

ENHANCED IMMOBILIZATION OF Pb(II) IN CONTAMINATED SOIL USING PHYSICOCHEMICALLY MODIFIED BENTONITE–SAPROPEL COMPOSITES

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Abstract:

This study evaluates physicochemically modified bentonite–sapropel composites for reducing mobile Pb(II) fractions in contaminated soil. Bentonite from the Navbahor deposit and sapropel were modified mechanically or thermally and subsequently used to prepare mineral–organic composites. Soil containing 1500 mg/kg Pb was treated at bentonite:sapropel ratios from 1:4 to 4:1 and doses of 10–50 g/kg. Immobilization was assessed after 1, 15 and 30 days using water extraction and 0.2 M Trilon B extraction. For B-12 + C-12, the 4:1 ratio at 50 g/kg after 30 days gave residual Pb fractions of 24.51% and 29.46%, respectively. Under the same conditions, B-11 + C-12 reduced the corresponding fractions to 22.48% and 27.12%. The results demonstrate that both modification route and composite composition affect Pb immobilization.

Keywords: bentonite; sapropel; Pb(II); soil immobilization; mechanical modification; thermal modification; composite sorbent; Trilon B.

Introduction

Heavy metals are among the most persistent inorganic contaminants of the terrestrial environment. Unlike organic pollutants they are not degraded, and once introduced into soil they are redistributed among solid-phase and solution-phase pools rather than removed, which underlies their environmental persistence, toxicity and capacity for bioaccumulation. Where contaminated soil is used for crop production, this persistence becomes a food-safety issue, because metals entering the soil–plant system may be transferred along the food chain; consequently the management of metal-contaminated agricultural soils has been identified as a sustainability priority. Lead is of particular concern in this group

because of its toxicity and its strong affinity for the soil solid phase, which makes conventional removal-based remediation of large contaminated areas difficult and expensive [1].

The environmental chemistry of hazardous heavy metals has been reviewed comprehensively by Ali et al., who emphasise environmental persistence, toxicity and bioaccumulation as the properties that distinguish this class of contaminants. Hou et al. [2] place the same problem in an agricultural context and review bioremediation of metal-contaminated agricultural soils from the perspective of food safety and sustainability. Wan et al. provide a recent synthesis of the sources of heavy metals in agricultural soils, the factors that influence their behaviour, and the remediation strategies currently in use, while Vareda et al. review anthropogenic pollution together with the corresponding remediation options[3][4].

Within the anthropogenic category, mining is one of the most significant contributors. Li et al. [5] reviewed soil heavy metal pollution originating from mines in China and carried out an associated health risk assessment, identifying lead among the metals of priority concern. Fertilizer application constitutes a second, more diffuse pathway: Niño-Savala et al. [6] documented cadmium input to arable soils and crops from phosphate fertilizers. Against these anthropogenic loads, geogenic contributions must also be accounted for. Kierczak et al. [7] reviewed ultramafic geoecosystems as a natural source of Ni, Cr and Co, and the regional-scale survey of Morrison et al. [8] demonstrated that lithologically controlled background concentrations of chromium and nickel can be high and spatially coherent over large areas. Taken together, these studies establish that a contaminated site must be characterised in terms of both its metal loading and the chemical condition of that loading before a treatment is selected.

The sequential extraction procedure introduced by Tessier et al. [9] established the operational framework within which trace metal mobility in solid matrices is still evaluated, by partitioning the metal among exchangeable, carbonate-bound, oxide-bound, organically bound and residual pools. The practical significance of this partitioning for agricultural systems was set out by Uchimiya et al. [10], who related the chemical speciation of heavy metals in agricultural soils to plant uptake and toxicity. The consequence for remediation assessment is direct: since immobilization does not remove metal from the soil, its effectiveness can only be demonstrated through a measured reduction in the mobile fractions. The water-soluble fraction and the fraction extractable by a complexing agent are therefore used in the present study as the response variables, in preference to total Pb content.

