



Adsorption of Metallic Ions in Lamellar Crystalline Compounds Intercalated with Organic Molecules

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Abstract: This work describes the synthesis and characterization of crystalline lamellar calcium phosphate intercalated with m-aminobenzoic acid (CaP/MABA), and results of a study of adsorption and preconcentration of Zn(II), Ni(II), Co(II) and Cu(II), and in ethanol medium. The adsorption isotherms from ethanol gave the maximum adsorption capacities of 1.43, 1.04, .030 and 0.19 mmol g⁻¹ for copper, nickel, cobalt and zinc, respectively, which average stability constants followed Zn(II) > Ni(II) > Co(II) > Cu(II); the number of ligands was determined as four for both cations. The results obtained in flow experiments showed a retention and recovery of ca. 100% of the metal ion with packed CaP/MABA columns from solution containing a mixture of these cations.

Keywords: Inorganic Compounds, Chemical Synthesis, Adsorption, Preconcentration

1. Introduction

Commercial ethanol is usually a mixed grade with low percentage of water. In use, other additives define its application in diverse fields such as food industry, alcohol chemistry or as automotive engine fuels. One positive aspect of ethanol research as a fuel has been the development of methods to determine traces of metals that result from the extraction process from sugar cane. The presence of cations in ethanol fuel can induce corrosion in the vehicle components in contact with the liquid. For cation determinations, the first step in the usual procedures has been evaporation of the liquid to dryness, which is obviously time-consuming [1]. Methods commonly found in the literature used in the separation of metallic ions: on-line flow preconcentration system, liquid-liquid extraction, adsorption and ion exchange [2-7].

The lamellar crystalline compounds intercalated with organic compounds have attracted interest since they can act as ligands for the coordination of metallic ions on their surface and also to be used in the adsorption and preconcentration of metallic ions from ethanol solutions [8-10]. Studies have shown that calcium phosphate intercalated with m-aminobenzoic acid exhibits high chemical stability and high velocity adsorption of metallic ions in ethanol when

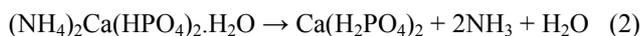
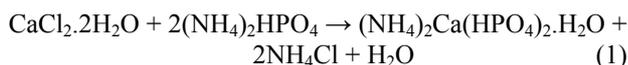
compared with other materials found in the literature. This material can be potentially used for analytical purposes.

This paper describes the preparation of crystalline lamellar calcium phosphate intercalated with m-aminobenzoic acid to find an efficient material for separation and determination of the metal ions present in ethanol, used as fuel for car engines. Primarily the material was tested with a synthetic ethanol solution containing some metal ions and further used in commercial ethanol.

2. Experimental

2.1. Synthesis of Calcium Phosphate (CaP)

Layered CaP was synthesized as described elsewhere [10]. Calcium phosphate was synthesized by slowly adding a dilute solution of calcium chloride dihydrated to a 1.50 mol.dm⁻³ dibasic ammonium phosphate solution. The mixture was heated to 353.15 K. The suspension formed was stirred for 1 h, when the solid started to settle out. This was filtered and dried at 323.15 K. Finally, the resulting compound was heated at 433.15 K for 48 hrs to eliminate ammonia. The reactions are given by equations 1 and 2.



2.2. Intercalation Procedure

About 50 mg of CaP was immersed in 25.0 cm³ of 0.50 mol dm⁻³ ethanolic m-aminobenzoic acid (MABA) and the suspension was shaken in an orbital mechanical stirrer for 8 hrs. The resulting solid was filtered, washed with distilled water and dried at 323.15 K. The solid was named CaP/MABA.

2.3. Characterization

Elemental analysis of calcium and phosphorus [11, 12] were performed by atomic absorption spectroscopy using a Perkin Elmer atomic absorption spectrometer, model 5100, and spectrophotometric methods using a Shimadzu spectrophotometer, model MultiSpec-1501.

The amount of 4-aminobenzoic acid intercalated into calcium phosphate was determined by nitrogen elemental analysis on a Perkin-Elmer Analyzer 2400 series H CHNS/O apparatus.

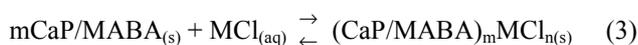
X-ray diffraction patterns were obtained with nickel-filtered CuK α (0.154 nm) radiation in the interval of 2 to 65° at a speed of 0.033° s⁻¹ and a step of 0.050° on a Shimadzu XD3-A diffractometer (30/20 kV/mA).

