



ELSEVIER

Contents lists available at ScienceDirect

MethodsX

journal homepage: [www.elsevier.com/locate/mex](http://www.elsevier.com/locate/mex)

## Method Article

## Functionalization of kaolinite for removal of phosphate from urban sewage

Camilla Carbinatti<sup>a</sup>, Fabiano Tomazini da Conceição<sup>a,\*</sup>,  
Rodrigo Braga Moruzzi<sup>a</sup>, Amauri Antônio Menegário<sup>b</sup><sup>a</sup>UNESP - Universidade Estadual Paulista, Instituto de Geociências e Ciências Exatas, Avenida 24-A, no 1515, CEP 13506-900, Bela Vista, Rio Claro, São Paulo, Brazil;<sup>b</sup>UNESP - Universidade Estadual Paulista, Centro de Estudos Ambientais, Rio Claro, Brazil.

## A B S T R A C T

The  $\text{PO}_4^{3-}$  widespread in urban sewages promotes eutrophication of water sources, with harmful effects to natural life and endanger human health. The removal of  $\text{PO}_4^{3-}$  from urban sewage requires treatment at tertiary level, with high costs and low efficiency in most cases. Thus, a functionalization method for surface modification of kaolinite was proposed to improve the removal of  $\text{PO}_4^{3-}$  from urban sewage. The kaolinite commercial did not remove  $\text{PO}_4^{3-}$  from aqueous solution. However, the functionalized kaolinite (FK) was efficient, with a maximum removal capacity of  $8.4 \pm 0.1$  mg  $\text{PO}_4^{3-}$ /L, within less than 1 min of reaction. The removal of  $\text{PO}_4^{3-}$  is associated with precipitation of pyromorphite, a mineral with low solubility ( $K_{sp} < 10^{-79.6}$ ). Finally, real urban sewage samples (raw and treated) were also tested for removal of  $\text{PO}_4^{3-}$  using FK, confirming its effectiveness. The central aspects of this development are:

- Functionalized kaolinite (FK), with Pb(II), for removal of  $\text{PO}_4^{3-}$  from urban sewage was studied.
- The FK was efficient for removal of up to 8.4 mg  $\text{PO}_4^{3-}$ /L from aqueous solution, within a short reaction time.
- The precipitation of pyromorphite was the mechanism responsible for removal of  $\text{PO}_4^{3-}$  and FK efficiency have been confirmed for real urban sewage samples.

© 2021 The Author(s). Published by Elsevier B.V.

This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>)

## A R T I C L E I N F O

*Method name:* Functionalization of kaolinite for removal of phosphate from urban sewage*Keywords:* Clay minerals, Surface functionalization, Phosphate removal, Mineral precipitation*Article history:* Received 26 April 2021; Accepted 17 June 2021; Available online 18 June 2021

\* Corresponding author.

*E-mail address:* [fabiano.tomazini@unesp.br](mailto:fabiano.tomazini@unesp.br) (F.T. da Conceição).

## Specifications table

Subject Area:	Environmental Science
More specific subject area:	Removal of phosphate from urban sewage
Method name:	Functionalization of kaolinite for removal of phosphate from urban sewage
Name and reference or original method:	S. Moharami & M. Jalali (2015). Use of modified clays for removal of phosphorous from aqueous solutions. Environ. Monit. Assess. 187:639.
Resources availability:	N/A

## Method details

### Background

The  $\text{PO}_4^{3-}$  present in urban sewage promotes eutrophication in the water bodies [1]. This anion is difficult to remove during the treatment of urban sewage, requiring treatment at the tertiary level [2]. The most used method for the removal of  $\text{PO}_4^{3-}$  from urban sewage is the chemical precipitation, involving the addition of bivalent or trivalent metal salts [3–5]. Recently, studies have shown the precipitation of pyromorphite ( $5\text{Pb}^{2+} + 3\text{PO}_4^{3-} + \text{H}_2\text{O} \rightarrow \text{Pb}_5(\text{PO}_4)_3(\text{OH})_{(\text{pyromorphite})} + \text{H}^+$ ) in natural surface waters due to presence of  $\text{PO}_4^{3-}$  and  $\text{Pb}(\text{II})$ , reducing the concentration of dissolved  $\text{Pb}(\text{II})$  [6,7]. The pyromorphite has a low solubility constant ( $K_{sp} < 10^{-79,6}$ ), preventing that the  $\text{Pb}(\text{II})$  returns to the environment as a dissolved cation [8–10].