Kumpiene et al. [11] reviewed amendment-based stabilization of As, Cr, Cu, Pb and Zn and attributed the observed decreases in leaching and bioavailability to adsorption, complex formation, precipitation and ion exchange. Clay minerals are well suited to several of these mechanisms because they combine a large reactive surface with a permanent structural charge. Sun et al. [12] applied bentonite to paddy soil co-contaminated with cadmium and lead under in situ conditions and reported stabilization of both metals, establishing bentonite as a practical soil amendment rather than solely a laboratory sorbent. More recently, Yang et al. [13] examined the adsorption and desorption behaviour of modified bentonite towards soil Pb and Cd and assessed the feasibility of reducing soil ecotoxicity by this route. These studies together justify the choice of bentonite as the mineral component of the composite examined here, and they also indicate that modification of the raw clay is the direction in which improvement is expected.

The characterisation of a modified clay is not a trivial matter, and reported surface areas must be interpreted with care. Macht et al. [14] compared specific surface areas of clay minerals obtained by atomic force microscopy with those from bulk gas (N₂) and liquid (EGME) adsorption and showed that the values are method-dependent. Surface area figures are therefore meaningful primarily as a relative measure within a single method, which is how the S_{BET} values reported in Section 4 of this article should be read.

For thermal modification, Sarikaya et al. [15] examined a calcium bentonite heated between 100 and 1300 °C and found that porosity reached a maximum at 500 °C, where dehydration was complete without alteration of the crystal structure; the specific surface area approximately doubled, from 43 to 89 m²/g, and decreased again at higher temperatures. Their results demonstrate that thermal treatment is effective only within a limited temperature window, beyond which structural collapse reduces the very properties the treatment is intended to develop. This is the basis for restricting the thermal treatment in the present work to the 200–500 °C range.

For mechanical modification, Kovalchuk et al. [16] studied the effect of high-energy ball milling of montmorillonite — the principal mineral of bentonite — on the adsorptive removal of caesium, strontium and uranium ions from aqueous solution, confirming that milling parameters are an effective means of altering the adsorption behaviour of the smectite structure. Milling and heating thus act on the material in different ways, and there is no a priori reason to expect them to yield equally effective sorbents for a given metal in a given matrix.

The organic component of the composite is provided by sapropel, a lacustrine organo-mineral sediment. Albrektienė-Plačakė and Paliulis [17] investigated the application of sapropel to the removal of cadmium, chromium, copper and zinc from aqueous solutions, establishing that sapropel itself possesses metal-binding capacity. Combining it with bentonite therefore produces a system in which mineral surface exchange and organic complexation may both operate.

The literature summarised above establishes three points: that bentonite is an effective in-situ amendment for Pb-contaminated soil ; that thermal and mechanical treatments modify its physicochemical properties in different and parameter-sensitive ways; and that sapropel has independent metal-binding capacity. What has not been reported is a direct comparison, under identical soil, dose and incubation conditions, of mechanically and thermally modified bentonite within the same bentonite–sapropel composite system, evaluated against the mobile Pb fractions rather than against total Pb. The present study addresses this gap using bentonite from the Navbahor deposit.

Materials and Methods

Natural bentonite from the Navbahor deposit and sapropel were subjected to mechanical and thermal modification. Mechanical treatment used 200 and 500 rpm, 30 and 90 min, ball-to-material ratios of 10:1 and 30:1, and dry or wet conditions. B-12 was prepared at 500 rpm for 30 min, BPR 30:1, under wet conditions. Its S_{BET} was 99.38 m²/g, pore volume 0.22 cm³/g, CEC 67.92 meq/100 g and absolute zeta potential 33.5 mV.

Thermal treatment of bentonite was conducted at 200–500 °C for 30–75 min. B-11, used for the composite study, was obtained at 400 °C for 60 min. Mechanically modified sapropel C-12 was prepared at 500 rpm for 30 min with BPR 30:1 under wet conditions.

