Beneficial use of meat and bone meal combustion residue: "an efficient low cost material to remove lead from aqueous effluent"

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Abstract

Meat and bone meal (MBM) combustion residues, a natural apatite-rich substance, was evaluated as a low cost substitute for hydroxyapatite in lead sequestration from water effluents. The thermal behaviour of crude meat and bone meal was followed by TGA and 24% inorganic residue was collected. The resulting ashes were characterised by powder X-ray diffraction (XRD), particle size distribution, specific surface area (BET), and elemental analysis confirming apatite contents, with high level of phosphate (56.3%) and calcium (36.8%). Mechanism and kinetics of lead removal by this bioinorganic material were investigated and compared to mechanisms and kinetics involved with synthetic apatite. Batch metal removal experiments were carried out with 500 and 1500 ppm (mg/kg) Pb^{2+} solutions. Lead concentration, calcium and pH were monitored. We observed that the mechanism is similar to that occurring for pure apatite, and involved both surface complexation and calcium hydroyapatite (CaHA), $Ca_{10}(PO_4)_6(OH)_2$, dissolution followed by less soluble $Pb_{10}(PO_4)_6(OH)_2$ precipitation, as confirmed by XRD analysis of ashes after incubation with lead solution. Our results show that this natural apatite-rich material removes in a few minutes a large quantity of lead (275 mg/g capacity) which remains however lower than the theoretical maximum capacity (if calcium were totally substituted by lead). Meat and bone meal combustion residues represent a valuable alternative apatite source for environmental application.
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1. Introduction

The presence of lead in aqueous effluents and the fate of meat and bone meal (MBM) stocks are two major environmental and health concerns. Like most other heavy metals, lead remains dangerous even at low concentration because it tends to bio-accumulate in the food chain. Therefore, several processes have been used and developed over the years to remove such metals from industrial wastewater: chemical precipitation–filtration, electrochemical recovery, ion exchange, membrane filtration or adsorption [1]. However, even if many of these processes can remove dissolved heavy metals, most present some disadvantages such as poor uptake capacity, low efficiency/cost ratio and/or ineffectiveness for low metal concentrations (ppb = μg/kg) as recommended by international standards [1,2].

Lead intoxication has been a problem throughout history [3,4], as it has been used for many years in products of every day life (paint, water pipes, . . .). Adverse health effects of lead are well documented: it may cause a range of physiological disorders from neuropsychologic dysfunction (headaches, hearing problems, learning disabilities, behavioural problems, brain damages, . . .) to death [4,5]. Human pharmacokinetic studies revealed that lead has an extremely long terminal elimination half time in blood of more than 30 days and a similar rate of uptake into tissues. But the major problem is its rate of elimination from bones, where it accumulates, estimated to years [5]. That is the reason why young children (less than 7 years old) are most at risk, their body growing quickly. Drug therapy with chelating agents removes lead primarily from blood and soft tissues, and so lowers its concentration in blood until deeply stored lead (bones) reequilibrates in circulation [4,5]. Therefore, treatment with chelating agents of chronically lead exposed individual is a long time therapy to lower body burden.

Calcium hydroxyapatite (CaHA), is the major inorganic constituent of bones and teeth. The strong efficiency of bones to store lead was rationalised by the ability of CaHA to exchange cations [6] and by the low solubility of lead phosphates [7–9] like lead hydroxyapatite (PbHA). Such ability has stimulated intensive research to understand the mechanisms involved in aqueous lead sequestration by synthetic apatites [10–14] and to evaluate environmental applications of this material. Immobilisation of lead on synthetic or natural (bones, rocks, . . .) calcium hydroxyapatite is becoming a promising way for remediation of contaminated water [10–16] and soil [17–20]. Some other research investigated the effectiveness of phosphate rocks to immobilise Pb by in situ formation of lead phosphate [21]. Hydroxyapatite is also widely used to trap other heavy metals [22–28].

