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Extremely fast and high Pb²⁺ removal capacity using a nanostructured hybrid material

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Ultra-fast toxic metals removal using a hybrid and nanostructured vaterite- poly(ethyleneimine) (NV-PEI) is reported. Especially for Pb²⁺ an extremely high and fast adsorption capacity without precedents is observed. Within a 3 min contact time (CT) 97-100% of Pb²⁺ contaminant in water samples at pH 6 with a large concentrations range (from 2 to 1000 ppm) and using a dosage of 0.5 g NV-PEI/L have been removed. The maximum adsorption capacity (q_{max}) calculated for a 1500 ppm Pb²⁺ initial concentration was 2762 mg of Pb²⁺/g NV-PEI. In addition to the excellent Pb²⁺ removal, this material is cheap, easy to be synthesized, biocompatible, biodegradable, which makes it superior to others reported so far and an attractive alternative for treatment of industrial wastewaters.

Introduction

Pure water progressively becomes a rare resource on Earth, because human activities release increasing amounts of soluble chemical species that are not appropriately removed before returning water to the environment. Among the number of polluting species heavy metals ions, especially mercury, cadmium and lead, are of special concern because of their high toxicity. Other less toxic ions such as copper or zinc may nevertheless prove harmful at slightly elevated concentrations. Wastewaters containing copper, lead, nickel, cadmium and zinc are produced by a variety of industries such as metal finishing, batteries manufacturing, non-ferrous metallurgical manufacturing, electrical industry, paper industry, printed wiring board industry and mining industry. Currently, water treatment technologies for the removal of toxic metals ions occurs through the use of several unit operations, such as chemical precipitation, sedimentation, filtration and sludge treatment.^{1,2} In a wastewater treatment plant in the basin of filtration ionic interchanger membranes or adsorption membranes, or mixture of both types are introduced to improve fundamentally the toxic metals removal at trace levels.¹⁻³ For the sake of sustainable development, the new environmental regulations will request wastewater treatment systems of increasing efficiency. In this aspect nanotechnology has been a useful tool in the fabrication of materials to remove toxic metals during the water treatment process.⁴ In this way many different nanoscale materials such as oxides, hydroxides or salts of metals such as iron⁵⁻⁹ and titanium,^{10,11} carbon nanotubes,¹²⁻¹⁶ various noble metals (mainly as nanoparticles),^{17,18} inorganic-organic hybrid materials,^{19,20} biomaterial as nanoporous silica,²¹ calcium carbonates²²⁻²⁵ and calcium phosphates,²⁶⁻²⁸ nanoscale networks (such as zeolites, metal-organic framework (MOF))²⁹ and others³⁰⁻³² have been explored as adsorbents for waters remediation.

Here a hybrid material composed of nanostructured vaterite-(poly)ethyleneimine (NV-PEI) microparticles has been evaluated

for toxic metals removal from model contaminated waters. New characterizations of the NV-PEI material and metal removal studies are reported here. For the first time, the results of metal adsorption onto the NV-PEI with the analysis of the N₂ adsorption-desorption isotherms, determination of the Pb²⁺ adsorption model and proposals of metal removing mechanisms are shown. An ultra fast removal capacity achieved within 6 min, never reached before, has been found for several metals at 100 ppm of initial concentration. A time of 3 min is completely sufficient to remove almost the 100% Pb²⁺ in a wide concentrations range from 2-1000 ppm using a dosage of 0.5 g NV-PEI/L at pH 6. Although there is a large number of studies using multiples nanostructure materials, this extremely rapid and high removal capacity to Pb²⁺ has never been achieved so far.^{5, 10-12, 14-16, 19, 21-23, 32} Generally, the toxic metal removal processes using the nanostructured microparticles (like fibres, sheet, tubes, rods, spheres, etc) are generally described by Langmuir isotherms^{9,10,21} that describes a superficial adsorption. In contrast, in the case of our material for the removal process by exchange of the Pb²⁺ with the Ca²⁺ of the vaterite structure only the Freundlich adsorption isotherm is the model that better fits with the experimental data. In addition to the excellent Pb²⁺ removal, the material here evaluated is cheap, easy to be synthesized, biocompatible, biodegradable, which makes it superior to others reported so far and an attractive alternative for treatment of industrial wastewaters.

