

Sorbent-embedded sheets for safe drinking water in developing countries: a case study of lead(II) removal by a zeolite-embedded sheet

Lester Botoman, Elvis Shukla, Erni Johan, Satoshi Mitsunobu and Naoto Matsue

ABSTRACT

Although many kinds of materials for water purification are known, easy-to-use methods that ensure the safety of drinking water for rural populations are not sufficiently available. Sorbent-embedded sheets provide methods for the easy removal of contaminants from drinking water in the home. As an example of such a sorbent-embedded sheet, we prepared a Linde type A (LTA) zeolite-embedded sheet (ZES) and examined its Pb(II) removal behaviour. Different amounts of LTA were added either as powder or as ZES to 0.3 mM Pb(NO₃)₂ solutions containing 2.5 mM Ca(NO₃)₂, in which the ratio of the negative charges in LTA to the positive charges in Pb(II) (LTA/Pb ratio) ranged from 1 to 20. After shaking, the mixtures were centrifuged to remove the powder, while the ZES was simply removed from the mixture by hand. The LTA powder removed more than 99% of the Pb(II) from the solution at all LTA/Pb ratios within 1 h, while the ZES removed >99% of the Pb(II) at LTA/Pb ratios of 2 and higher; at the highest LTA/Pb ratio of 20, the ZES removed >99% of the Pb(II) in 30 s. Therefore, the use of appropriate sorbent-embedded sheets enable the facile removal of contaminants from water.

Key words | lead(II) removal, safe drinking water, sorbent, zeolite-embedded sheet

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INTRODUCTION

Lack of safe drinking water is one of the most serious global health problems. WHO/UNICEF have reported that nearly 663 million people worldwide do not have access to clean water and 80% of people living in rural areas lack safe drinking water (WHO/UNICEF 2015). The types and amounts of contaminants in drinking water differ by country and region, and consist mainly of *Escherichia coli*, heavy metals and arsenic, along with many other kinds of substances and microbes (Amin *et al.* 2014). Among these contaminants, heavy metals are natural and become concentrated because of weathering, mining and industries, as well as other factors (Nagajyoti *et al.* 2010; Chao & Chen 2012), and millions of

people have been reported to suffer from chronic heavy metal poisoning (Fernández-Luqueño *et al.* 2013).

Heavy metals in water are usually removed by a variety of methods that include precipitation, filtration, coagulation, flotation, electrochemical methods and sorption (Fu & Wang 2011). Sorption is the most widely used technique, and studies have reported a variety of effective adsorbents for the removal of heavy metals (Wang & Peng 2010; Fu & Wang 2011; Hua *et al.* 2012; Khan *et al.* 2012). However, despite the knowledge gained from these studies, only a few methods exist for the removal of heavy metals from water in the home.

Here, we introduce the use of a sorbent-embedded sheet as a new method for the removal of contaminants on a small scale from, for example, a glass of drinking water. The sorbent-embedded sheet facilitates the addition of the sorbent to water, as well as its removal. As a case study, we prepared

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a Linde type A (LTA) zeolite-embedded sheet and compared its Pb(II) removal behaviour with that of the LTA powder. We selected Pb(II) as a universally harmful heavy metal and used LTA because Pb(II) is adsorbed to it with high selectivity (Kabwadza-Corner *et al.* 2015).

MATERIALS AND METHODS

Materials

All chemical reagents were purchased from Nacalai Tesque, Inc., Japan. LTA was purchased from Wako Pure Chemical Industries, Ltd, Japan, and was washed with 1 M NaCl solution, followed by water, and air-dried prior to use.

Ten non-woven fabrics normally used for filtering kitchen sink waste, each composed of polypropylene and polyethylene (24 × 30 cm; Platec, Ltd, Japan), were sandwiched by 100 g of the LTA powder on an aluminium dish, and gently pressed by hand to loosely attach the LTA powder to the fabric. The dish was placed in an oven at 160°C and removed after 8 min. After cooling, each fabric sample was vigorously washed with water to remove any unattached LTA powder, followed by drying in air. The sheets obtained in this manner were used as LTA zeolite-embedded sheets (ZES). Unembedded LTA powder was also heated prior to use as described for the ZES.