In our search for new low-cost materials to extract heavy metals from aqueous effluents, we investigated the use of low risk MBM combustion residues, which contain a high amount of phosphate. Among the different processes studied, valorisation of MBM can be realised by a thermal treatment. During high temperature combustion (over 800 °C), thermal energy is recovered and proteins such as prions are destroyed (as all organic matter is converted to CO_2, H_2O, . . .) [29]. In France, for example, 850 000 t of MBM are produced each year but actually only 45% can be burned by cement plants [30]. The remaining 55% are stored waiting for further destruction. Ashes produced by meat and bone meal combustion representing up to 30% in weight, a thermal treatment of the whole MBM production could lead to an important amount of ashes (nearly 250 000 t per year). Therefore, valorisation of ashes is of major concern. We report here a study on the ability of meat and bone meal

combustion residues, to uptake and immobilise lead from aqueous effluents. Mechanism, capacity and kinetic experiments are compared to published results on synthetic apatite.

2. Materials and methods

Meat and bone meal were burned by calcination in an electric furnace programmed to reach 800 °C at 2 °C/min. The residues were washed with water, and the pH adjusted to 7 with nitric acid, before filtration to remove all water soluble residues. Ashes were used after drying 24 h at 50 °C.

Thermogravimetric analysis was performed with a Setaram TG-DTA92, in platinum crucible, under air atmosphere, from 20 to 900 °C with an increasing temperature rate of 3 °C/min.

Total C, H and N were determined by elemental analysis on a Thermoquest CHN EA 1108W.

Specific surface area measurements were realised applying one-point BET method (nitrogen adsorption) on Micrometrics Model 2100E Accusorb.

Infrared spectra were recorded with an ATI Mattson (Genesis series FTIR) spectrometer.

The aqueous solutions of lead were prepared with deionised water (Millipore Milli-Q) and crystallised $Pb(NO_3)_2$ (99% minimum) provided from Labosi. Lead analysis was performed by atomic adsorption with electrothermal atomisation (Perkin—SIMAA6000). Calcium analysis was performed by atomic adsorption with flame atomisation (Unicam—Solar) and N_2O/C_2H_2 gas mixture. Certified aqueous standards were obtained from Aldrich.

Solids were analysed by X-ray diffractometry using a Siemens D501 diffractometer operating with Cu Kα radiation. Measurements were made using a step-scanning technique with 2θ step interval of 0.05° from 15° $< 2\theta < 80°$ and an acquisition time of 1 s per step.

Kinetics were conducted in a 1 L thermostated reactor, at 20 °C, by mixing 200 mL of metal solution at various concentrations with 500 mg of ashes. A mechanical agitator at 400 rpm provided mixing (Urostar digital IKA). pH was monitored. Aliquots of the supernatant solution were taken using a 2 ml propylene syringe equipped with a 0.45 μm filter. Collected samples were acidified with nitric acid and diluted before analysis. The amount of sorbed metal/g of ashes (q_t) at time t was calculated as follows:

$$q_t = \frac{C_0 - C_t}{m_{\text{ads}}} \tag{1}$$

where C_0 and C_t are the metal concentration in liquid phase at the initial and any time t (in ppm (mg/kg) or mmol/L), and m_{ads} the sorbent amount in solution (g/L).

3. Results and discussion

As expected, the lead extraction efficiency of meat and bone meal is closely related to its composition and so to its origin, combustion temperature, washing procedure, particle size, ... In our experiments we used low fat MBM coming from slaughterhouse waste. These

products were dehydrated (110 °C/4–5 h) and sterilised (133 °C/(20 min at 3×10^5 Pa)) according to European standards by Fersobio.

Thermal analysis shows a three-step mass loss with nearly 24% inorganic residue available. In a first step we observed water (6%) evaporation around 100 °C and then combustion of organic material (70%) between 250 and 525 °C. Under our conditions, thermal decomposition is complete at 550 °C. After washing, ashes represent 22% in weight of the initial meat and bone meal used. Elemental analysis shows a high yield of phosphate (56.3%) and calcium (36.8%), with Ca/P ratio of 1.55, compared to small amounts of carbon (0.17%), hydrogen (0.15%) and nitrogen (0.36%). In IR analysis (ATR), only the strong characteristic phosphate bands are observed. X-ray diffraction (XRD) analysis confirms the presence of calcium hydroxyapatite (Fig. 1). The surface area is found to be $11 \, \text{m}^2/\text{g}$ with 99% of the residue containing particle size lower than 0.25 mm. In this work we used the crude washed ashes, without further purification, sieving or grinding.