Experimental Section

75 Synthesis of the adsorbent material

The NV-PEI adsorbent material was synthesized mixing under 45 min sonication equal volumes (5 mL) and concentrations (0.33 M) of CaCl₂ and Na₂CO₃ solutions that contain PEI (4 mg mL⁻¹). To prepare the CaCl₂/PEI solution a mixed solvent of water/ethanol 1:1 (v/v) was used. The precipitate product was washed three times by centrifugation, air dried and collected.³³

Metal removal experiments

In a typical metal removal experiment the used Pb^{2+} , Cu^{2+} , Hg^{2+} , Zn^{2+} , Cd^{2+} and Ni^{2+} solutions at different concentrations were prepared by dissolving a weighed quantity of $\text{Pb}(\text{NO}_3)_2$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, HgCl_2 , ZnCl_2 , CdCl_2 and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, respectively, in Milli-Q water (resistivity $18.2 \Omega \cdot \text{cm}$ at 25°C) and pH adjusted to 6. As-prepared hybrid NV-PEI microparticles (25 mg) were added to 50 mL of the metal solutions under stirring. To follow the experiments aqueous samples (500 μL) were taken during 6 h using a homemade filter-collector sample at several fixed time intervals. The metal ions concentrations were analyzed by using an inductively coupled plasma mass spectrometry (ICPMS) Agilent 7500ce model system. The amount q_t (mg g^{-1}) of metal adsorption onto microparticles surface at the time interval t was calculated by:

$$q_t = \frac{C_0 - C_t}{W} V$$

where C_0 and C_t (mg L^{-1}) are the liquid phase concentrations of Pb^{2+} ions at initial and any time interval t , respectively, V is the volume of the solution (L) and W is the mass of NV-PEI used as adsorbent (g).

Results and Discussion

Synthesis and characterization of the adsorbent material. Metal removal assays.

Our previous experimental results demonstrated the high loading capacity of the NV-PEI for a large variety of (bio)molecules.³³ Based on these preliminary results we decided to test the NV-PEI particles in model assays for water treatment purposes to evaluate for the first time the behaviour of this material versus toxic metals and carry out removal studies. Figure 1A-D shows SEM and TEM images of the NV-PEI particles used as water treatment material in the tested removing experiments. The CaCO_3 product is 100% of vaterite polymorph (Fig. S1) formed by microellipsoids and microspheres of about $1 \mu\text{m}$ (Fig. 1A), which are compounded of nanostructures of about 40-70 nm (Fig. 1B, C). The surface of this nanostructured vaterite is covered by PEI polymer as corroborated by TGA and EDX analyses (Fig. S2 A and B). The weight loss of about 4% that appears in the TGA diagram at range of $150\text{-}350^\circ\text{C}$ corresponds to the PEI delivery from CaCO_3 structure. Simultaneously, the PEI presence in this material was also observed by the nitrogen appearing at the EDX pattern. Taking into account these evidences, the nebulous zones (indicated by the red arrows) in the Fig. 1D could be related with the presence of the PEI organic phase. These results indicate that the NV-PEI hybrid material was synthesized.

The first removing probes were carried out in multi-metal competitive assays. The evaluated metals have been chosen based on their toxicity and the fact that these are reported as usual contaminants in waters. The NV-PEI adsorbent material exhibited the highest selectivity and removal capacity for Pb^{2+} and Cu^{2+} , followed for Hg^{2+} , Zn^{2+} and Cd^{2+} with a similar removal preference between them. The NV-PEI showed the lowest selectivity and removal for Ni^{2+} between all the assayed metals (Fig. 1E). The change of colour from white to blue in the