Infrared spectra of the samples were acquired on a Perkin-Elmer FTIR spectrophotometer, model 1600, by using pressed KBr pellets in the 4000-400 cm⁻¹ range with 4 cm⁻¹ of resolution.

Scanning electron microscopy (SEM) images were obtained for samples dispersed on a double-faced conducting tape adhered to an aluminum support. The samples were coated with gold using a Balzer MED 020 low-voltage sputtering apparatus. The measurements were carried out on a JEOL JSM-T300 scanning electron microscope.

2.4. Adsorption Isotherms

Adsorption of MCl_n by CaP/MABA from a solution can be described by equilibrium equation [13]:



The time required for this reaction to achieve the equilibrium condition was previously determined immersing 50 mg of CaP/MABA in 25.0 cm³ of 1.0 x 10⁻² mol dm⁻³ of the metal solution and shaken. At different time intervals, an aliquot of the supernatant solution was separated and the metal ion analysed by complexometric titration using EDTA as the titrant [14]. The amount of cations adsorbed, n_f, was determined by applying the equation: n_f = (n_a - n_s)/m, where m is the mass of the adsorbent and n_a and n_s are the initial and the equilibrium amounts of the metal in the solution phase in number of mols, respectively [15].

The adsorption capacity for CuCl₂, ZnCl₂, CoCl₂ and

NiCl₂ from ethanol solutions were performed by using the batchwise method. For each isotherm a series of samples containing 50 mg of the calcium phosphate intercalated with m-aminobenzoic acid was shaken for 8 h in an orbital bath with variable concentrations of each metal halide at a constant temperature of 298.15 ± 0.10 K. The concentration of the metal ion in solution, in equilibrium with solid phase, was determined by complexometric titration. The most commonly used isotherms are those related to the Langmuir model, which was originally derived for gas adsorption on planar surfaces such as glass, mica and platinum. The process was successfully extended to heavy metal ion adsorptions on porous surfaces. For this adsorption model the quantity adsorbed is related to the equilibrium solution concentration of the adsorbate, after adjusting to K_L and b parameters. From this procedure, the plateau of the isotherm enables K_L determination that reflects the affinity of the active sites on the surface. On the other hand, the b value is the upper limit and represents the maximum adsorption, determined by the number of reactive surface sites [16], as represented by equation 4:

$$n_f = K_L \cdot C_b / (1 + C_b) \quad (4)$$

Taking into account the experimental data, C_s/n_f and the so-called distribution coefficient K_L can be plotted against the concentration of the supernatant. If the Langmuir equation can be adjusted to the studied system, the measured data should fall on a straight line, whose slope gives K_L and the intercept the b values, derived from 1/K_Lb and 1/b, resulting from the angular and linear coefficients [16-18], as represented by equation 5.

$$C_s/n_f = 1/K_L \cdot b + C_s/b \quad (5)$$

Another fitting for the adsorption process is established by the Redlich-Peterson (equation 6) and Toth (equation 7) equations [19]:

$$n_f = K_{RP} a_{RP} C_s / (1 + K_{RP} C_s^\beta) \quad (6)$$

$$n_f = K_T a_T C_s / (1 + K_T C_s^\beta)^{1/\beta} \quad (7)$$

where K_{RP} and K_T are constants related to adsorption capacity, a_{RP} is the Redlich-Peterson capacity constant, a_T is the Toth capacity constant and β is an affinity constant of the adsorbent, with 0 < β < 1. Although these equations were previously employed empirically, they can be derived with the assumption of a continuous variation in thermal effects during the adsorption process. There is no assurance that the derivations of the Redlich-Peterson and Toth equations are unique; consequently, if the collected data can fit to the equations, it is only likely, but not proven, that the surface is heterogeneous. The Redlich-Peterson and Toth models unfortunately predict both infinite adsorption at infinite concentration and a corresponding thermal effect related to the adsorption at zero coverage [19].

Non-linear regression was compared to obtain the optimum kinetic sorption and isothermal parameters. A trial

and error procedure was employed for non-linear methods using the solver add-in functions of Microsoft Excel software. In the trial and error procedure, isotherm and thermodynamic parameters were determined by maximizing the coefficient of determination values [20]. The least squares method was used to analyze the linear forms of the thermodynamic and isotherm models.