Lead immobilisation efficiency of meat and bone meal combustion residues is evaluated by kinetic studies. Metal concentrations in solutions are determined at different times with 500 and 1500 ppm starting solutions and ashes concentration of 2.5 g/L. Solutions are prepared with $Pb(NO_3)_2$, in distilled water, as Ma et al. showed that nitrate anions do not interfere with the apatite cation exchange reaction [11]. Their pH are 5.15 and 4.95 for lead initial concentration of 500 and 1500 ppm, respectively. This slightly acid pH is a result of
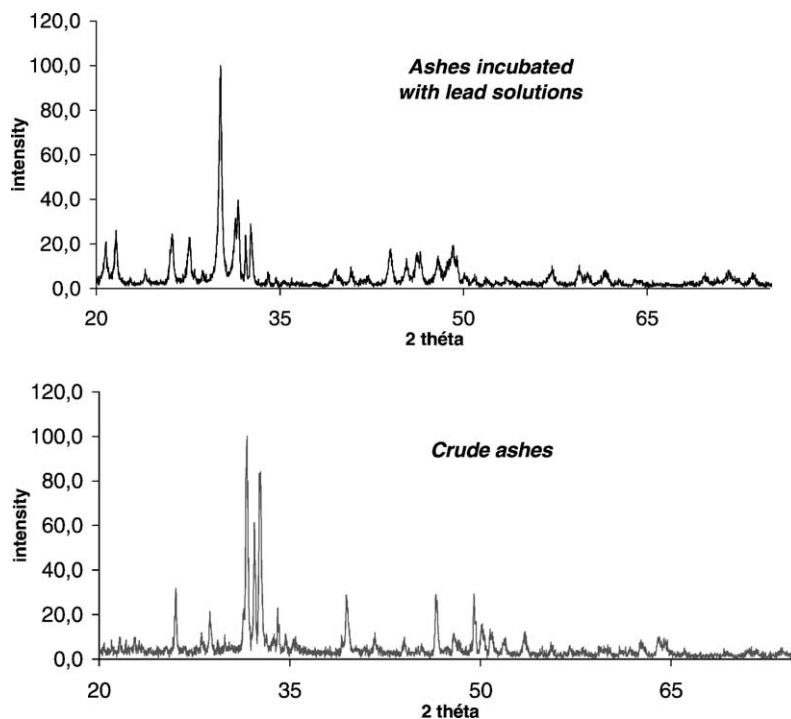

Fig. 1. XRD patterns of crude ashes and after 6 h incubation with lead solutions.
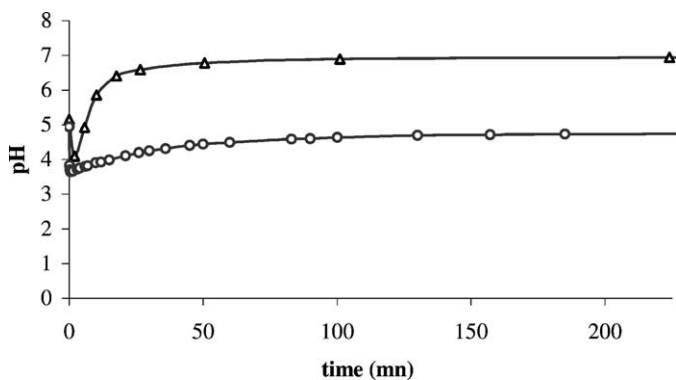
Fig. 2. pH evolution during lead uptake for Pb^{2+} initial concentration of ($\triangle$) 500 ppm and ($\bigcirc$) 1500 ppm.

Pb^{2+} hydrolysis which produces $(PbOH)^+$ and H^+ ions [14]. Results for lead uptake and pH evolution versus time are shown in Figs. 2 and 3.