adsorbent material after 6 min of CT with the metal solution is related to the adsorption of Cu^{2+} and Ni^{2+} onto this material (Fig. 1F). The q_{max} for the six assayed metals using both 20 and 100 ppm as initial concentration is reached at 6 min of sample collection time or CT of the material with the metal dissolution (lower times of sample collection or CT were not assayed). It indicates that the whole removal process is very fast (Fig. 1E). The q_{max} for the total metal concentration of 120 ppm was around 152 mg/g which corresponds to 63% of total metal removal, meanwhile it was around 430 mg/g for the total initial metal concentration of 600 ppm which corresponds to 31% of removal. When 20 ppm of each metal is used as initial concentration, almost 100% of Pb^{2+} and Cu^{2+} are removed followed by around 50-60% of removal for Hg^{2+} , Zn^{2+} and Cd^{2+} and 20% for Ni^{2+} . While using 100 ppm of each metal as initial concentration, around 60% of Pb^{2+} and Cu^{2+} , 20% of Hg^{2+} , Zn^{2+} , Cd^{2+} and 10% of Ni^{2+} are removed. The decreasing in the removal percentage using mixture of different metal contaminants with respect to the removal percentage obtained using each metal by separated at the

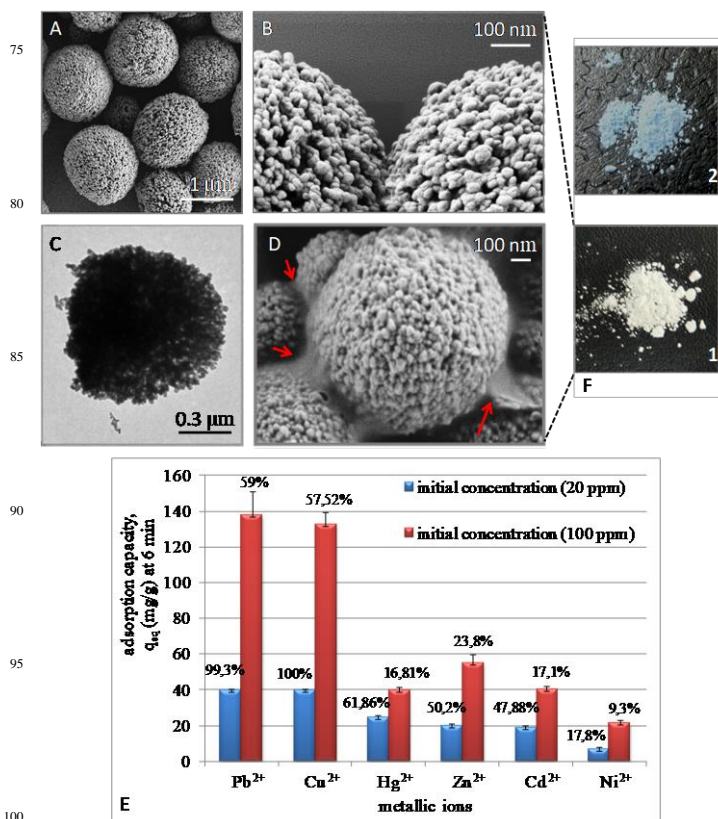


Fig. 1. A, B and D, SEM images and C, TEM image of the synthesized NV-PEI microparticles. (B) Close up to the NV-PEI surface that displays the large macroporous caverns like structure that composes this material. (E) Adsorption capacities of NV-PEI (0.5 g/L dosage) obtained during 6 min of CT for different metallic ions in a competitive assay using 20 and 100 ppm of initial concentration for each metal. The number over the bar is the percentage of removal. (F) Photos of the adsorbent material of the NV-PEI before (1) and after (2) the removal process.

same total initial metal concentration of 120 or 600 ppm (results not shown here) could be related with the fact that especially at high concentrations the different removing mechanisms for these metals start blocking/interfering each other and some removal

mechanisms could to reach the saturation onto the NV-PEI surface (as for example the removal by surface adsorption),

allowing a major removal for each metal in comparison to the case when only one metal should be present.