Coefficient of determination values (r^2) were used in order to find the fitting degrees of isotherm adsorption models and thermodynamics by considering the experimental data [20], as defined by equation 8:

$$r^2 = S(n_f^{\text{CAL}} - \bar{n}_f^{\text{EXP}})^2 / \sum (n_f^{\text{CAL}} - \bar{n}_f^{\text{EXP}})^2 + \sum (n_f^{\text{CAL}} - n_f^{\text{EXP}})^2 \quad (8)$$

where n_f^{EXP} (mmol g⁻¹) is the experimental amount of divalent cations exchanged by the natural and the intercalated compound, \bar{n}_f^{EXP} is the average of n_f^{EXP} and n_f^{CAL} is the amount of cations obtained by isotherm models [20].

2.5. Metal Retention

A column with dimensions of 10.0 mm length and 5.0 mm internal diameter was filled with about one gram of the material and connected on line with a peristaltic pump. Ethanol solutions containing 6.5, 6.5, 6.1 and 5.8 mg dm⁻³ for CuCl₂, ZnCl₂, CoCl₂ and NiCl₂, respectively, were passed through the column with a flow rate of 0.65 cm³ min⁻¹. The column was initially washed with pure ethanol and afterwards the cations were eluted with a mixture of ethanol/0.10 mol dm⁻³ aqueous hydrochloric acid solution in a 4:1 (v/v) proportion. The eluted metals were analyzed by atomic absorption spectrometry. Three independent cations solutions were passed through the column and then each cation was determined in triplicate.

3. Results and Discussion

3.1. Characterizations

Calcium and phosphorus elemental analysis determinations for the synthesized compound gave 26.3 and 17.2%, respectively, values which are very close to the expected amounts, 26.5 and 17.1%, for the proposed formula Ca(H₂PO₄)₂. Based on these values, the corresponding molar amounts of these elements were calculated to give phosphorus to calcium ratio equal to two. The quantity of MABA intercalated into CaP was determined through the 9.08% of nitrogen atoms of this guest molecule, respectively, which corresponds to 6.48 mmol g⁻¹. The mechanism of intercalation of amine into the inorganic layers presumes the protonation of the basic centers by the acidic P-OH groups located in the inorganic matrix, in a typical acid-base interaction. On entrance of the amine into the lamellar cavity, it interacts with the monohydrogenphosphate group (O₃P-OH), enabling proton transfer to the base to form the organic cation. This species is electrostatically bonded to the inorganic sheets with amine in the original free interlamellar

space [17, 21, 22]. A proposed intercalation scheme for *m*-aminobenzoic acid inside the free inorganic host cavity is shown in Fig. 1.

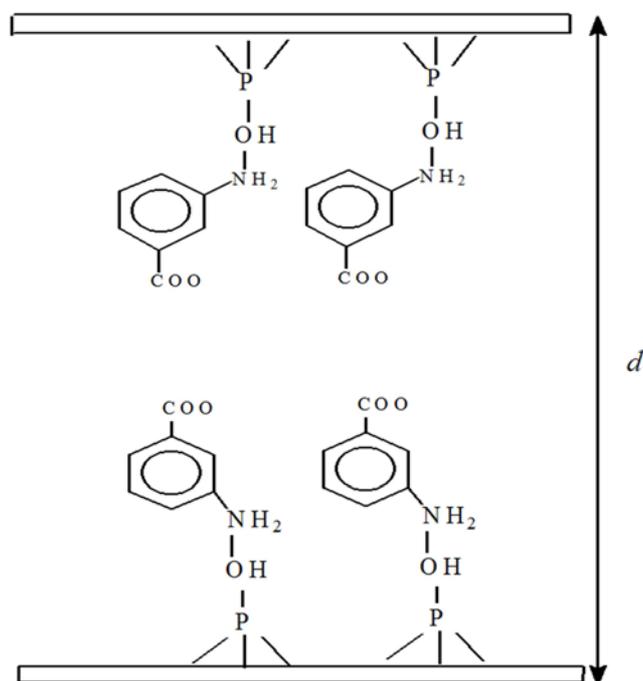


Fig. 1. Schematic representation of calcium phosphate intercalated with *m*-aminobenzoic acid.

