Allophane nanoclay for the removal of phosphorus in water and wastewater

Guodong Yuan\textsuperscript{a,}\textsuperscript{*}, Longhua Wu\textsuperscript{b,1}

\textsuperscript{a}Landcare Research, Cnr Riddet Road and University Avenue, Private Bag 11052, Palmerston North, New Zealand
\textsuperscript{b}Institute of Soil Science, Chinese Academy of Sciences, PO Box 821, Nanjing, China

Received 22 July 2006; received in revised form 29 August 2006; accepted 1 September 2006
Available online 20 October 2006

Abstract

We have assessed the capacity of an allophane nanoclay to take up phosphorus (P) from aqueous solutions and meatwork effluent. The data of adsorption in aqueous solutions were fitted to the Freundlich equation: \( q = 5.620C^{0.264} \) (g/kg). The nanoclay effectively removed P from a wide range of concentrations at high solution/nanoclay ratios. This finding together with the low cost and environmentally friendly nature of allophane make this material a superior candidate for the remediation of eutrophic water and the treatment of P-rich effluent and sewage. An added advantage is that allophane does not disperse in water, and hence can be recovered after use.

Keywords: Nanoclays; Phosphorus; Sorption; Eutrophication; Remediation; Allophane

1. Introduction

In many parts of the world, runoff from farmlands, discharge of sewage and industrial effluents, and accidental spills of toxic chemicals contribute to the pollution of lakes, rivers, and groundwater by nutrients (e.g., phosphorus), trace metals (e.g., cadmium), and organic contaminants (e.g., polycyclic aromatic hydrocarbons). The demand for clean water and increased awareness of the adverse effects of pollution on human and ecosystem health call for the development of effective and affordable technologies and materials for pollution control and water treatment.

Because of their widespread occurrence and availability in soil and sediment, clays have long been used as a flocculate and sorbent of suspended particles, disease-bearing organisms, and toxic compounds in water [1]. The use of clays and clay minerals (in their natural state, or after chemical and surface modification) for water treatment has been widely investigated over the past three decades. Examples of such applications are the removal of oil and grease from water, the construction of clay liners to intercept organic leachates from waste disposal sites, the uptake of heavy metals and endocrine-disrupting chemicals, and the recovery of nitrogen from nitrogen-rich effluents [1–6].

Since clays and clay minerals have primary particles with at least one dimension in the nanometre scale, they may be regarded as nanomaterials of geological and pedological origins [4,7–8]. The elementary layers of smectite are a few hundreds of nanometres in length and width and about 1 nm in thickness. The unit particles of allophane consist of hollow aluminosilicate nanoballs with an outer diameter of 3.5–5.0 nm, and those of imogolite are slender, hollow aluminosilicate tubules 2 nm in diameter [9]. Because of their small particle size, the specific surface area (external and internal) of clays and clay minerals extends to a few hundred m\(^2\)/g. Clays and clay minerals also carry electric charges from substitution of Al\(^{3+}\) and/or Si\(^{4+}\) by cations of lower valency, and the gain or loss of protons as solution pH changes. The nano-size dimension, extensive surface area, and peculiar charge characteristics of clay materials...
lie behind their large propensity for taking up ions and organic compounds from their immediate environment.

Here we assess the capacity of an allophane nanoclay to take up phosphate from aqueous solution, and its suitability for the remediation of eutrophic water and the treatment of meatworks effluent.

2. Materials and methods

Allophane nanoclay was obtained from a deposit in New Zealand. The field moist samples were air-dried, crushed, and analysed for allophane by extraction with acid ammonium oxalate. The sample with the highest allophane content (39%) was used for the sorption experiments described below.

Sorption of phosphorus (P) was determined in duplicate using the batch equilibrium method. Briefly, 30 mL solutions, containing 2–700 mg P/L (prepared from KH₂PO₄) and 1 mM CaCl₂ as background electrolyte, were added to a series of centrifuge tubes containing 0.0500 g allophane nanoclay. The capped tubes were shaken for 24 h at 20°C and then centrifuged for 12 min at 5000 rpm. Phosphorus concentrations in the supernatant solutions were determined colorimetrically using a Lachart instrument. Phosphorus adsorbed was calculated from the difference between the amount of P initially added to, and that measured at equilibrium with, the allophane nanoclay.

For comparison, sorption of P by a commercial product ‘Phoslock™’ was also determined. Phoslock™ is a surface-modified bentonite (dominated by montmorillonite), produced by replacing the natural exchangeable cations (Ca and Na ions) of montmorillonite with a rare earth element (lanthanum). It works as a sink for phosphorus in water by forming lanthanum phosphate, a compound with low solubility.

To assess the capacity of an allophane nanoclay to remove P from eutrophic lakes 0.2000 g of the material was placed in a flask with a 2 L solution of 1 mg P/L and 0.5 mM CaCl₂. The flask was left on a bench at 20 °C, and shaken three times before sampling for P analysis.

To test the effectiveness of allophane nanoclay for removing P from meatworks effluent having a total P concentration of 14.2 mg/L. After shaking the mixture for 24 h and centrifuging at 5000 rpm for 12 min, the total P concentration in the supernatant was determined.