Kaolinite [ $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ] has its negatively-charged surface, becoming this mineral an important adsorbent for cationic ions [11]. The functionalization of kaolinite with acid treatment [12] and bivalent trace elements can promote the removal of anionic molecules, such as  $\text{PO}_4^{3-}$ , present in the urban sewage [13–15]. Based on the functionalization of commercial kaolinite (CK) with bivalent trace elements, the functionalized kaolinite (FK) with  $\text{Pb}(\text{II})$  was produced. The efficiency for removal of  $\text{PO}_4^{3-}$  from aqueous solution using FK was studied and compared with CK. Furthermore, the reaction time and maximum removal capacity of  $\text{PO}_4^{3-}$  was determined using FK. Finally, the FK was applied in real urban sewage samples, attesting its effectiveness.

### Functionalization of commercial kaolinite

The CK (Sigma-Aldrich®, CAS Number 1318-74-7) was used in this study. The following procedures have been applied for the functionalization:

- 1 – About 1.0 g of CK was placed in a beaker;
- 2 – 10 mL of aqueous solution with  $\text{Pb}(\text{II})$  initial concentration of 40 mg/L was added;
- 3 – The beaker was agitated (digital shaker Biothec – model BT 645) for 24 h at 145 rpm;
- 4 – The solution was centrifuged (centrifuge Excelsa II® – model 206-BL) for 25 min at 3000 rpm;
- 5 – The FK was separated and washed three times, using ultrapure water (Milli-Q® system - model IQ 7000) with electrical conductivity lower than 0.02  $\mu\text{S}/\text{cm}$ ;
- 6 – Finally, the FK was dried for 12 h at 40 °C.

### Method validation

For validation purposes, 1.0 g of each sample (CK and FK) was mixed with 10 mL of aqueous solution containing  $\text{PO}_4^{3-}$  in the initial concentration ( $C_0$ ) of 1 mg/L at pH 6 [9]. The suspension was shaken for 24 h at 145 rpm, and then centrifuged at 3000 rpm for 25 min. The supernatant was separated and the  $\text{PO}_4^{3-}$  concentration remaining in solution ( $C_e$ ) was measured using a Hach DR-2800 spectrophotometer, with a detection limit of 0.1 mg/L. The removal efficiency of  $\text{PO}_4^{3-}$  (%A – in percentage) was determined according to the Eq. 1. The experimental procedures were carried out in triplicate.

$$\%A = [(C_0 - C_e)/C_0] \cdot 100 \quad (1)$$

**Table 1**Removal efficiency (%A) of  $\text{PO}_4^{3-}$  (mg/L) using FK and CK in aqueous solution.

CK			FK		
$C_0$	$C_e$	%A	$C_0$	$C_e$	%A
1.0	$1.0 \pm 0.1$	0	1.0	< 0.1	100

**Table 2**Reaction time (min) and removal efficiency (%A) of  $\text{PO}_4^{3-}$  (mg/L) using FK in aqueous solution.

Time	$C_0$	$C_e$	%A
0	1.0	$1.0 \pm 0.1$	0
1	1.0	< 0.1	100
5	1.0	< 0.1	100
15	1.0	< 0.1	100
30	1.0	< 0.1	100
60	1.0	< 0.1	100

**Table 3**Maximum removal capacity of  $\text{PO}_4^{3-}$  using FK and concentration of residual Pb(II) in aqueous solution.