The X-ray diffractogram provides the angle between the incidence of the diffracted radii and the sample (2θ) still showing the relative intensity. The technique is non-destructive and only small amount of powder sample is sufficient for the identification of the crystal phase present. Through the Bragg equation,

$$2d \sin\theta = n\lambda \quad (9)$$

where $\lambda = 1.5406 \text{ \AA}$ is the wavelength of the radiation used, it is possible to determine the distance interlayer d (\AA) between the atomic planes of the crystal lattice.

The high degree of crystallinity of the calcium phosphate compound reflects in well-formed X-ray diffraction powder patterns, showing the presence of a sharp and intense peak attributed to the 001 plane, with an interlayer spacing that corresponds to 2θ value of 16.73° , giving a basal distance of 535 pm [23] as illustrated in Fig. 2a. As expected, this distance increases when the inorganic support is suspended in ethanolic solution containing dissolved MABA guest molecule, to give, in the present case, a sharp peak at $2\theta = 9.36^\circ$, which corresponds to an interlayer distance of 947 pm, as illustrated in Fig. 2b, an increase of 412 pm in comparison to that of the original host, under such conditions, the experimental values suggested that MABA is perpendicular orientation to the inorganic layer, to form a bilayer arrangement in the cavity, as considered in the Fig. 1.

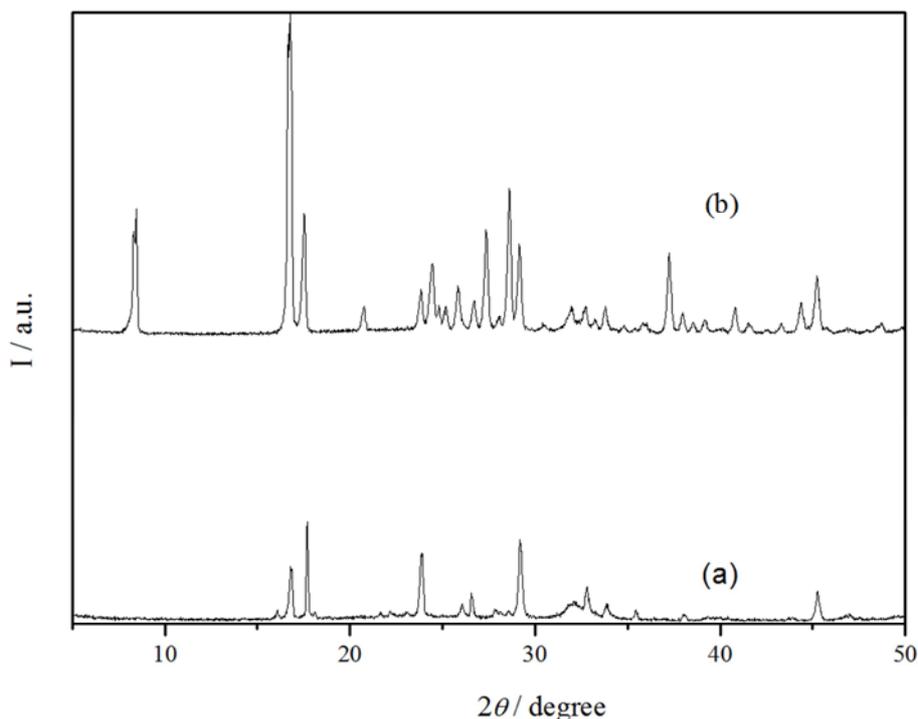
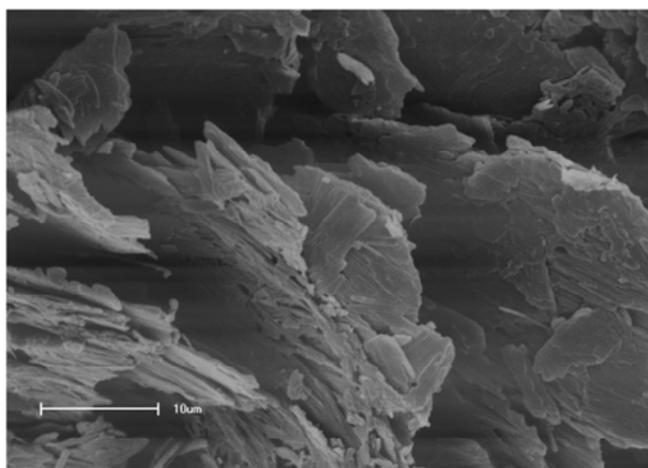


Fig. 2. X-ray diffraction of calcium phosphate (a) and the respective intercalated compound with *m*-aminobenzoic acid (b).