The immobilization experiment used soil contaminated with 1500 mg/kg Pb. Composite ratios were 1:4, 1:3, 1:2, 1:1, 2:1, 3:1 and 4:1; doses were 10–50 g/kg; incubation periods were 1, 15 and 30 days. Residual Pb was determined by water extraction and 0.2 M Trilon B extraction and expressed as a percentage of the initial Pb content.

Results and Discussion

Mechanical modification increased bentonite S_{BET} from 50.13 m²/g in B-0 to 99.38 m²/g in B-12, while CEC decreased from 120.30 to 67.92 meq/100 g. The data demonstrate that increasing surface area was accompanied by changes in exchange capacity; therefore, optimization requires simultaneous consideration of several physicochemical characteristics. This trade-off is consistent with the parameter sensitivity reported for milled and heated smectites in the literature, and the S_{BET} values should be read as method-internal relative measures.

Table 1. Selected physicochemical characteristics of bentonite samples

Sample	Treatment	S_{BET} , m ² /g	CEC, meq/100 g	$ \zeta $, mV
B-0	Natural	50.13	120.30	15.0
B-12	500 rpm, 30 min, 30:1, wet	99.38	67.92	33.5
B-11	400 °C, 60 min	87.72	85.21	22.0

For B-12 + C-12, increasing the bentonite fraction resulted in progressively lower residual Pb at 30 days. At 50 g/kg and a 4:1 ratio, residual water-soluble Pb was 24.51%, whereas Trilon B-extractable Pb was 29.46%.

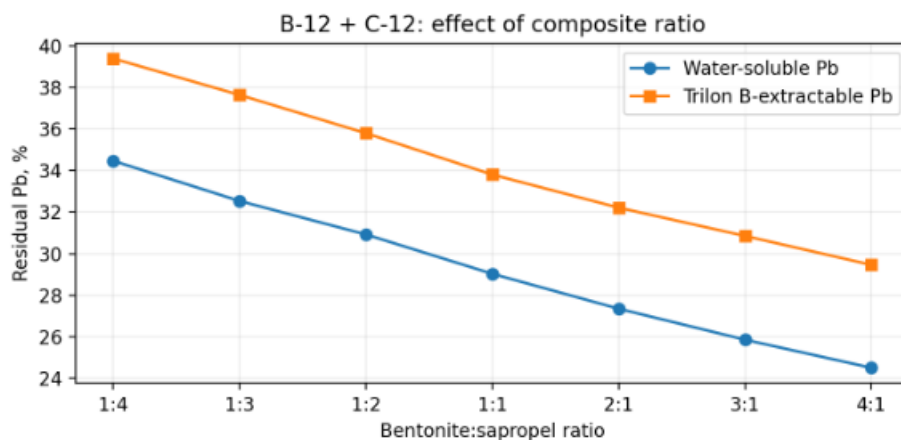


Figure 1. Effect of bentonite:sapropel ratio on residual Pb for B-12 + C-12 (30 days, 50 g/kg).

Table 2. Residual Pb fractions for B-12 + C-12 at 30 days and 50 g/kg

B:S ratio	Water-soluble Pb, %	Trilon B-extractable Pb, %
1:4	34.46	39.38
1:3	32.53	37.63
1:2	30.92	35.79
1:1	29.03	33.80
2:1	27.35	32.21
3:1	25.86	30.85
4:1	24.51	29.46

Thermal modification produced a more effective bentonite component under the investigated conditions. At 4:1, 50 g/kg and 30 days, B-11 + C-12 produced residual water-soluble and Trilon B-extractable Pb fractions of 22.48% and 27.12%, respectively, compared with 24.51% and 29.46% for B-12 + C-12.

