Lead confinement and fluorimetric detection using zeolites: towards a rapid and cost-effective detection of lead in water

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Abstract
Metal clusters stabilized in zeolites have emerged as promising candidates for optoelectronic applications due to their remarkable luminescent properties. These optical properties have been exploited to develop fast and highly sensitive methods for optical sensing in environmental monitoring. However, to date, these materials have not been proposed as a detection method based on their luminescent response for sensing toxic metal ions. In this report, we synthesized luminescent lead (Pb) clusters into the cavities of synthetic F9-NaX zeolites, which were used as scaffolds to confine and detect Pb2+ ions in water through a fluorimetric mode. These Pb-F9 samples display an intense cyan emission in dehydrated form. Also, a correlation between the luminescence intensity of the materials and the lead loadings was observed, obtaining a low limit of detection of 1.248 ppb and a limit of quantification of 3.782 ppb. The results clearly demonstrate the potential of luminescent lead-exchanged F9 zeolites as one-step method for lead monitoring in water using a rapid and low-cost strategy.

1. Introduction

Lead ions (Pb2+) can cause serious damage to the environment and public health; it can accumulate in high levels in the human body affecting the brain, nervous and hematopoietic system, and digestive system during long-term expositions [1, 2]. Besides, it is one of the top five main heavy metals (Hg, Pb, As, Cr, and Cd) present in water [3, 4]. For such reasons it is important to monitor water quality to protect public health and the environment. Most common analytical techniques for quantitative detection of lead ions comprise UV–VIS absorption spectrometry, atomic absorption spectrometry, atomic emission spectroscopy, inductively coupled plasma mass spectrometry, thermal ionization mass spectrometry, x-ray fluorescence spectrometry and anodic stripping voltammetry. However, even though they display high sensitivity and selectivity, the use of sophisticated instruments and complicated sample preparation processes is required, which limits their direct and on-the-spot applications [5]. Therefore, it is of paramount importance to develop simple, fast and sensitive methods to detect and quantify lead ions in water. Several analytical methods for the detection of heavy metal ions based on optical properties, such as fluorimetric and colorimetric responses, have recently emerged due to their simplicity and low detection limits [6–8].

Microporous aluminosilicate zeolites have proven to be effective materials for the removal of heavy metal ions in water due to their excellent adsorption properties derived from their ion-exchange capabilities [9–12]. Besides, the zeolite framework possesses molecular-size pores and cages that have been used as an ideal scaffold to confine and stabilize sub-nanometric metallic clusters. Metal exchanged zeolites have emerged in recent years as materials with unique optical properties that originate from the electronic
configuration and molecular-like discrete energy levels of metal clusters [13, 14]. An activation step, such as heat treatment [15], photoactivation [16] and x-ray irradiation [17–19], is required to induce the formation (reduction and migration of metal ions within the scaffold) of luminescent metal clusters within zeolites. Therefore, the fluorimetric response of this new class of luminescent materials has been suggested as a promising alternative for pollutants sensing applications. For instance, Yao et al [20] reported the use of highly luminescent silver clusters confined in FAU-Y as an effective sensor for detecting formaldehyde based on a colorimetric and fluorimetric dual mode. Besides luminescent silver clusters stabilized in zeolites [21–25], Baekelant et al [26] recently demonstrated the self-assembly of highly luminescent Pb clusters confined in Lynde Type A (LTA) zeolites, opening up possibilities to use such strategy to, in one hand, confine lead ions within the microporous cavities of zeolites; and on the other hand, to use the fluorimetric response of lead clusters stabilized in zeolites to detect and quantify their presence in water.