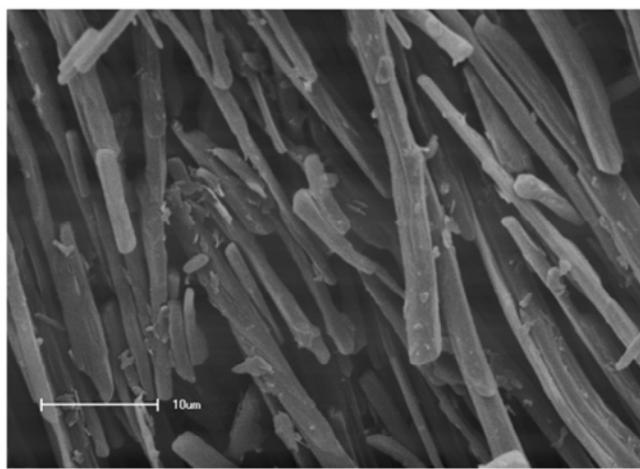
The infrared spectra indicate that the amines interact strongly with the proton of the P-OH groups. The OH band at 1250 cm^{-1} in spectra except indicates partial saturation of the host. The presence of OH group on phosphate in the lamellar calcium phosphate exhibits stretching at 3400 cm^{-1} and weak deformation at 1630 cm^{-1} bands in the infrared spectrum. The intense characteristic stretching bands for phosphate groups are located at 1033 and 1010 cm^{-1} [17]. However, after MABA intercalation the bands attributed to OH vibrations remain in the spectrum, with a decrease in intensity, mainly

the deformation band as observed before for other systems [24] and no clear evidence of NH vibration bands at 3580 and 3077 cm^{-1} could be attributed.

The scanning electron microscopic (SEM) photograph of the calcium phosphate and also for the sample intercalated with *m*-aminobenzoic acid were obtained as shown in Fig. 3. The crystal morphology of this compound is clearly lamellar, in good agreement with the expected structural characteristics. These results are very important in order to obtain pillared compounds with a high degree of crystallinity.



(a)



(b)

Fig. 3. SEM photographs of CaP (a) and intercalated with MABA (b).

3.2. Adsorption Isotherms

Taking into account a property associated with the intercalated crystalline lamellar compound for adsorbing

metal ions from ethanol solution, the corresponding isotherm for the selected cations, Zn^{2+} , Ni^{2+} , Co^{2+} and Cu^{2+} , was investigated. Initially, investigation demonstrated that the original matrix, without MABA, does not adsorb this cation.

The Langmuir, Redlich-Peterson and Toth nonlinear adsorption models were used to explain the significant capacity of these matrices to quantify divalent metal interactions on this polymeric inorganic structure.

The nonlinear Langmuir model presents a significant advantage when used with such experimental data, allowing the determination of the capacity of cations bonded to basic centers and to evaluate the constant related to the binding energy [25-28]. The Redlich-Peterson and Toth models were similar to the Langmuir model with coefficient r^2 over 0.98. The large capacity of CaP/MABA sample was confirmed through constant values obtained with these models in the nonlinear form, whose results gave the best approximation to the experimental data. The adsorption isotherm of the CaP/MABA system is illustrated in Fig. 4.

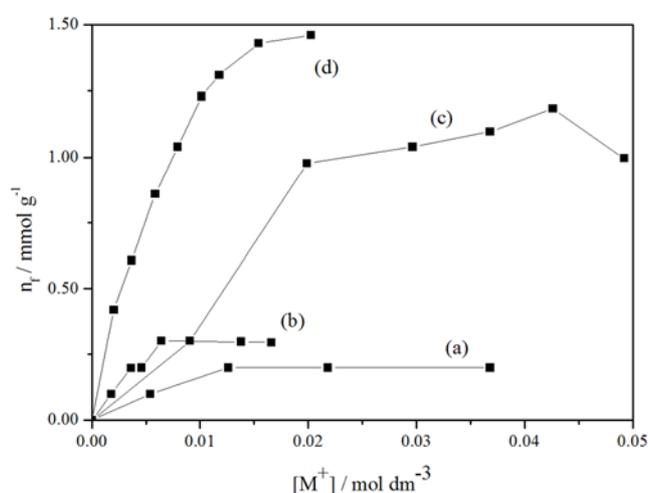


Fig. 4. Isotherms of zinc (a), cobalt (b), nickel (c) and copper (c) adsorption on the intercalated compound.