$\text{PO}_4^{3-}$ (mg/L)			Pb(II) (mg/L)
$C_0$	$C_e$	%A	
1	< 0.1	100	$692 \pm 20$
2	< 0.1	100	$91 \pm 4$
3	< 0.1	100	$63 \pm 3$
4	< 0.1	100	< 0.006
7	< 0.1	100	< 0.006
9	$0.6 \pm 0.1$	93.3	< 0.006

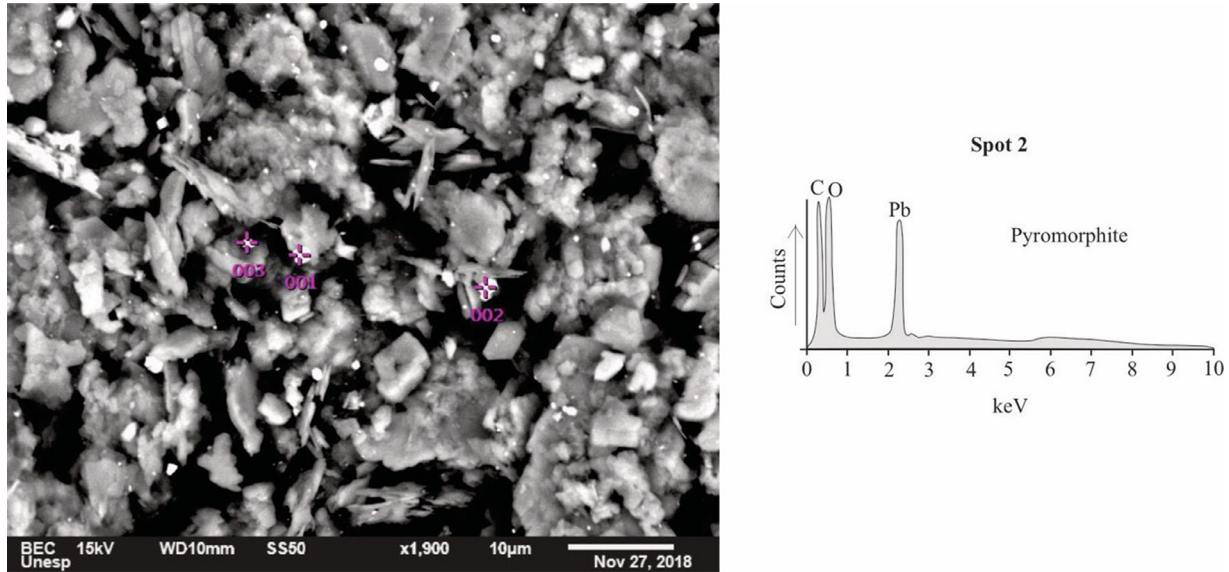
The results are presented in Table 1. The removal efficiencies of  $\text{PO}_4^{3-}$  were 0 and 100% using CK and FK, respectively. These results evidenced the functionalization plays a crucial role on the removal of  $\text{PO}_4^{3-}$ . The precipitation of pyromorphite was the main mechanism associated with  $\text{PO}_4^{3-}$  removal using FK with Pb(II), as shown in Fig. 1.

### Reaction time and maximum removal capacity of $\text{PO}_4^{3-}$ using functionalized kaolinite

The reaction time for removal of  $\text{PO}_4^{3-}$  using KF has been investigated, according the following procedures carried out in triplicate. The FK (1.0 g) was mixed in 10 mL of an aqueous solution with  $C_0$  of 1 mg  $\text{PO}_4^{3-}$ /L at pH 6 [9]. The suspension was shaken at 145 rpm, with samples taken after 1, 5, 15, 30 and 60 min. The solution was centrifuged at 3000 rpm for 25 min, with the supernatant separated and the  $C_e$  determined. The experiments have shown no residuals of  $\text{PO}_4^{3-}$  after 1 min of reaction time (Table 2), showing a fast reaction time for removal of  $\text{PO}_4^{3-}$  associated to the mineral pyromorphite precipitation.