Herein, we present a one-step and cost-effective strategy based on the luminescent response of partially lead exchanged F9-NaX zeolites for sensitive sensing of Pb^2+ ions. Particularly, zeolite Na-X has been shown to have a high affinity for Pb^2+ ions, as previously reported [27]. These materials were synthesized through a cation-exchanged process followed by heating at 450 °C. A strong relationship between the emission color and the hydration level was observed in these materials, which has been already described in silver-exchanged zeolites [28–31]. Furthermore, we found a strong correlation between the emission intensity and lead loadings in luminescent Pb-F9 zeolites, displaying a remarkable trend where the maximum emission intensities were observed at low lead loadings, depicting the potential of our strategy to detect lead ions in water at very low concentrations. To the best of our knowledge, this is the first time that zeolites are used in a dual way to confine and detect lead ions through a fluorimetric strategy.

2. Experimental section

2.1. Reagents and sample preparation
Lead(II) acetate trihydrate (Pb(CH₃COO)₂·3H₂O, Sigma-Aldrich, 99.9% purity) was used as received, zeolite F9 (Tosoh zeolites, figure S1 (available online at stacks.iop.org/JPHOTON/3/034003/mmedia), supporting information) was calcined at 450 °C for one day (with 15 min stops at 80 and 120 °C to avoid zeolite structure damage) to remove organic impurities before utilization. An aqueous lead acetate solution was used to perform the cation exchange of the original counter-ion. Different degrees of lead loadings were achieved by varying the concentration of the lead acetate (0.001, 0.005, 0.01, 0.05 and 0.1 M). The lead-loaded zeolites are named according to their lead content and hydration level as follows; F9Pb_y-X, where ‘y’ refers to the lead acetate concentration (0.001 up to 0.1 M) and ‘X’ stands for the hydration level (D: dehydrated, H: hydrated). Briefly, the zeolites were suspended in a solution containing the adequate amount of lead acetate and then stirred for 30 min at 50 °C. After recovery of the lead loaded zeolites by filtration, the powder was preheated at 100 °C for 1 h, and then transferred to a muffle for its further calcination at 450 °C overnight, using a temperature ramp of 5 °C min⁻¹. After heat treatment the samples were cooled under ambient conditions, allowing the samples to reach a fully hydrated state, and stored in the dark for further analysis. In the case of dehydrated samples, the activated materials were re-heated at 250 °C for 2 h and kept in a sealed container.

2.2. Samples characterization
For the emission-excitation characterization, the heat-treated samples were placed in a quartz cuvette (1 mm path length) and covered with a teflon stopper. Emission and excitation spectra were recorded using a Horiba Jobin Yvon fluorolog FL3-22 fluorimeter. Long pass filters were used, when appropriate, to avoid influence from scattering. Absolute emission spectra were measured by using an integrating sphere coupled to a commercial spectrofluorimeter (figure S2, supporting information). The device is based upon a Labsphere optical Spectralon integrating sphere (100 mm diameter), which provides high reflectance in the UV–visible and near infrared region [32]. The sphere accessories were made from Teflon (rod and sample holders) or Spectralon (baffle). Excitation was provided by a xenon lamp with a monochromator. Emission was collected in right angle and sent to a photon multiplier tube through the side port of the sphere after passing a monochromator. In the sphere, a baffle between the sample holder and the detection port was placed to avoid direct observation of the scattered light and the fluorescence from the sample. Diffuse reflectance spectra (DRS) were measured on a Perkin Elmer Lambda 950 instrument equipped with a 150 mm integrating sphere, using barium sulfate powder as 100% reflective reference sample. The reflectance percentage of the DRS spectrum was finally converted to Kubelka-Munk [33]. Powder samples were analyzed by Raman spectroscopy using a Micro Raman Spectrometer Dilon Labram II with an excitation line of 632.8 nm, a 50× objective and 25 mW laser power at room temperature. SEM images were recorded using a JEOL-6010LV SEM (non-coated samples).
3. Results and discussion