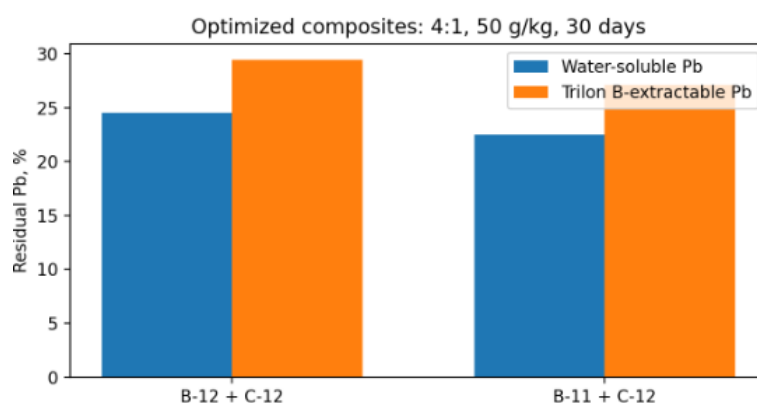


Figure 2. Comparison of optimized composites under identical conditions

The higher performance of B-11 + C-12 is consistent with the higher CEC retained by B-11 (85.21 meq/100 g) compared with B-12 (67.92 meq/100 g). The dissertation results therefore show that the highest S_{BET} does not necessarily correspond to the strongest Pb immobilization; preservation of exchange capacity is also important. This observation is in line with the mechanistic account of amendment-based stabilization given by Kumpiene et al. in which ion exchange operates alongside adsorption, and with the temperature-window behaviour reported for thermally treated bentonite. Incubation time contributed to further stabilization. For B-11 + C-12 at a 1:1 ratio and 30 g/kg dose, the Trilon B-extractable Pb fraction decreased from 57.64% after 1 day to 41.82% after 15 days and 35.23% after 30 days. Under identical conditions, B-12 + C-12 gave 62.59%, 45.42% and 38.26%, respectively.

Because the response variables are the water-soluble and complexant-extractable fractions rather than total Pb, the reductions reported above describe a change in the chemical condition of the lead present in the soil, in the sense established by Tessier et al and applied to agricultural soils by Uchimiya et al. The magnitude of the effect is comparable in kind to that reported for bentonite and modified bentonite applied to metal-contaminated soils, although the extraction schemes and soil matrices differ between studies and the numerical values are not directly transferable.

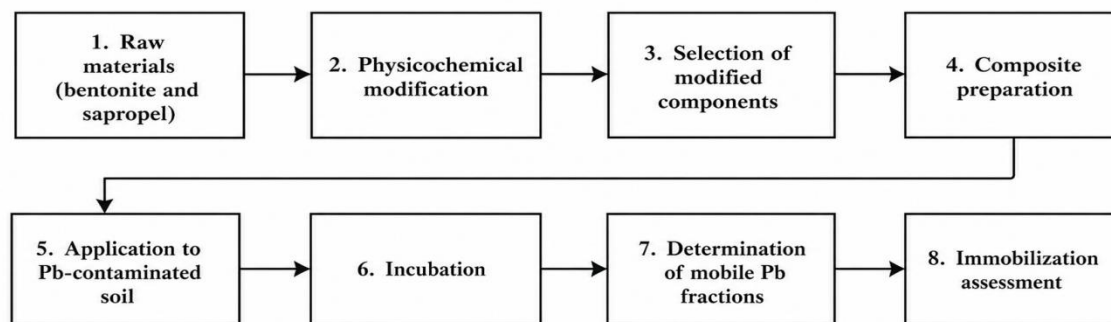


Figure 3. Technological scheme for Pb(II) immobilization in contaminated soil using physicochemically modified bentonite–sapropel composites

Conclusion

The investigated physicochemically modified bentonite–sapropel composites reduced mobile Pb fractions in contaminated soil. For B-12 + C-12, the best investigated condition was a 4:1 ratio, 50 g/kg dose and 30-day incubation, giving 24.51% water-soluble and 29.46% Trilon B-extractable residual Pb. B-11 + C-12 showed a stronger effect under the same conditions, with residual fractions of 22.48% and 27.12%. The comparison indicates that preservation of cation-exchange capacity is an important factor in addition to development of specific surface area. This finding complements the existing literature, in which bentonite modification is usually optimised with respect to surface area alone, and it supports the mechanistic role assigned to ion exchange in amendment-based stabilization. The technological sequence presented here is directly derived from the experimental procedure and results of the dissertation and does not introduce additional experimental assumptions.

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