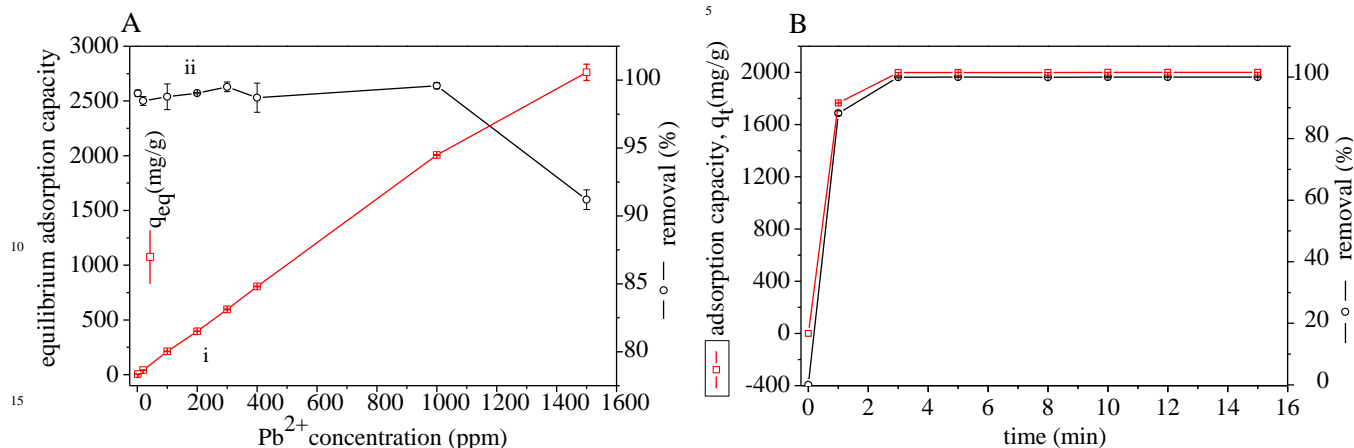


Fig. 2. Adsorption rate for Pb²⁺ cations onto NV-PEI. (—□—) Curve of adsorption capacity reached at 3 min of CT when initial metal concentration is increased. (—○—) Metal removal percentage when the equilibrium adsorption capacity is reached at different metal initial concentrations using 0.5 g NV-PEI/L dosage and 3 min of contact time. (B) Kinetic behaviour of the adsorption capacity and the percentage of removal of the NV-PEI particles using 1000 ppm of Pb²⁺ as initial concentration in the system.

As NV-PEI material in the multi-metal competitive removal assay showed the highest removal capacity for Pb²⁺, the following adsorption studies for the Pb²⁺ removal as shown below were performed.

The equilibrium adsorption capacity increases dramatically by increasing of Pb²⁺ initial concentration, until it reaches the q_{max} of 2762 mg Pb²⁺/g NV-PEI at 1500 ppm of Pb²⁺ initial concentration (Fig. 2A-i). For concentrations from 2 to 1000 ppm, 3 min of CT is enough to remove around 97-100% of the total Pb²⁺ initial mass using a dose of 0.5 g NV-PEI/L (Fig. 2A-ii). CTs longer than 3 min don't change significantly the adsorption capacity (see Fig. 2B), because all the Pb²⁺ contaminant from 2 to 1000 ppm is completely removed in the first 3 min of reaction reaching the q_{max}. This fast and high Pb²⁺ removal capacity has not been reported so far as shown in table S1.

The N₂ adsorption-desorption isotherms

The nitrogen adsorption and desorption isotherms of the NV-PEI adsorbent material exhibit type II isotherm with a type III

hysteresis loop in the relative pressure range of 0.45–1 P/P₀ (Fig. 3 A), suggesting that the adsorbing material structure is composed in majority by macropores with good pore connectivity associated with slit-like pores.^{34,35} In addition, as shown in Fig. 3 A and B, some mesoporous part in the size range of 2-50 nm for low relative pressures (P/P₀ < 0.4) is also present. The nitrogen amount adsorbed rises very steeply at high relative pressure (P/P₀ > 0.85), which also suggests the presence of an appreciable amount of very large pores in the material.^{34,35} The distribution curve of BJH pore size derived from the adsorption branch of the isotherm shows one very narrow distribution with a peak at 2.1 nm and one broad distribution in the range of 2.8–191 nm with a peak at 40 nm. It indicates that few microporous parts make up the material structure and a high percentage of the structure porosity are mesoporous and macroporous morphologies (see Fig. 3 B). It is interesting to highlight that the final part of the adsorption branch reaches large macropores diameter (50-190 nm). Moreover the material has a BET surface area of 20 m²/g and a BJH pore volume of around 0.07 mL/g.