3.1. Photoluminescence characterization

Figure 1 displays the emission profiles of the F9-Pb samples obtained at different lead acetate concentrations (from 0.001 to 0.1 M) and digital photographs under UV irradiation, in their hydrated and dehydrated states. Upon calcination of the samples at 450 °C, an intense emission peak centered at 480 nm (cyan emission color) with an excitation maximum of 255 nm was observed for all samples in their dehydrated state (figures 1(a) and (b)), however, upon hydration of the samples a second emission band at 445 nm (deep blue emission color) was spotted (figures 1(c) and (d)). The same trend was also observed by Baekelant et al [26] with increasing the concentration of Pb in LTA zeolites in partially dehydrated state treated at 200 °C, nevertheless, no direct correlation between the emission intensity and lead loadings was reported in this contribution. It should be noted that no significant changes in the emission intensity of hydrated samples were recorded, as compared to the emission intensity of samples in their dehydrated state (figures 1(a) and (c)). Thus, dehydrated samples were selected to further investigate the correlation between the emission intensity and Pb loadings, which shows a decrease trend of the emission intensity with respect to the increase of lead loadings. Although, this change in luminescence intensity is more evident in the pictures of the hydrated samples under UV excitations of 256 and 366 nm (figure 1(d)) displaying the formation of emitting species of deep-blue color, except for the samples with high Pb content (F9-Pb₀.₀₅ and F9-Pb₀.₁) where there is a quasi-total decrease of the luminescence intensity. Figure S3 (supporting information) shows the 2D excitation-emission spectra of the samples in their dehydrated and hydrated states with different Pb contents, displaying the formation of well-defined luminescent lead clusters, similar to those previously reported [26]. These results show that a full dehydration of the samples is necessary to obtain a correlation between lead concentrations and emission intensities in lead loaded F9 zeolites.

3.2. Optical and structural characterization

To elucidate the origin of the different absorbing species, we measured the DRS for each sample with different Pb loadings, after cation-exchange (non-luminescent samples) process and in the calcined samples (dehydrated/hydrated states) and performed a spectral deconvolution of the experimental absorption spectra.
ions in Pb(ClO$_2$) solutions containing sodium formate employing pulse radiolysis, where the agglomeration in samples with high Pb loadings, these experimental results atoms to form Pb$^{4+}$ and Pb$^{4+}$ and F$_9$-Pb$^{4+}$-Pb$^{4+}$ species, respectively, encapsulated within the cavities of the atoms was observed. Also, they 35 Pb ions, displaying two main Pb$^{4+}$ ions, except for sample 39 Pb$^{4+}$ species and suggested that a further agglomeration process would cluster formation encapsulated into the sodalite cages in Pb species. Finally, they concluded that small metal particles with less and Pb$^{4+}$ cluster as the responsible of the luminescence in Pb$^{4+}$ species within F9 zeolite matrix [34, 35].

Upon dehydration of the calcined samples, a small red-shift of the two main absorption bands was spotted indicating the possible reduction of lead ions to lead atoms (figure 2(b)) [35]. An intense absorption band centered at 230 nm was observed for all samples, this band has been associated to Pb$^{0}$ atoms [35–37]. When increasing the Pb content, the formation of a second absorption band was observed. For sample F9-Pb$_{b001}$, a broad band centered at approximately 266 nm was recorded, then for F9-Pb$_{b005}$ and F9-Pb$_{b01}$ samples a blue-shift with the respective formation of well-defined bands at around 251 and 253 nm, respectively, was observed. However, for samples F9-Pb$_{b05}$ and F9-Pb$_{b01}$, a red-shift occurs again, with well-defined bands centered at about 268 and 272 nm, respectively, with a notably increase of absorbance intensity, that can be due to Pb$^{0}$ agglomeration in samples with high Pb loadings, these experimental results can be comparable with those reported by Henglein and collaborators [38]. They investigated the reduction of Pb$^{2+}$ ions in Pb(ClO$_2$)$_2$ solutions containing sodium formate employing pulse radiolysis, where the formation of absorption bands at 290 and 220 nm associated to Pb$^{0}$ atoms was observed. Also, they measured kinetic curves for the decay of the absorptions, where the rate of radiolytic reduction leads to the agglomeration of Pb$^{0}$ atoms to form Pb$_2$ species and suggested that a further agglomeration process would result in the formation of Pb$_4$ and Pb$_8$ species. Finally, they concluded that small metal particles with less than ten atoms already possess strong UV absorption bands associated to lead clusters.