The maximum removal capacity of  $\text{PO}_4^{3-}$  using FK was also determined (in triplicate). The samples with 1.0 g: 10 mL of an aqueous solution with  $C_0$  of 1 mg/L were stirred at 145 rpm for 5 min at pH 6 [9], with  $C_0$  of 1, 2, 3, 4, 7 and 9 mg/L. The solutions were centrifuged for 25 min at 3000 rpm and the  $C_e$  determined in the supernatants. The maximum removal capacity of  $\text{PO}_4^{3-}$  using FK was  $8.4 \pm 0.1$  mg/L (Table 3) or 8.4 mg/g, indicating an efficiency of 93.3% for removal of  $\text{PO}_4^{3-}$  from aqueous solutions with  $C_0$  of 9 mg/L. The value of 8.4 mg/g is higher than the removal capacities obtained for natural or functionalized kaolinite, i.e., CK used in this study (< 0.1 mg/g), kaolinite from Linthipe (ca. 0.15 mg/g) [12], modified kaolinite with  $\text{FeCl}_3$  (1.31 mg/g) [13] and modified kaolinite with seawater in different temperatures (4.07 mg/g at 600 °C) [15].

Trace levels of residual Pb(II) in the treated effluent can pose a serious environmental risk for aquatic systems due to its toxicity. Thus, the concentration of Pb(II) were also determined in the



**Fig. 1.** SEM-EDS images of functionalized kaolinite after the removal of  $\text{PO}_4^{3-}$ , showing the precipitation of small grains (lower than  $5 \mu\text{m}$ ) of pyromorphite (spots 1, 2 and 3).

**Table 4**

$C_0$  and  $C_e$  averages of  $\text{PO}_4^{3-}$  and Pb(II) (in mg/L) measured in the urban sewage collected in a WWTP located in Rio Claro.

Sample	$C_0$ of $\text{PO}_4^{3-}$	$C_e$ of $\text{PO}_4^{3-}$	$C_0$ of Pb(II)	$C_e$ of Pb(II)
Raw	$6.1 \pm 0.1$	< 0.1	< 0.006	< 0.006
Treated	$3.8 \pm 0.1$	< 0.1	< 0.006	< 0.006

supernatants by inductively coupled plasma optical emission spectrometry (ICP OES), iCAP 6000 SERIES machine Thermo Scientific, with detection limit of 0.006 mg/L. The presence of residual Pb(II) in aqueous solutions was measured in aqueous solutions with  $C_0$  of 1, 2 e 3 mg/L of  $\text{PO}_4^{3-}$ . Residual Pb(II) was not detected for  $C_0$  of  $\text{PO}_4^{3-} \geq 4$  mg/L, indicating the use of FK for removal of  $\text{PO}_4^{3-}$  only in urban sewage with  $C_0 \geq 4$  mg/L. Further studies for lower  $C_0$  concentrations in urban sewage are encouraged before application.

### Removal of $\text{PO}_4^{3-}$ using functionalized kaolinite in real urban sewage samples

Three samples of raw and treated urban sewage were collected in a wastewater treatment plant (WWTP) located in Rio Claro, São Paulo State, Brazil. These samples were stored in labeled amber container at 4°C and transported immediately to the laboratory, where they were filtered, using 0.45  $\mu\text{m}$  MF-Millipore® membrane filter, and the  $C_0$  of  $\text{PO}_4^{3-}$  and Pb(II) measured (Table 4). In order to verify the real removal efficiency of  $\text{PO}_4^{3-}$  from urban sewage (raw and treated), 10 mL of each filtered sample were mixed with 1.0 g of FK. The solutions were shaken at 145 rpm for 5 min at pH 6 [9], centrifuged at 3000 rpm for 25 min, and then the  $C_e$  of  $\text{PO}_4^{3-}$  and Pb(II) were determined in the supernatants (Table 4).

The  $C_0$  averages of  $\text{PO}_4^{3-}$  were  $6.1 \pm 0.1$  e  $3.8 \pm 0.1$  mg/L, respectively, for raw and treated urban sewage. After the use of FK,  $C_e$  averages of  $\text{PO}_4^{3-}$  were lower than 0.1 mg/L. In addition, the  $C_0$  and  $C_e$  averages of Pb(II) were always lower than the detection limit of 0.006 mg/L. These results show the efficiency during the use of FK for removal of  $\text{PO}_4^{3-}$  from urban sewage in real samples collected in a WWTP.