ZES characterisation

Scanning electron microscopy (SEM) was performed with a JEOL JSM-5310 instrument. Cation-exchange capacity (CEC; equal to the amount of negative charge) was obtained as

follows (Ming & Dixon 1987; Kang & Egashira 1997): 1 g of the LTA powder, and ZES embedded with 1 g of LTA were separately washed three times with 30 mL aliquots of a 1 M KCl solution (1 h each wash), then five times with 30 mL aliquots of 80% ethanol (1 h each wash) and three times with 30 mL aliquots of a 1 M NH₄Cl solution (1 h each wash), and the amount of K⁺ extracted by NH₄⁺ was determined by atomic absorption spectrophotometry (AAS; Hitachi, Z-5000).

Pb(II) removal experiments

In 250-mL polypropylene centrifuge bottles, 0.01–0.2 g of LTA, either as the LTA powder or ZES, were added to 100 mL aliquots of 0.3 mM Pb(NO₃)₂ solution containing 2.5 mM Ca(NO₃)₂ at pH 5. The presence of Ca(NO₃)₂ served to simulate hard water, and the experiments were performed in duplicate. The mixtures were shaken reciprocally at 125 rpm at an amplitude of 3 cm and at 20°C for up to 6 h. For the LTA powder-containing samples, the bottles were centrifuged at 2,500 × g for 10 min and the supernatants (LTA-s) were collected. For the experiments using ZES, the ZES was simply removed from the bottles by hand to obtain the treated solutions (ZES-s). The concentrations of Pb(II) in the LTA-s and ZES-s were determined by AAS, the percentages of removed Pb(II) calculated, and the final pH values of the solutions measured.

RESULTS AND DISCUSSION

ZES characterisation

The physical appearances of the non-woven fabric sheet and the ZES are shown in Figure 1(a). There was almost no

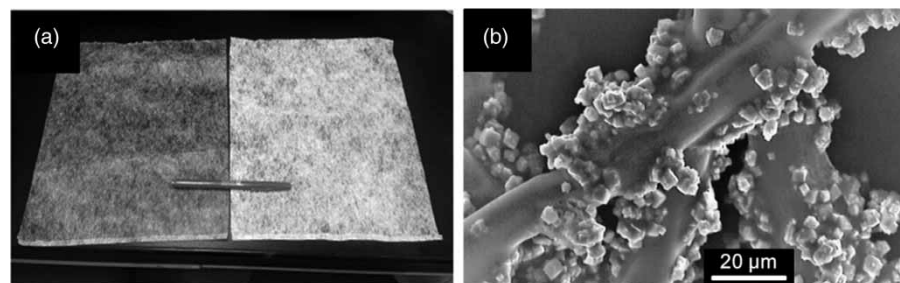


Figure 1 | (a) Physical appearance of the non-woven fabric sheet (left) and ZES (right), and (b) SEM image of ZES.

shrinkage of the sheet following heat treatment during the preparation of the ZES, and it had similar water-permeability to the fabric sheet. The fabric sheet had an area density of 15.4 g m^{-2} , while that of the ZES was 27.8 g m^{-2} ; consequently, the LTA content in the ZES was 44.6%. The SEM image of the ZES is shown in Figure 1(b). The non-woven fabric sheet consists of 15–20 μm -diameter fibres, and the attachments of the LTA particles to these fibres are clearly observable. Particle aggregation is observed; however, the detachment of these particles from the ZES was not observed during the Pb(II) removal experiments. The CEC values of the LTA powder and the LTA embedded in the ZES were determined to be 5.95 and $5.83 \text{ mol}_c \text{ kg}^{-1}$, respectively, which indicates that the attachment of the LTA particles onto the fibres did not significantly affect the sorption capacity of the LTA zeolite embedded in the sheet.