The shapes of the curves representing ratio of lead concentration in solution at time t ($[Pb]_t$) over initial lead concentration ($[Pb]_0$) versus time demonstrate that a two-step mechanism occurs (Fig. 3). The first portion indicates that a rapid uptake occurs during the first 15 min. Then, the metal uptake slowly reaches equilibrium. With initial lead concentration of 1500 ppm the metal removal percentage reaches 45%. This result gives a capacity of 275 mg of lead/g of ashes. With starting lead solution of 500 ppm, the removal percentage is 100%. In this case, lead concentration in solution remains below the detection limit
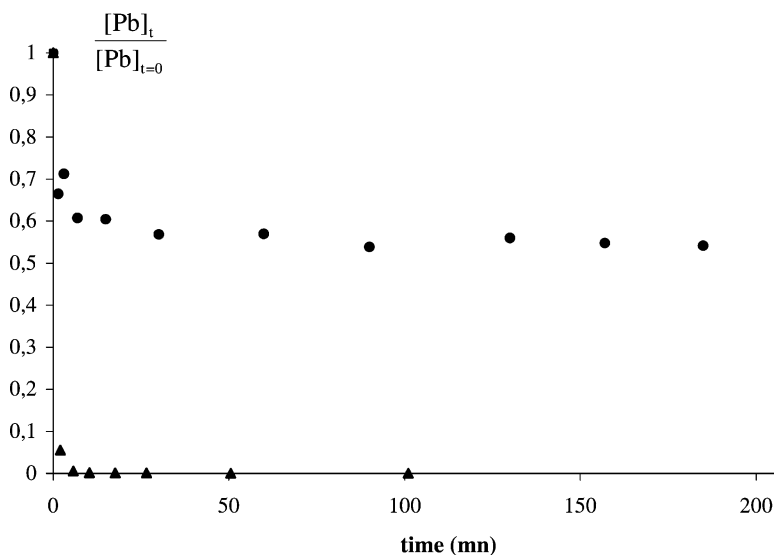

Fig. 3. $[Pb]_t/[Pb]_{t=0}$ evolution during lead uptake for Pb^{2+} initial concentration of ($\blacktriangle$) 500 ppm and ($\bullet$) 1500 ppm.

and so cannot exceed 1 ppb. This result underlines the high immobilisation ability of the material.

The addition of meat and bone meal ashes onto a solution containing Pb^{2+} causes an immediate pH decrease (Fig. 2). In a second step, pH increases to an equilibrium value depending on initial lead concentration in solution. One can notice that the shape of the two types of curves, pH and percent of lead immobilisation (Figs. 2 and 3), are similar and reach equilibrium at the same time. These results are in agreement with previous studies on the mechanism of metal immobilisation on synthetic hydroxyapatites [13,14].

The immediate pH drop induced by the addition of ashes in lead solution (Fig. 2) has been observed by Wu et al. in studies on acid–base properties of apatite surface in water [31]. They showed that dominant surface species are pH or point zero charge (PZC) dependent (PZC is defined as the pH at which the total surface charges become zero) and measured a PZC of 7 for the synthetic apatites they used. They showed that dominant surface species are (P)-OH when pH < PZC, (P)-O$^-$ for pH close to PZC and (Ca)-OH for pH > PZC. According to these authors, in the first stage of lead uptake (pH <5), (P)-OH should be the predominant form. The rapid pH decrease can then be explained by a fast surface complexation reaction which liberates phosphate bound protons:

$$(P)\text{-}OH + Pb^{2+} \rightarrow (P)\text{-}O\text{-}Pb^+ + H^+ \tag{2}$$

In the second step, when pH increases, a new mechanism [13–15] dominates the reaction. As low pH and the presence of Pb^{2+} ions both accelerate $Ca_{10}(PO_4)_6(OH)_2$ dissolution [13], released phosphates combine with Pb^{2+} ions to form the less soluble Pb-hydroxyapatite $Pb_{10}(PO_4)_6(OH)_2$. Mavropoulos et al. showed that this dissolution/precipitation produces first a solid solution (Ca/PbHA) until all the Ca atoms have been substituted by Pb:

$$Ca_{10}(PO_4)_6(OH)_2 + xPb^{2+} \rightarrow Pb_xCa_{(10-x)}(PO_4)_6(OH)_2 + xCa^{2+} \tag{3}$$
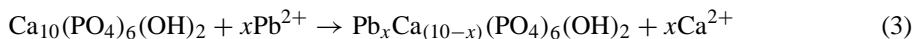
Even if there is no H^+ or OH^- ions involved in this reaction, pH will increase. Indeed Pb^{2+} ions concentration will decrease, and so will the H^+ ions concentration produced by lead(II) hydrolysis. If so, the final pH (at equilibrium) will depend on remaining lead concentration in solution, or on initial lead concentration as we used the same quantities of ashes for each experiment. Higher is the Pb^{2+} ions concentration and lower is the pH. This is in agreement with our experimental results (Fig. 2), as we obtained at equilibrium pH values of 7.0 and 4.9 for initial lead concentration of 500 and 1500 ppm, respectively.

Moreover, the appearance of peaks belonging to Pb-apatite (Fig. 1) on filtered ashes XRD analysis (after an incubation time of 6 h with lead solution) confirms the production of $Pb_xCa_{(10-x)}(PO_4)_6(OH)_2$ [32–34]. At last, monitoring lead and calcium concentrations shows that calcium release follows lead uptake with time (Figs. 3 and 4). Both results support a dissolution/precipitation mechanism.

Addition of ashes to pure water induces calcium release with pH increase (Fig. 4). Similar behaviour has been described by Valsami-Jones et al. who worked on apatite dissolution and can be illustrated by a simplistic equation:

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 10Ca^{2+} + 6PO_4{}^{3-} + 2OH^- \tag{4}$$
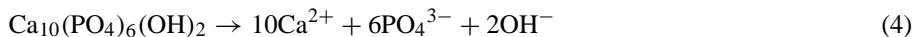
However, as we work with pH between 4 and 7, and according to H_3PO_4 pK_a values, $H_2PO_4{}^-$ should be the dominant species. Therefore, pH increase will not be induced by
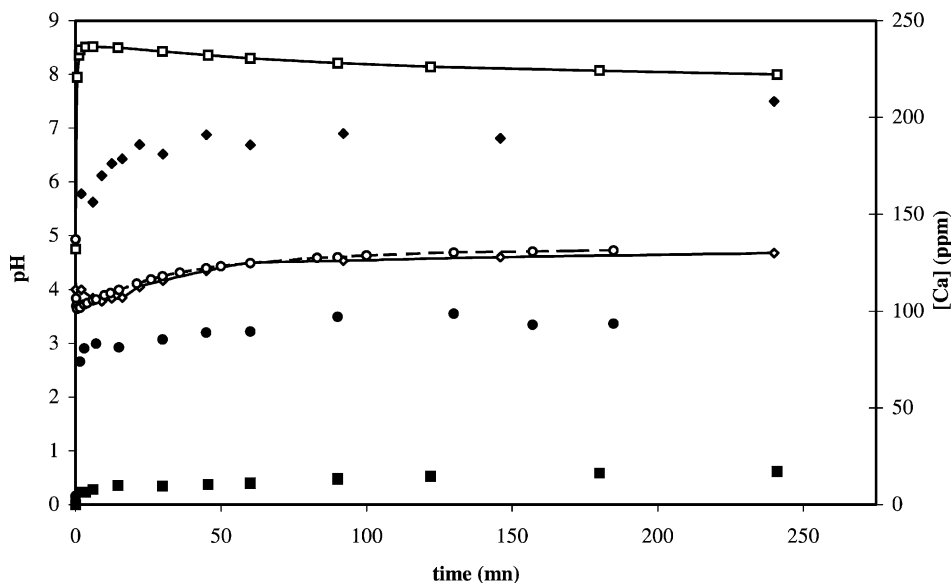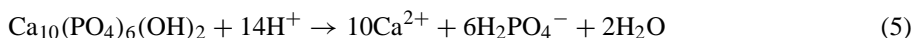
Fig. 4. Variation of calcium concentration and pH in solution ([Ca], pH) after addition of ashes in distilled water ($\blacksquare$, $\square$), 1500 ppm Pb^{2+} solution ($\bullet$, $\bigcirc$) and distilled water with pH regulation ($\blacklozenge$, $\diamondsuit$).