### Conclusions

A method for functionalization of kaolinite for removal of  $\text{PO}_4^{3-}$  from urban sewage was studied. The functionalized kaolinite (FK) with Pb(II) have shown a promising alternative for removal of  $\text{PO}_4^{3-}$  in aqueous solution, with maximum removal capacity of 8.4 mg/L, within a reaction time lower than 1 min. The precipitation of  $\text{PO}_4^{3-}$  is associated with pyromorphite, a mineral with low solubility ( $K_{sp} < 10^{-79.6}$ ). Finally, real urban sewage samples (raw and treated) were also tested for removal of  $\text{PO}_4^{3-}$  using KF, confirming its effectiveness for removal of  $\text{PO}_4^{3-}$  from urban sewage with  $C_0 \geq 4$  mg/L.

### Acknowledgments

This investigation was performed under a scholarship from Coordination of Superior Level Staff Improvement - CAPES, Brazil. Dr. Moruzzi is grateful to National Council for Scientific and Technological Development - CNPq (grant 301210/2018-7) and to CAPES (grant code 001) for financing support. We thank Dr. Damià Barceló (Editor-in-chief) and all the referees for their detailed and insightful review's comments, whom helped to improve the manuscript.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## References

- [1] V.H. Smith, Eutrophication of freshwater and coastal marine ecosystems a global problem, *Environ. Sci. Pollut. Res.* 10 (2003) 126–139.
- [2] S. Yeoman, The removal of phosphorus during wastewater treatment: a review, *Environ. Pollut.* 49 (1988) 183–233.
- [3] J.T. Bunce, et al., A review of phosphorous removal technologies and their applicability to small-scale domestic wastewater treatment systems, *Front. Environ. Sci.* 6 (2018) 8.
- [4] Morse G.K., et al., Phosphorus removal and recovery technologies, *Sci. Total Environ.* 212 (1998) 69–81.
- [5] B.E. Rittmann, et al., Capturing the lost phosphorus, *Chemosphere* 84 (2011) 846–853.
- [6] J. Zhao, et al., Formation and aggregation of lead phosphate particles: implications for lead immobilization in water supply systems, *Environ. Sci. Technol.* 52 (2018) 12612–12623.
- [7] Q. Shi, et al., Lead immobilization by phosphate in the presence of iron oxides: adsorption versus precipitation, *Water Res.* 179 (2020) 115853.
- [8] Q.Y. Ma, T.J. Logan, S.J. Traina, Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks, *Environ. Sci. Technol.* 29 (1995) 1118–1126.
- [9] R.X. Cao, et al., Phosphate-induced metal immobilization in a contaminated site, *Environ. Pollut.* 122 (2003) 19–28.
- [10] P. Miretzky, A. Fernandez-Cirelli, Phosphates for Pb immobilization in soils: a review, *Environ. Chem. Lett.* 6 (2008) 121–133.
- [11] M. Raji, A.E. Qaiss, R. Bouhfid, Effects of bleaching and functionalization of kaolinite on the mechanical and thermal properties of polyamide 6 nanocomposites, *RSC Adv.* 10 (2020) 4916–4926.
- [12] M.W. Kamiyango, et al., Phosphate removal from aqueous solutions using kaolinite obtained from Linthipe, Malawi. *Phys. Chem. Earth* 34 (2009) 850–856.
- [13] S. Moharami, M. Jalali, Use of modified clays for removal of phosphorous from aqueous solutions, *Environ. Monit. Assess.* 187 (2015) 639.
- [14] L. Deng, Z. Shi, Synthesis and characterization of a novel Mg-Al hydrotalcite-loaded kaolin clay and its adsorption properties for phosphate in aqueous solution, *J. Alloy. Compd.* 637 (2015) 188–196.
- [15] J. Li, et al., Enhancement of kaolin adsorption affinity toward phosphate by sequestering naturally abundant Ca/Mg from seawater, *Clean* 46 (2018) 1700662.