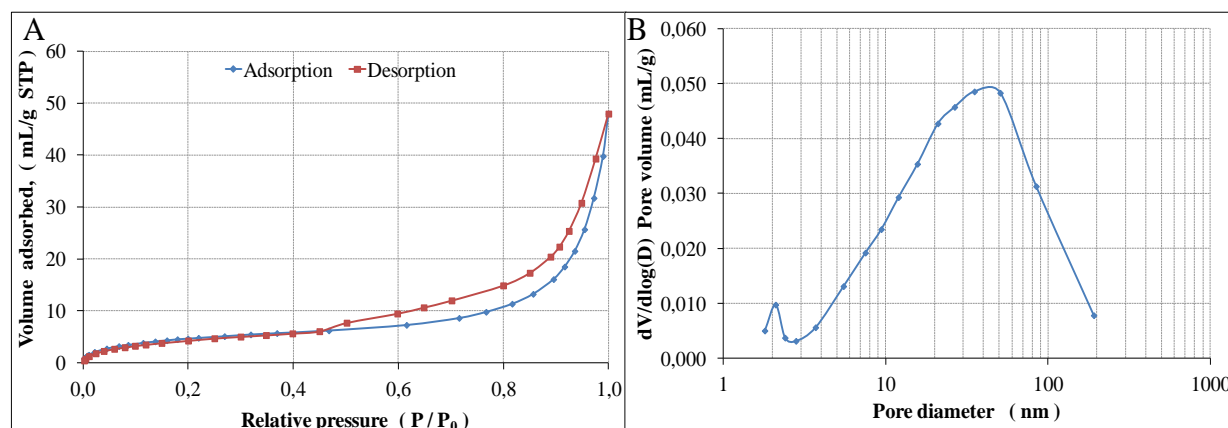


Fig. 3. N₂ adsorption and desorption isotherms (A) and the corresponding BJH pore size distribution curve for the synthesized product (B).

Pb²⁺ removing mechanisms.

XRD patterns and SEM images in Fig. 4 A and B, respectively, indicate that a new precipitation process is taking place during the treatment process of contaminated water with Pb²⁺. Fig. 4 A-1 shows the pattern of vaterite before its contact with Pb²⁺ solutions while its corresponding SEM images of spherical/ellipsoidal microparticles are shown in Fig. 4 B-1. After the contact of the NV-PEI material with Pb²⁺ solutions of increasing initial concentration a transformation of part of vaterite in cerussite (orthorhombic PbCO₃) (Fig. 4 A-2 and B-2) occurs, until that using 1500 ppm of Pb²⁺ solution a complete vaterite transformation into cerussite takes place (Fig. 4 A-3 and B-3).

The recrystallization process is mediated via ionic exchange, where the NV-PEI behaves like an ionic exchanger network of Ca²⁺ by Pb²⁺ cations. The exchanging process takes place both at superficial level as well as at the interior of NV-PEI material. The structure of NV-PEI collapses during the ion exchange, resulting in a recrystallization process by an irreversible ion exchange. The SEM images in Fig. 4B-3 display the orthorhombic PbCO₃

precipitate appeared from the starting NV-PEI microspheres/ellipsoids.

The curves represented in Fig. 5A show the increase of Ca²⁺ concentration in the solution during the removal process while that of Pb²⁺ was decreased. The equivalent molar concentration (Meq) of Ca²⁺ that is delivered from the NV-PEI material to the solution is statistically equal with that of Pb²⁺ which in turn disappeared from the solution by incorporation of the Pb²⁺ to the removing material when the removal equilibrium is reached. It means that a 1:1 ionic exchange between Ca²⁺ and Pb²⁺ occurs being this the principal mechanism for Pb²⁺ removal. As shown in Fig. 5B, equal Pb²⁺ Meqs are exchanged by Ca²⁺ at 3 min of contact time during the treatment process over a range of 20 to 1000 ppm of Pb²⁺ initial concentration. Under these conditions the residual quantity of Pb²⁺ in the solution varies from 0.8 to 0.1 ppm. It suggests that the NV-PEI material could be very useful to remove large Pb²⁺ quantity from industrial wastewaters allowing that the wastewaters reach the permissible maximum discharge limit of Pb²⁺ in sewers, rivers and seas (500 ppb).³⁶⁻³⁸ After 3 min