The excitation spectra of dehydrated samples exhibit a well-defined excitation maximum (figure S5(a), supporting information) located between 255 and 260 nm (4.86 and 4.76 eV) which are comparable to those observed in the absorption spectra, indicating that the origin of the emission can be ascribed to a single lead species confined in the cavities of the synthetic zeolite F9. This was further corroborated by the absence of such absorption bands in pure F9 zeolites (figure S6, supporting information). Such excitation energies have been previously assigned to a cubane-like Pb$_4$O$_4$ cluster as the responsible of the luminescence in Pb containing LTA zeolites [26, 39]. The neutral Pb$_4$O$_4$ cluster formation encapsulated into the sodalite cages in Pb$^{2+}$-exchanged zeolite X followed by dehydration at elevated temperatures has also been observed in previous reports [40, 41]. Therefore, based in previous studies, the absorptions bands found between 251 and 272 nm in our samples can be assigned to Pb$_4$O$_4$ clusters. In addition, the deconvolution analysis of the absorption spectra (figure S4(b), supporting information) revealed a third band between 234 and 244 nm that can be attributed to presence of Pb$^{4+}$ ions, which could be formed upon evacuation at elevated temperatures, as previously reported [34, 40, 41]. Such lead ions inside the zeolite framework are not participating in the formation of luminescent clusters but rather compensating the negative character of the zeolite framework [40], such species could be absorbing UV light without displaying luminescence.

Likewise, we analyzed the absorption spectra after hydration of the calcined samples exposed to ambient conditions. As shown in figure 2(c), lead atoms are re-oxidized to Pb$^{4+}$ and Pb$^{2+}$ ions, displaying two main absorption bands, suggesting that the reduction is fully reversible. In DRS spectra we observed an intense band located at around 210 nm for all samples that can be attributed to Pb$^{2+}$ ions, except for sample

![Figure 2. Normalized Kubelka-Munk spectra of samples (a) lead exchanged (non-luminescent), (b) dehydrated and (c) hydrated state with different Pb contents.](image-url)
Figure 3. Normalized Raman spectra of samples with different lead loadings in hydrated state.

F9-Pb_{0.005} (figure 1(d)). Additionally, deconvolution analysis (figure S4(c), supporting information) revealed a small shoulder located around 220 nm that could be assigned to Pb^0 atoms [35, 36]. For all samples a second absorption band was located at around 240 nm, that can be associated to Pb^{4+} ions [34]. However, an evident decrease in the intensity of the absorption band for samples F9-Pb_{0.001} and F9-Pb_{0.05} was observed; whereas for samples F9-Pb_{0.01}, F9-Pb_{0.5} and F9-Pb_{0.1}, higher intensities were recorded.

From the excitation spectra of hydrated samples (figure S5(b), supporting information) a well-defined excitation maximum located around 250 nm (comparable to the absorption band observed at 240 nm) and two more bands centered at about 310 and 370 nm were identified. Nevertheless, a decrease in the intensity of the 250 nm excitation maximum at higher Pb loadings was recorded, reaching even a total decrease in the intensity for samples F9-Pb_{0.05} and F9-Pb_{0.1}. This could indicate that at higher Pb loadings the formation of competing species (which absorb UV irradiation without displaying luminescence) is more relevant [26]. It is worth noting that the other two bands at 310 and 370 nm, could be also associated to other luminescent species, since under 366 nm UV excitation, the samples displayed a dim luminescence (figure 1(d)).

[Pb_{4}(OH)_{4}]^{4+} clusters have been reported inside the sodalite cages of hydrated Pb^{2+}-exchanged zeolite X [42]. Therefore, we can assume that our results could be related to presence of this type of clusters.