Removal of Pb(II)

In this study, we added different amounts of LTA in the powder or ZES form to a consistent amount of Pb(II). From the mass of added LTA and the measured CEC values of the two materials, we calculated the ratios of the negative charges in LTA to the positive charges in Pb(II) (LTA/Pb ratio) for all samples; this ratio ranged from approximately 1 to 20. The final pH of the LTA-s or ZES-s was observed to increase with increasing shaking time and LTA/Pb ratio. After shaking for 6 h, the final pH ranged from 5.85 to 8.62 for the LTA-s and from 5.32 to 7.53 for the ZES-s; the pH values were lower for the ZES-s than for the LTA-s at each LTA/Pb ratio. The observed increases in pH are due to the replacement of Na^+ by H^+ ; this phenomenon is generally observed when Na^+ -saturated zeolites are added to aqueous solutions. The increase in pH is reported to cause the formation of PbOH^+ species having stronger affinity to negatively charged surfaces than that of Pb^{2+} , which may increase Pb(II) adsorption selectivity to the LTA (Renatunga et al. 2008). On the one hand, preliminary experiments indicated that the Pb(II) in a 0.3 mM Pb (NO_3)₂ solution began to precipitate as hydroxides at pH 6.5; however, pH values higher than 6.5 were observed for the LTA-s and ZES-s, as discussed above. In the case of the ZES-s, no Pb(II) precipitate was observed at least in

the solution phase, even at the highest LTA/Pb ratio of 20 (pH 7.53); Pb(II) was not detected by AAS after nitric acid was added to the solution, confirming its absence.

Figure 2(a) shows the concentrations of Pb(II) as functions of shaking time for the LTA-s at different LTA/Pb ratios. The concentrations of Pb(II) in the LTA-s decreased to below $3 \mu\text{M}$ at all LTA/Pb ratios. We assumed that >99% of the Pb(II) was removed when the concentration of Pb(II) fell below $3 \mu\text{M}$, because the initial concentration