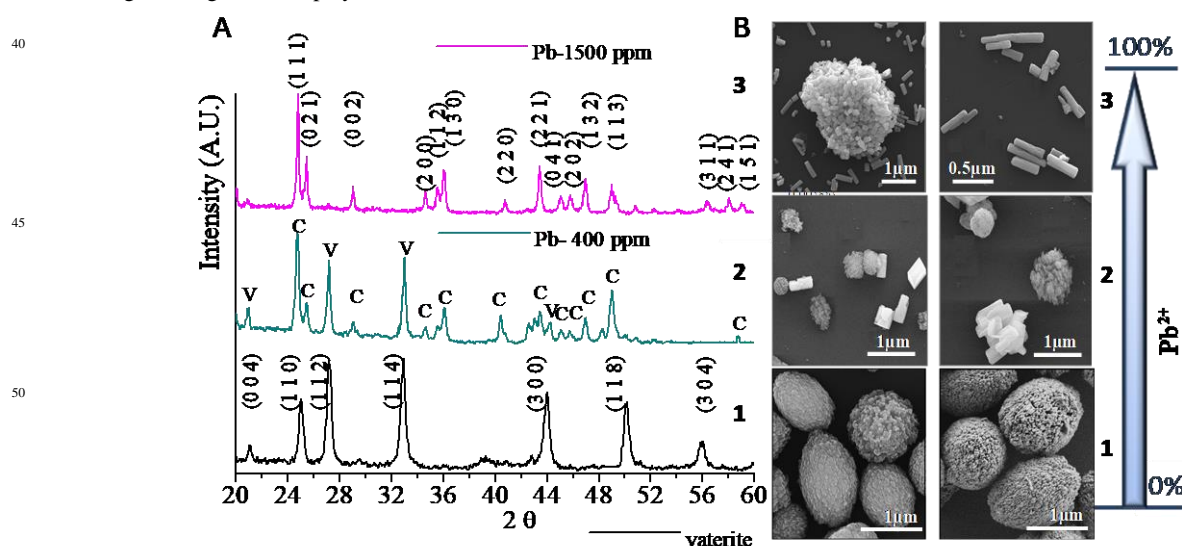


Fig. 4. (A) XRD patterns correspond to the NV-PEI product at different CTs and Pb²⁺ initial concentrations (1) before treatment at initial time when there is not contact with Pb²⁺ solution, (2) after 6 min of treatment in contact with 400 ppm of Pb²⁺ solution, (3) after 6 min of treatment in contact with 1500 ppm of Pb²⁺ solution. V means vaterite and C cerussite. (B) SEM images of the corresponding products.