Raman spectroscopy is a powerful technique widely used in the characterization of zeolites despite the strong background fluorescence exhibited by luminescent materials [43]. Additionally, UV-Raman has been employed to monitor zeolites growth, showing that the Si/Al ratio strongly influences the position and intensity of the Raman peaks, which is directly related to the structural order of the zeolite framework [44]. Using this technique, local low-frequency translational vibrations of cations in zeolites and framework bending modes can be analyzed [45, 46]. The synthetic F9-NaX zeolite did not display vibration modes at low frequencies, which makes it ideal for determining the presence of exchanged cations. Moreover, Pb–Pb vibration modes of Pbₙ structures at low frequencies between 92 and 124 cm⁻¹ have been determined [47] in such zeolites.

Experimental Raman microspectroscopy was measured for samples in hydrated state and pristine zeolites (as reference). As can be seen in figure 3, Raman spectrum of zeolite F9-NaX exhibits two bands between 250 and 400 cm⁻¹, straightforward assigned to the bending mode of the six-membered rings (6MR) and a more intense band at 507 cm⁻¹ related to the bending mode of the characteristic four-membered rings (4MR), as previously reported for zeolite X [44]. Raman spectra of lead loaded zeolites showed slight changes in the position and intensity of the most prominent bands near 507 and 376 cm⁻¹ with the increase of lead concentrations where a blue-shift was recorded, this could be considered as an indication of ion exchange.
In addition, a very low-frequency peak appears at about 117 cm\(^{-1}\) starting from F9Pb\(_{0.01}\) and steadily increase with respect to the lead loading. This peak has been assigned to Pb–Pb vibration modes \([37, 47]\) and is considered as an indicator of lead cation exchange in zeolites.

It is worth noting that the bandwidth at around 507 cm\(^{-1}\) of pristine F9 zeolites increased progressively with respect to lead concentration. This trend has been associated with the redistribution of the cations location and the coordination with water molecules after hydration \([45, 49]\), and produces a substantial level of disorder into the system, as observed in figure S3 (supporting information). Furthermore, it is indicative of the formation of [Pb\(_4\)(OH)\(_4\)]\(^{4+}\) clusters that are probably positioned in the axis of the 4MR of the sodalite cage in their hydrated form, which is in very good agreement with Nardin \(et\) \(al\) \([42]\) that observed fully occupied sodalite cages with lead hydroxide clusters [Pb\(_4\)(OH)\(_4\)]\(^{4+}\) in zeolite X. Hence, the changes observed for the band around 376 cm\(^{-1}\) can be related to the evidence of individual Pb cations placed in the S6R of sodalite cages containing both clusters and non-clusters species, as previously reported by Baekelant \(et\) \(al\) \([26]\). Thereby strengthening the explanation that this percentage of cations does not participate in the formation of luminescent clusters, causing a decrease in luminescence intensity when the Pb content increases.

### 3.3. Fluorimetric detection of lead

To evaluate the sensitive detection of Pb\(^{2+}\) ions, a deconvolution of the emission spectra was performed using a Gaussian fit (figure S7, table S2 and S3, supporting information). We used the emission intensity at 480 nm peak of the dehydrated F9Pb samples (figure 1(a)), since it exhibited a direct correlation with respect to lead loadings. The results are depicted in figure 4(a) where a decrease of the luminescence intensity at high lead concentrations was observed, while the opposite is true for low loaded samples, indicating the excellent fluorimetric response for low lead concentrations, considering that the luminescence of the samples was collected using an integrating sphere to achieve absolute measurements. As the concentration response curve is not a linear for the entire lead loading range, we employed a logarithmic scale to adjust the experimental data \([20]\). Figure 4(b) displays the calibration curve showing that the luminescence emission of the lead loaded zeolites exhibit a linear response in the range of 207 200–2.072 \(\times\) \(10^5\) ppb \((y = -0.38922 \log (x) + 9.89701, R^2 = 0.997)\). The limit of detection (LOD) and limit of quantification (LOQ) (estimation based on LOD = 3.3\(\sigma\)/S and LOQ = 10\(\sigma\)/S, the procedure is explained in detail in the supporting information) of lead emitting species, as obtained from the calibration curve, were of 1.248 and 3.782 ppb, respectively \((n = 5)\). LOD was lower than the maximum allowable concentration (15 ppb) for Pb\(^{2+}\) in drinking water, as defined by the United States Environmental Protection Agency (EPA) \([50]\). This suggests that our material can be used as a fluorimetric sensor for the detection of lead ions in the analysis of polluted water. Nevertheless, further investigation is needed to develop an analytical protocol based on the proof of principle presented in this report.

