mild acidic solutions. Under such conditions, most of the metal chalcogenide compounds can be digested into free ions. At the same time, due to the high stability of the PDMS in acidic conditions, no damage or modification is caused to the polymeric network.<sup>31</sup> In this way, the NCs are dissolved, while the PDMS foams still retain their porous structure, with similar physical appearance as the unused nonfunctionalized ones. Therefore, they can be reutilized after being loaded with new non reacted NCs for further exchange reactions.

To prove the effectiveness and the synergistic nature of the presented nanocomposite system, the interaction of the bare PDMS foam with the metal ions solution and the interaction of the nanocomposite foam with pure water were studied. The bare PDMS foam, i.e., without loading of ZnSe NCs, was

introduced in a 70 ppm  $\text{Pb}^{2+}$  ion solution, and after 24 h, an insignificant variation of the  $\text{Pb}^{2+}$  ions concentration was measured (see Supporting Information Figure S5), proving that the decrease of the concentration of the ions observed in the case of nanocomposite foams was exclusively attributed to the presence of the ZnSe NCs. Additionally, when ZnSe–PDMS foams were dipped in clean water (without any metal ions; see Supporting Information Figure S6) for 24 h, there was a minor release of  $\text{Zn}^{2+}$  that proves that the  $\text{Zn}^{2+}$  presence in water, in the cases described above, was exclusively due to the exchange process with  $\text{Pb}^{2+}$  ions.

The developed ZnSe–PDMS foams were further tested for the removal of  $\text{Hg}^{2+}$  ions from water. Even if a lower concentration of the ZnSe NCs in foams was used (1 wt %), the removal of  $\text{Hg}^{2+}$  ions was successfully demonstrated, with a removal percentage above 99.5% within the first hour of reaction. This was confirmed in two different  $\text{Hg}^{2+}$  ion concentrations in water, i.e., 19.37 and 39.90 ppm (Figure 5).



**Figure 5.** Kinetics of removal of (a) 19.37 ppm of  $\text{Hg}^{2+}$  and (b) 39.90 ppm of  $\text{Hg}^{2+}$  ion concentration (for both the cases, 1 wt % of ZnSe–PDMS foam was used).

In particular, the concentration of  $\text{Hg}^{2+}$  ions decreases to 0.0863 and 0.0607 ppm, within 1 h, whereas their final concentration after 24 h is 0.04 and 0.03 ppm for initial concentrations of 19.37 and 39.90 ppm, respectively. This indicates a highly efficient removal of  $\text{Hg}^{2+}$  (above 99.8%), and “very good” and “outstanding”  $K_d$  values (22 183.195 mL/g and 55 072.53 mL/g for the lower and higher concentration, respectively). The simultaneous increase of  $\text{Zn}^{2+}$  in water confirms the ion exchange mechanism, with the  $\text{Zn}^{2+}$  concentration always lower than 10 ppm in the first hour of reaction.

The efficiency of the ZnSe–PDMS foam to remove  $\text{Hg}^{2+}$  was further tested under the presence of other metal ions in the wastewater. In particular, the presence of  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$  and  $\text{In}^{3+}$  did not affect the  $\text{Hg}^{2+}$  removal efficiency of the foam which was 99.7% after 24 h, although the removal rate was slower (30% in 1 h) (Supporting Information Figure S7). In parallel, the removal efficiencies of  $\text{In}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  were about 98.8%, 98.3%, 91.2%, 69.1% and 64.6%, respectively. This experiment verifies the versatility of the

developed foams, because they are capable of removing the metal ions of interest under diverse conditions.

## CONCLUSIONS

In conclusion, the present study demonstrates that ZnSe–PDMS foams can be successfully used for the fast removal of heavy metal ions from water by a cation exchange reaction. Compared to other studies of similar systems, we show a faster and more efficient removal of the ions, using elastic nanocomposite foams fabricated by a facile method. In particular, the PDMS foams were fabricated by the leaching technique, whereas the loading of NCs was performed by dip adsorption method that requires no specific reaction conditions. As shown by the systematic study presented, the ~96% of the  $\text{Pb}^{2+}$  ions were efficiently removed from solutions with ion concentrations 20–40 ppm within the first hour of reaction, whereas in the case of  $\text{Hg}^{2+}$ , the removal percentage was even higher and reached the ~99.8%. After 24 h, the removal percentage was further increased indicating that the proposed ZnSe–PDMS foams are an effective tool for the water cleaning process. Also, their fast color change indicates the presence in the aqueous media of metal ions that upon cation exchange form metal selenides with a band gap in the visible/IR region of the spectrum. Therefore, the proposed foams can be used not only as media for the removal of the harmful ions but also as fast indicators for the presence of these metals in water.

## ASSOCIATED CONTENT

### Supporting Information

TEM analysis for ZnSe NCs (first and second method), SEM image of the pristine PDMS foam, compression tests of PDMS foams (four cycles), EDS spectra (ZnSe–PDMS foams before and after reaction with  $\text{Pb}^{2+}$ ), ICP analysis of  $\text{Pb}^{2+}$  ions in water after dipping pristine PDMS foams, ICP analysis of pure water after dipping ZnSe–PDMS foams, ICP analysis of  $\text{Hg}^{2+}$  removed by the foams from wastewater containing diverse metal ions. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03003.

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### Notes

The authors declare no competing financial interest.

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