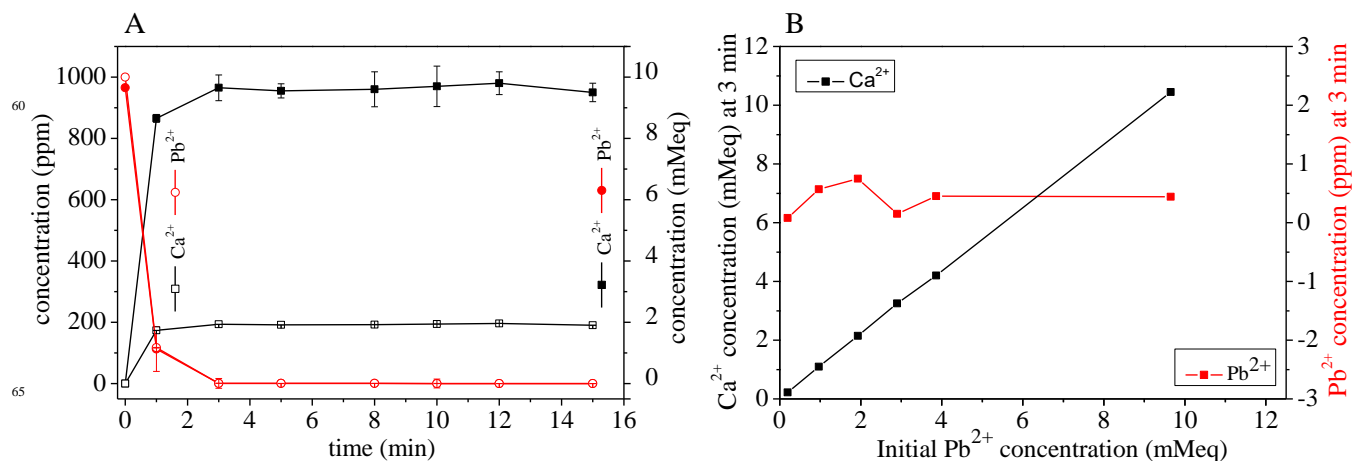


Fig. 5. (A) Kinetic behaviour of the Ca²⁺ and Pb²⁺ concentrations during the water treatment process with the NV-PEI material using 1000 ppm of Pb²⁺ as

initial contamination. (B) Behaviour of the Ca^{2+} and Pb^{2+} concentrations over the range of Pb^{2+} initial concentration (20-1000 ppm) at 3 min of CT with the NV-PEI material.

of use of this material in model assays for waters treatment with around 2 ppm of Pb^{2+} initial concentration, the residual quantity of Pb^{2+} in the solution is about 50 to 10 ppb, which additionally suggests that this material could be adequate to treat waters for uses as irrigation water, groundwater and agricultural and livestock considering the fact that 50 ppb is the acceptable maximum limit of Pb^{2+} for these waters (Table S2).³⁶⁻³⁸

The obtained results show that the NV-PEI hybrid material has powerful capability for fast and high removal of Pb^{2+} toxic ions (nearly 100% of Pb^{2+} removal after 3 min of CT). This phenomenon is related with three factors: the large pore size in the NV-PEI structure, the PEI presence in the material surface that entraps metallic cations through the adsorption via electrophilic-nucleophilic interactions and the recrystallization process mediated by the ionic exchange of Pb^{2+} contaminant through the entire calcite structure. Fig. 6 is a representative scheme of the proposed principle of the Pb^{2+} removing mechanism.

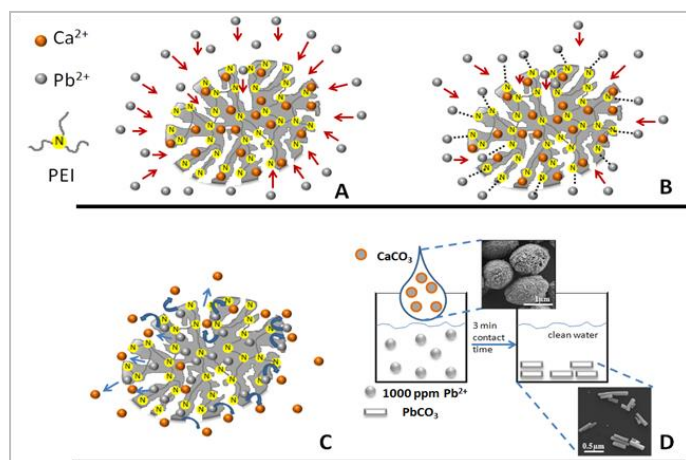


Fig. 6. Schematic representation of the Pb^{2+} removing mechanism by use of NV-PEI material. A) Pb^{2+} cations diffusion toward the NV-PEI structure occurs. B) The PEI layer onto the material surface entraps cations via electrophilic-nucleophilic interactions between PEI's nitrogen and Pb^{2+} . The slit macroporous structure permits a rapid accessibility to the inner parts in the NV-PEI structure. The red arrows indicate the movement of the Pb^{2+} cations into the adsorbent structure. C) Ionic exchange of Ca^{2+} by Pb^{2+} cations leading to the recrystallization process. The blue arrows indicate the movement of released Ca^{2+} ions after exchanging with Pb^{2+} ions. D) General scheme of the whole removing process.