The solid adsorption capacity of metal halide on CaP/MABA depends on the nature of the complex formed on the surface and the affinity of any particular attached ligand for the metal. In the present case, the maximum adsorption capacity, n_f^{\max} , for Cu^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+} was 1.43, 1.04, 0.30 and 0.19 mmol g^{-1} , respectively. The sequence of the number of metallic cation that enters into the inorganic sheet decreases in the order $\text{Zn}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+}$. This sequence is the opposite of that of hydrated cation size $\text{Cu}^{2+} \cong \text{Ni}^{2+}$ (147.8) $< \text{Co}^{2+}$ (169.6) $< \text{Zn}^{2+}$ (178.2) ($\text{cm}^3 \text{mol}^{-1}$) [29,

Table 2. Determination of metal ions in ethanol fuel after preconcentration by the proposed method and by the conventional preconcentration method [1].

Plant	Concentration found / $\mu\text{g dm}^{-3}$					
	Cu (II)		Ni (II)		Zn (II)	
	Proposed	Conventional	Proposed	Conventional	Proposed	Conventional
A	50 ± 5	48 ± 4	9 ± 1	11 ± 2	10 ± 3	7 ± 2
B	55 ± 7	50 ± 3	12 ± 1	10 ± 3	11 ± 2	9 ± 3
C	68 ± 6	65 ± 3	8 ± 1	9 ± 2	12 ± 3	10 ± 3

4. Conclusions

Elemental analysis data enabled the calculation of the molecular formula for the crystalline lamellar $\text{Ca}(\text{H}_2\text{PO}_4)_2$

[30]. The small volumes of hydration displayed by nickel make it easier to access the interlamellar positions. On contrary, the volume of zinc is prone to give it the largest hindrance to the basic centres within the lamella. The average stability constant (Γ) and the average number of ligands bonded and coordinated to the metallic ion (\bar{n}) were determined from the plot of $1/n_f$ and $1/C$. The average stability values of Cu^{2+} , Ni^{2+} , Co^{2+} and Zn^{2+} in CaP/MABA were 516, 920, 2027 and 3406 $\text{dm}^3 \text{mol}^{-1}$, respectively, and the average number of ligands (\bar{n}) for CaP/MABA were four for both metallic ions. The values of the calculated constants indicate the formation of a stable complex.

3.3. Recovery and Determination of the Metal Ions

The results obtained from the experiments carried out by passing a mixture of the four metals through the column packed with CaP/MABA matrices are summarized in Table 1. Experiments carried out in triplicate for each material, showed that in every case, the column retained the cations and are then released by an acidic solution with nearly 100% efficiency. Thus, the same efficiency is observed in all experiments.

The recovery experiments for each metal ion from synthetic solutions served as basis for a rapid method for preconcentration and determination of metal ions a fuel ethanol.

Table 1. Recoveries of metal ions from ethanol solution by CaP/MABA matrix using the column method.

Ion	Recovered / %
Co(II)	98 ± 2
Cu(II)	99 ± 2
Ni(II)	99 ± 2
Zn(II)	99 ± 2

Table 2 shows the concentration of the metal ions in samples of fuel ethanol produced in three different plants. The metal Co^{2+} is not found in detectable amount. The concentrations of Cu^{2+} are the highest in the analysed samples, and correspond to the contents of this metal normally found in fuel ethanol [31]. These results are in accordance with results obtained using the conventional preconcentration method [1].

compound. The expansion of the basal distance was detected in X-ray diffraction patterns; the lamellar structure was maintained after intercalation, and so was the morphology of the microcrystals. The availability of the basic centers in the intercalated compound gives this

material the property of adsorbing cations from ethanol solution at the solid/liquid interface, a behavior that may be useful in cation removal. It is relatively high chemical stability in ethanol, and the velocity with which the metal ions were adsorbed, turns this material potentially used for analytical purposes.

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