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Enhancing radiostrontium uptake by a pillared montmorillonite, modified by organic acids

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Abstract

The possibility to increase strontium uptake by an aluminum pillared montmorillonite has been studied by introducing organic acids in the interlayer space of the PILC. The effect of the acid was found to depend on its acid strength and the pH of the exchange solution. Oxalic acid proved the most successful agent, leading to an increase in Sr^{2+} uptake ranging from 0.3 to 0.4 meq g^{-1} at $\text{pH} \approx 8$, compared to the rest of the acids used. Furthermore, the amount of Sr^{2+} ions retained by the PILC-oxalic acid sample, after decreasing the pH from 8 to 3, was measured to be higher by a factor of 9 compared to the unmodified material.

1. Introduction

The separation and removal of radiostrontium from diverse types of radioactive environments has been the objective of numerous studies during the last decades. Pillared clays (PILCs) are found among the materials that have been proposed for applications such as nuclear waste management and decontamination of biological systems. Although, these materials are inorganic ion exchangers, highly resistant to thermal and radiation degradation, characterized by fast kinetics and potentially low cost production, they do not exhibit high cation exchange capacity (CEC) compared to several resins and synthetic metal oxides used for the same applications. Furthermore, they suffer from a marked decrease in their CEC at solutions of low pH, while they also allow desorption of interlayer cations in acidic conditions. Nevertheless, PILCs allow the fine-tuning of their adsorption properties, by adequately modifying their preparation process.

In the present work, an aluminum pillared montmorillonite was prepared, to be used for the absorption of radiostrontium from aqueous solutions. The possibility to

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increase strontium uptake as well as decrease strontium desorption in highly acidic solutions, was tested by introducing organic acids in the pore structure of the PILC.

2. Experimental

2.1 PILC characterization

An aluminum pillared montmorillonite was prepared from a greek bentonite, as described extensively elsewhere [1]. The XRD measurements showed a d_{001} -spacing of 16.7 Å. The specific surface area was determined to 190 m² g⁻¹ through nitrogen adsorption-desorption isotherms using the BET method. The specific pore volume of the material is 0.16 cm³ g⁻¹, out of which ~15% is in the microporous region (width less than 20 Å) while the rest consists of mesopores. The CEC of the PILC was measured through strontium adsorption isotherms and was found to be ~0.64 meq g⁻¹ at neutral pH.

2.2 Intercalation of organic acids

The chemical formulas and the first pK value of the organic acids used in the present study are listed in table 1. Samples of 0.5 g PILC were contacted with 0.01 M acid solutions for 15 h, under mild stirring. The modified PILCs were then separated by centrifugation, washed twice with de-ionized water and dried at 50°C.

Table 1: Chemical formulas and pK₁ values of the acids used.

Acid	Chemical formula	pK ₁
acetic	CH ₃ CO ₂ H	4.75
oxalic	HO ₂ C-CO ₂ H	1.23
malonic	HO ₂ C-CH ₂ -CO ₂ H	2.83
citric	HOC-(CH ₂ -CO ₂ H) ₂ -CO ₂ H	3.14

2.3 Strontium adsorption

Strontium adsorption from aqueous solutions of several pH values was studied through ion exchange isotherms, using the batch technique and radioactive ⁸⁵Sr as a tracer. The pH was adjusted by addition of HCl or Sr(OH)₂ solution. The amount of strontium ions uptaken by the PILC was determined by counting the γ-radioactivity of the solution,

both before and after the exchange. An intrinsic 22% efficiency Ge-detector was used for the radioactivity measurements.