OH$^-$ ions release but by H$^+$ ions consumption and the overall reaction should be better illustrated by following equation:

$$Ca_{10}(PO_4)_6(OH)_2 + 14H^+ \rightarrow 10Ca^{2+} + 6H_2PO_4^- + 2H_2O \tag{5}$$

To go a little further into the mechanism, we can notice that after 3 h (Fig. 4), calcium release is much lower when ashes are added to pure water than to 1500 ppm lead solution whereas pH is higher. To differentiate pH influence from lead influence on CaHA dissolution we added ashes to pure water and imposed a pH adjustment identical to the pH evolution observed in the previous experiment (ashes in contact with 1500 ppm lead solution). We observe then a very important calcium release, which is almost twice larger than in the experiment with 1500 ppm lead solution. These results are in agreement with a dissolution/precipitation mechanism, excluding a simple apatite dissolution mechanism induced by low pH.

However, even if lead uptake seems to near an equilibrium after 3 h (with 1500 ppm solution), XRD (Fig. 1) and chemical analysis show that calcium is not totally exchanged by lead. We obtained a final lead uptake of 275 mg/g of ashes after a 3 h lead extraction experiment. The theoretical maximum capacity is calculated to be nearby 1665 mg of lead/g of initial apatite according to the formal stoichiometry of reaction 6.

$$Ca_{10}(PO_4)_6(OH)_2 + 10Pb^{2+} \rightarrow Pb_{10}(PO_4)_6(OH)_2 + 10Ca^{2+} \tag{6}$$
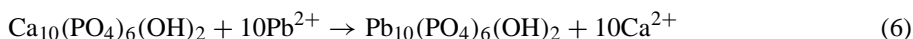
Moreover, lead concentration and pH monitoring for longer periods (up to 24 h) show that the lead uptake reaction is going on but with a very slower rate. Assuming this uptake

rate to remain constant, total immobilisation of lead would require at least 10 days with 1500 ppm initial solution. Obviously, a very slow third step occurs. This could be explained by insoluble $Pb_{10}(PO_4)_6(OH)_2$ coating the particles surface. The $Pb_{10}(PO_4)_6(OH)_2$ layer would act as a shield, dramatically decreasing phosphate dissolution rate and consequently Pb^{2+} ions uptake. As proposed by Valsami-Jones et al., this third step could be explained by slow diffusion of lead in the solid, thus making lead phosphate an effective barrier [13].

4. Conclusion

The above results show that meat and bone meal combustion residues are Ca-hydroxyapatite rich. The lead uptake by this bio-inorganic material involves at least three successive steps: surface complexation of lead, $Ca_{10}(PO_4)_6(OH)_2$ dissolution followed by precipitation of $Pb_{10}(PO_4)_6(OH)_2$ and slow Pb diffusion/substitution of Ca. These results are comparable to those involved in lead uptake by synthetic apatite.

Comparison of lead uptake and calcium release shows that Ca^{2+} ions are not totally substituted by $Pb_{10}(PO_4)_6(OH)_2$ formation. This could be explained by surface coating as a $Pb_{10}(PO_4)_6(OH)_2$ layer would decrease phosphates dissolution. The rate of this third step (lead diffusion in solid) could be modified and improved by working on the physical property of the particles such as size, porosity, or specific surface.

The first two steps occur rapidly and a high lead uptake capacity of 275 mg/g ashes is reached in less than 3 h, whereas reaching the total lead immobilisation capacity would require more than 10 days. The initial rate is in a reasonable range to assess a batch or column lead removal process involving meat and bone meal combustion residues, as 95% of the capacity is reached within 10 min.

This work underlines the efficiency of this natural material as a low cost substitute for synthetic apatite. However, as we used the crude washed combustion product, without further sieving or chemical treatment, additional studies should be carried out on this bio-inorganic material to optimise its heavy metal removal efficiency and get a better understanding of the underlying mechanism involved.

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