The large size of the macropores that dominates in the structure (typical SEM images are displayed in Fig. 1A, B and D where large pore sizes of this material can be observed) as found by BJH method (see section *The N_2 adsorption-desorption isotherms*), and the high affinity power of the PEI with metallic cations as part of this hybrid material can explain the ultra rapid metal adsorption process that takes place in this system. The large size of the pores of this material permits large accessibility, as well as a fast and simultaneous penetration of a high quantity of

ions toward the inner parts of the NV-PEI microparticles. In addition to the pore size, the high affinity of PEI for metal cations acting as ionic entrapment network of chemical adsorption (Fig. 6 A and B) is another important and determinant factor in the fast Pb^{2+} removal process. The fast uptake of toxic metal ions indicates a high affinity rate between the Pb^{2+} ions and the amine groups of PEI that cover the material, as well as a rapid mass transference to the inner parts of the structure propitiated by the large size of the pores.

On the other hand, the recrystallization process mediated by the ionic exchange between the Pb^{2+} and the Ca^{2+} in the particle structure (see Fig. 6 C and D) is associated to the high removal capacity of this material. The value of BET surface area for the NV-PEI material, as obtained from N_2 adsorption and desorption isotherms (see section: *The N_2 adsorption-desorption isotherms*), is discrete in comparison with the reported ones for other materials (see table S1) and it doesn't justify the high Pb^{2+} removal capacity. This reasonably suggests that the high BET is not the only criterion that would explain the high Pb^{2+} removal capacity. The removal capacity sometimes is greatly affected by the surface quality/property. We suggest that the Pb^{2+} removal mechanism is based on a recrystallization via ionic exchange which is far a way of a simple superficial adsorption. This recrystallization via ionic exchange that happens here could be considered as a multilayer adsorption through the whole NV-PEI material, which consequently produces a superior removal capacity. The Pb^{2+} removal process onto the as-obtained NV-PEI microparticles, as explained in the section of *Adsorption isotherm of Pb^{2+} onto the NV-PEI material at SI*, obeys well the Freundlich isotherm model rather than the Langmuir one.^{39,40}

Additional discussion about the mechanisms of removing for other assayed metals appears in the corresponding section at SI.

Conclusions

In summary, a very fast toxic metals removal by using the hybrid NV-PEI is here reported. Metal removal studies such as the results of metal adsorption onto the NV-PEI, the analysis of the N_2 adsorption-desorption isotherms, the determination of the Pb^{2+} adsorption model and the proposals of removing mechanisms are shown for the first time for this material. Many results related to metal adsorbent materials reported in the literature for water treatment are obtained using an optimized pH value (usually pH 3-4) with long times of adsorption duration that end up to 2 h. Therefore, we believe that the exceptionally fast and high removal capacities obtained by using the NV-PEI under pH 6 are more indicative for a promising use of this material in real water treatment applications. Although the obtained results are in the laboratory scale, we expect satisfactory removal efficiencies at industrial scale especially for Pb^{2+} . This material could be useful to remove efficiently Pb^{2+} (almost 100% of removal) between 2 and 1000 ppm (using the discrete dosage of 0.5 g NV-PEI/L and just 3 min of CT) from industrial wastewater and transforming this residual water to an adequate one (with Pb^{2+} content under 500 ppb) able to be discharged into rivers, seas and sewers, or even (depending of the Pb^{2+} initial contamination) to use the

treated water for the reuse in agriculture or livestock, taking into account the maximum acceptable limit of Pb²⁺ for these waters (table S2). Moreover, this material could be easily produced at industrial amounts because it is facile to synthesize, cheap, biodegradable and environmentally friendly. In addition, it has a high loading capacity for organic molecules (dyes such as bromocresol green and methyl orange) through the hydrogen bond interaction of acid hydrogens in the contaminants molecules and the nitrogen's PEI onto the vaterite microparticles surface as reported previously.³³ This would increase the NV-PEI interest as potential adsorbent for simultaneous removing of many co-existing pollutants that usually appear in industrial effluents. The development of such multipurpose adsorbent which can remove both organic and toxic metal pollution would improve the cost / efficiency of water treatment process and might have impact on both the wastewater treatment technology as well as the science behind the phenomena occurring during the operation of such integrated and hybrid nanostructured materials.

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