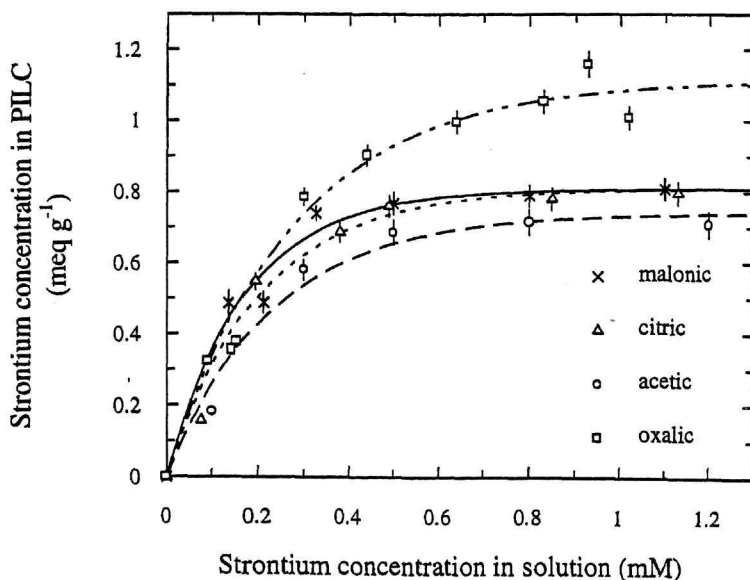
3. Results and discussion

3.1 Weak acid groups and strontium adsorption

All modified PILCs were tested for strontium adsorption at pH 8. Adsorption isotherms given in fig. 1, reveal that the PILC-oxalic sample is saturated with ~ 1.14 meq Sr^{2+} per g, while the saturation concentration ranges from ~ 0.73 to 0.81 meq g^{-1} for the rest of the modified PILCs. This increase in strontium adsorption is attributed to the higher acid strength of oxalic acid compared the other acids. As shown in table 1, the dissociation constant (K) of oxalic acid is one to three orders of magnitude higher. In general, weak acids (RCOOH) are expected to contribute to the negative charge of the PILC through dissociation reactions of the form:



The carboxylate anions (RCOO^-) formed may act as fixed charges which must be balanced by counter ions. However, reaction (1) is a pH-dependent process and takes place only when the pH inside the PILC (pH_{PILC}) rises above the pK value of the acid. Several studies^[2] have concluded that pH_{PILC} usually ranges from 1.5 to 3 and is related to the pH of the external solution. Therefore, the condition $\text{pH}_{\text{PILC}} > \text{pK}$ is more probable to be valid the stronger the acid, thus the smaller its pK value.



3.2 Effect of pH on strontium adsorption by the oxalic acid-modified PILC

The considerations above have been tested by studying Sr^{2+} adsorption by the PILC-oxalic sample in solutions of pH from 3 to 9. Saturation levels (meq g^{-1}) at each pH value used are given in fig. 2. In the same figure, saturation levels for the pristine PILC are drawn for comparison^[3]. Strontium uptake is practically the same for both PILCs at $\text{pH} < 5$, but an increase in adsorption is noticed for the PILC-oxalic in solutions of higher pH. This enhancement in strontium uptake supports the idea that additional exchange sites, arising from the dissociation of oxalic molecules, are formed inside the PILC. In fact, the increase in the pH of the exchange solution causes a decrease in the surface acidity of the PILC, thus allowing reaction (1) to proceed.

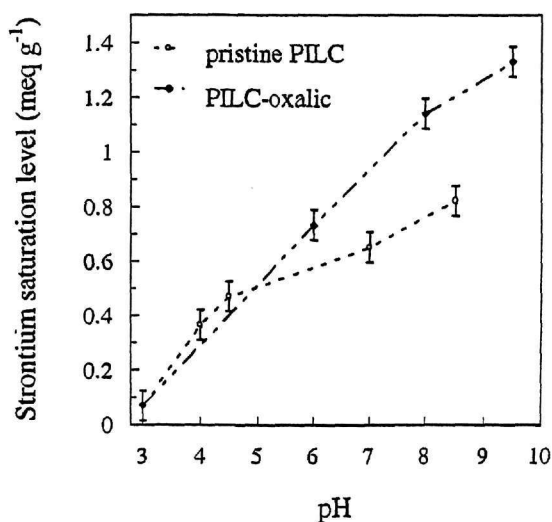


Fig. 2: Strontium saturation levels of the pristine and oxalic acid-modified PILCs, as a function of the pH of the exchange solution.

3.3 Strontium desorption from the oxalic acid-modified PILC

To examine the influence of oxalic acid on the desorption of Sr^{2+} in acidic solutions, strontium adsorption-desorption experiments were carried out. Samples of PILC-oxalic were first saturated with strontium ions at $\text{pH}\approx 8$. Upon reduction of pH to the value of 3, strontium desorption from the material was determined. Saturation levels at both pHs for the PILC-oxalic and pristine PILC are given in table 2. The modified sample was found to retain ~9 times more strontium than the pristine PILC upon decrease of the solution pH. Such an improved performance indicates that the oxalate group acts as a chelating agent for the strontium cation, forming compounds that resist solvation in acid media.

Table 2: Strontium saturation levels at pH 8 and 3, for pristine and oxalic acid-PILC.

Sample	Sr^{2+} saturation (meq g^{-1})	
	pH~8	pH~3
pristine-PILC	0.76	0.03
PILC-oxalic	1.14	0.27

4. Conclusions

The cation exchange properties of the pillared clay prepared in the present study, can be modified by introducing ionogenic groups, such as organic acids, in the interlayer space of the material. These pH-dependent sites improve the material properties in that: a) they contribute to its cation exchange capacity by adequately adjusting the pH of the exchange solution and b) they limit the desorption of the cation in acidic conditions, provided that they form an acid-resistant salt with the cation.

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