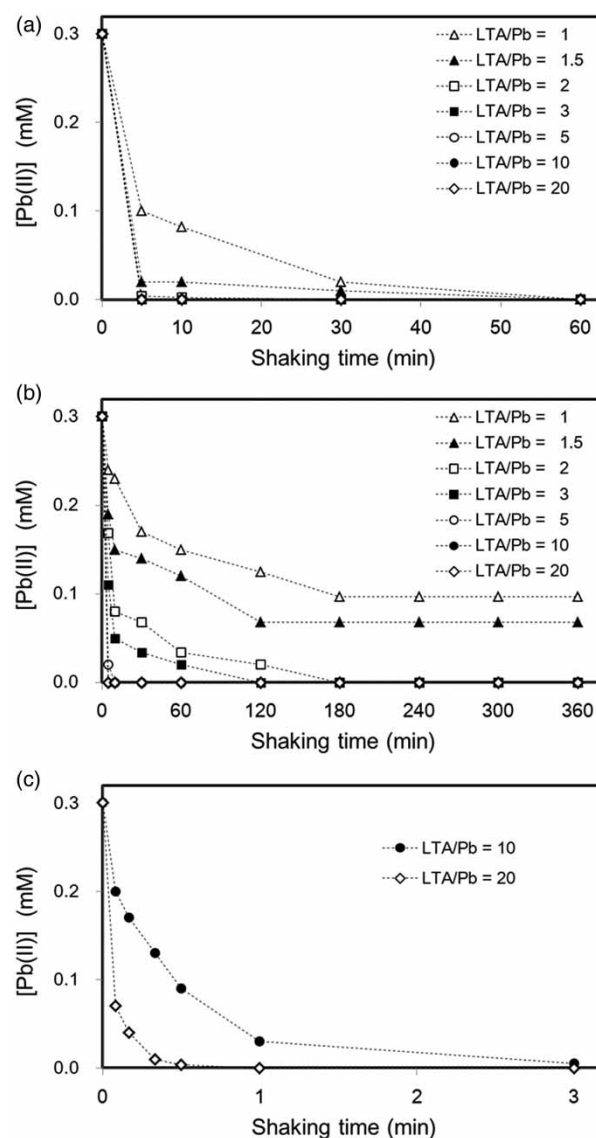


Figure 2 | Concentrations of Pb(II) as a function of shaking time for (a) LTA-s and (b) ZES-s at different LTA/Pb ratios; and (c) ZES-s at LTA/Pb ratios of 10 and 20 over shorter shaking times.

of Pb(II) was 0.3 mM. Even at the lowest LTA/Pb ratio of 1 (pH 5.85), >99% of the Pb(II) was removed after 60 min of shaking.

The concentrations of Pb(II) in the various ZES-s samples as functions of shaking time are shown in Figure 2(b). At LTA/Pb ratios of 2 and higher, >99% of the Pb(II) was removed, but the shaking time required to achieve this was longer than that for the LTA-s at each LTA/Pb ratio. In addition, at LTA/Pb ratios of 1 and 1.5, more than 20% of the Pb(II) remained in the ZES-s even after 6 h of shaking. These results indicate that the ZES has a lower Pb(II) sorption capacity and rate than those of the LTA powder, and this is ascribed to the fact that Pb(II) in the bulk solution is incapable of directly contacting the outer surface regions of the LTA particles in the ZES, namely, regions attached to the fibres and regions located inside the aggregates. In addition to the effect of attachment and aggregation, lower contact frequencies between the LTA particles and Pb(II) in the batch system might reduce the Pb(II) accessibility to the LTA in ZES. In other words, the LTA-powder particles are evenly distributed throughout the solution during shaking, whereas for ZES, these particles are more localised. The attachment, aggregation and limited distribution also affect the replacement of Na⁺ by H⁺; consequently, the ZES-s samples were more acidic (lower pH values) than the LTA-s, as previously mentioned.

The lower accessibility of cations to the LTA particles in the ZES mentioned above is, however, inconsistent with the CEC results that reveal almost identical values for the LTA powder and ZES. The high concentrations of KCl and NH₄Cl and the repeated washing during the determination of CEC, in which the adsorption and replacement of K⁺ and NH₄⁺ proceed almost to completion even for the ZES, are likely to be responsible for this observation.

Although the accessibility of Pb(II) to the LTA in ZES is lower than that of the LTA powder, the ZES removed >99% of the Pb(II) in solution, except at low LTA/Pb ratios, and the shaking time needed to achieve >99% Pb(II) removal decreased with the increasing LTA/Pb ratio (Figure 2(b)). Since the Pb(II) concentrations at higher LTA/Pb ratios decreased very rapidly with the reaction time (Figure 2(b)), the results obtained at LTA/Pb ratios of 10 and 20 were re-plotted by restricting the shaking times to 3 min, as shown in Figure 2(c). This figure reveals that the Pb(II)

concentrations decrease dramatically over the first minute, and that >99% of the Pb(II) was removed in 30 s at an LTA/Pb ratio of 20. This suggests that Pb(II) in water is easily removed by LTA without the need for any equipment to separate the LTA powder from the water.

CONCLUSION

The use of an appropriate sorbent-embedded sheet provides an easy way of removing contaminants from the drinking water of rural communities in developing countries. Our case study demonstrated that the ZES removes Pb(II) from Pb(II)-polluted drinking water without the need for centrifugation and other separation techniques. Nonetheless, the selection of cheap and effective sorbents, optimisation of the embedding method, and use of sorbent-embedded sheets by rural communities need to be further studied since community cultures, including lifestyle, differ from one country or region to another, which affect the efficacy of any water purification method.

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