To verify the specificity of the approach presented in this study, a cation exchanged experiment using Ag\(^+\) was conducted (F9-Ag samples), varying the concentration of silver nitrate (0.001, 0.005, 0.01 and 0.05 M), and heat-treating the samples following the same procedure utilized for F9-Pb samples. Several reports have demonstrated the formation of luminescent silver clusters incorporated in zeolite matrices.
[21–25], therefore, these materials are good candidates to analyse a possible spectral interference with respect to F9-Pb samples. The obtained F9-Ag samples were irradiated under a 366 nm UV lamp revealing different luminescent colors (figure S8, supporting information). Figure S9(a) (supporting information), depicts the emission spectra of the samples in their dehydrated state with different Ag contents excited at 310 nm, displaying a broad emission in the visible region ranging from 420 to 690 nm with a maximum band between 555 and 580 nm. Nonetheless, the results showed the lack of a lineal correlation between the emission intensities and silver concentrations in luminescent F9-Ag zeolites (figure S9(b), supporting information). This finding further reflects the important role played by zeolite F9 in the confinement of lead clusters to obtain a linear behavior between the luminescent response and the concentration of the lead species, demonstrating the potential of this system to be employed as a fluorimetric sensor to capture and detect lead ions in water.

In previous reports, the utilization of noble metal nanoclusters as sensors for the optical detection of toxic metal ions has been proposed. However, for the stabilization of nanoclusters other types of scaffolds have been used, including polymers, dendrimers, oligonucleotides, DNA, peptides, proteins and small molecules [51]. For instance, Burratti et al [52] prepared a colloidal water solution of polymer polymethacrylic acid-encapsulated Ag nanoclusters, by UV irradiation process. They used the fluorescent Ag nanoclusters as heavy metal ions sensing probes and found a remarkable sensitivity mainly towards Pb$^{2+}$ ions that produced a strong fluorescence enhancement with respect to the lead concentration and showed a relatively low LOD of 12 ppb. Nevertheless, in the majority of the developed sensing strategies a two-step process is required, one to produce the sensing agent (luminescent species) and the second to bring it in contact with the species to detect. In the proposal presented in this report zeolites are used as adsorbents to confine lead ions and at the same time as stabilization scaffolds to convert the lead ions into highly luminescent lead clusters, simplifying the sensing strategy.

4. Conclusions

In summary, we have synthesized luminescent lead-exchanged zeolites through Pb$^{2+}$ cation exchange and thermal treatment using F9 zeolites. The results of the photoluminescence, optical and structural characterization of the samples showed that F9 zeolites have a high affinity for Pb$^{2+}$ ions and that the luminescent properties originate from the formation of Pb$_4$O$_4$ clusters inside the sodalite cages of the F9 zeolite in their dehydrated state displaying an intense cyan emission; whereas in hydrated samples a dim deep blue emission was observed attributed to [Pb$_4$(OH)$_4$]$^{4+}$ species. We found a strong correlation between the emission intensity of dehydrated samples and lead loadings, displaying a remarkable trend where the maximum emission intensities were observed at low lead loadings, demonstrating the potential use of these materials as fluorimetric sensors to detect Pb$^{2+}$ ions in water through a one-step approach, exhibiting a LOD of 1.248 ppb, complying with the maximum allowable limit of the EPA for Pb$^{2+}$ in drinking water. To the best of our knowledge, this is the first time that zeolites are used in a dual way to confine and detect lead ions through a fluorimetric methodology, opening up possibilities to apply this strategy to other heavy metals.

Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: https://dataverse.harvard.edu/dataset.xhtml?persistentId=doi:10.7910/DVN/8A3ZK9.

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