3. Results and discussion

Fig. 1 shows the isotherms for the sorption of P by allophane nanoclay and Phoslock. When the initial P concentration was ≤5 ppm, both materials were able to reduce the equilibrium P concentration to ppb levels at a solution:solid ratio of 600 ml:1 g. At higher initial P concentrations, however, Phoslock and allophane nanoclay showed different sorption behaviours. The isotherm for Phoslock had a long, flat plateau, suggesting that its capacity for P sorption was limited to 11–12 g P/kg. On the other hand, the allophane nanoclay showed a curvilinear increase in sorption with P concentration. The data for allophane fit the Freundlich equation: 

\[ q = KC^n \]

where \( q \) is the amount adsorbed (g/kg), \( C \) the equilibrium concentration of P (mg/L), \( K \) the distribution coefficient, and \( n \) a correction factor, indicating the degree of linearity of isotherm [10].

Fig. 2 shows the residual concentrations of P in the flask after contacting the solution with allophane nanoclay for different periods of time. After 24 h of contact, the P concentration decreased from 0.96 to 0.55 mg/L. The P concentration continued to decrease as contact time increased.

Likewise, the allophane nanoclay was effective in reducing the concentration of P in a meatwork effluent from 14.2 to 4.2 mg/L, a reduction of 70%.

Since allophane nanoclay is capable of sorbing P at high solution:solid ratios (600 in sorption experiments, 10 000 in simulated eutrophic water, and 400 in effluent treatment), this material is well suited for remediating eutrophic water and treating effluents and sewage. Allophane nanoclay has a large capacity for adsorbing and precipitating P because
of its high concentration of active aluminum (acid oxalate extractable Al). For example, the nanoclay used in this study contains 11.2% of active Al. In contrast, the concentration of lanthanum in Phoslock™, the active constituent for P removal, is about ten times lower. Besides its large capacity for P removal, allophane nanoclay has other advantages over Phoslock™. Firstly, allophane is cheap because it can be obtained in large quantities from deposits that are close to major roads. Indeed, its cost could be an order of magnitude lower than that of Phoslock™. Secondly, allophane is safe to use because it is a natural material and does not require extensive chemical modifications before usage. Thirdly, allophane nanoclay is recoverable after use because it occurs as granules that do not disperse in aqueous media. Applying dispersible materials (e.g., Phoslock™) to eutrophic lakes or wastewater ponds for P removal is not ideal because the adsorbed P remains within, and could again be released into the system. By contrast, allophane nanoclay can be removed from wastewater or eutrophic water bodies by settling or packaging, and the adsorbed P can be recycled to farmland.

4. Conclusions

Allophane nanoclay is a natural, inexpensive, and environmentally friendly material suitable for removing phosphorus from water and wastewater. It has a strong propensity for adsorbing phosphate over a wide range of solution concentrations, and can be recovered from wastewater after use. Because of these attributes allophane is superior to some commercial products for the treatment and purification of water bodies.

Acknowledgements

This research was supported by a grant from Technology New Zealand. G. Yuan thanks colleagues, Mr G. Salt for technical assistance in the analyses of phosphate, and Dr B.K.G. Theng for valuable comments and discussion. The comments and suggestions from two anonymous reviewers are appreciated.

References

[1] G.J. Churchman, W.P. Gates, B.K.G. Theng, G. Yuan, Clays and clay minerals for pollution control, in: F. Bergaya, B.K.G. Theng, G. Lagaly (Eds.), Handbook of Clay Science, Elsevier Ltd., Amsterdam, 2006, pp. 625–675.
[2] S. Kemnetz, C.A. Cody, Oil spill flocculating agent and method of remediating oil spills, US Patent 5558777, 1996.
[3] G.J. Churchman, The role of clays in the restoration of perturbed ecosystems, Dev. in Soil Sci. 28A (2002) 333–350.
[4] G. Yuan, Natural and modified nanomaterials as sorbents of environmental contaminants, J. Environm. Sci. Heal A 39 (2004) 2661–2670.
[5] I.M.C. Lo, Solidification/stabilization of phenolic waste using organic-clay complex, J. Environ. Eng. 12 (1996) 850–855.
[6] B.K.G. Theng, G.J. Churchman, W.P. Gates, G. Yuan, Organically modified clays for pollution uptake and environmental protection, in: Q. Huang, P.M. Huang, J.-M. Bollag (Eds.), Soil Mineral-Organic Matter-Microorganism Interactions: Fundamentals and Impacts, Springer, Heidelberg, 2006, in press.
[7] L.A. Bursill, J.L. Peng, L.N. Bourgeois, Imogolite: an aluminosilicate nanotube material, Philos. Mag. A 80 (2000) 105–117.
[8] R.A. Schoonheydt, Smectite-type clay minerals as nanomaterials, Clay. Clay Miner. 50 (2002) 411–420.
[9] M.F. Brigatti, E. Galán, B.K.G. Theng, Structures and mineralogy of clay minerals, in: F. Bergaya, B.K.G. Theng, G. Lagaly (Eds.), Handbook of Clay Science, Elsevier, Amsterdam, 2006, pp. 19–86.
[10] G. Yuan, Defining the distribution coefficient of heavy metals introduced to soils, Commun. Soil Sci. Plan Analysis 34 (2003) 2315–2326.