



Performance of phosphoric acid activated montmorillonite as buffer materials for radioactive waste repository

Tsing-Hai Wang^a, Tsung-Ying Liu^b, Ding-Chiang Wu^c, Ming-Hsu Li^d, Jiann-Ruey Chen^b, Shi-Ping Teng^{a,c,*}

^a Institute of Nuclear Engineering and Science, National Tsing Hua University, Hsinchu 300, Taiwan

^b Department of Material Sciences and Engineering, National Tsing Hua University, Hsinchu 300, Taiwan

^c Department of Engineering and System Science, National Tsing Hua University, Hsinchu 300, Taiwan

^d Institute of Hydrological and Oceanic Sciences, National Central University, Jungli 320, Taiwan

ARTICLE INFO

Article history:

Received 9 April 2009

Received in revised form 15 August 2009

Accepted 19 August 2009

Available online 26 August 2009

Keywords:

Montmorillonite

Radioactive waste repository

Acid activation

Cesium

Safety assessment

ABSTRACT

In this study, the performance of phosphoric acid activated montmorillonite (PAmmt) was evaluated by cesium ions adsorption experiments. The PAmmt samples were obtained by activating with 1, 3 and 5 mol L⁻¹ of phosphoric acid, respectively under reflux for 3, 12, and 24 h. Experimental results demonstrated that the treatment of raw K-10 montmorillonite with phosphoric acid increased the materials' affinity for Cs uptake and no significant amount of suspension solids were produced. A relatively insignificant variation in the CEC value was observed. Furthermore, PAmmt also showed high adsorption selectivity toward Cs ions. The improved sorptive properties were mainly related to the increased surface area and the relatively higher surface charge density. Increased specific surface area was the result from partial decomposition of lamellar structure of mmt; while the higher surface charge density was caused by the protonation of octahedral Al–OH sites during the acid activation. Generally speaking, stronger acid concentration and longer activation times would produce relatively more decomposed PAmmt particles. However, as the activation exceeds 3 h, the precipitation of Si⁴⁺ would passivate PAmmt against further acid attacks. Based upon our results, acid activation by phosphoric acid could produce PAmmt samples with high sorption capacity and selectivity, and good structural integrity, which are beneficial to be used at radioactive waste repository.

Crown Copyright © 2009 Published by Elsevier B.V. All rights reserved.

1. Introduction

Activation by either chemical (acid/alkaline) or physical (thermal) treatment is widely applied to clay minerals such as montmorillonite (mmt) for preparation of functional materials such as sorbent toward environmental contaminants or radionuclides of concern. The thermal treatment, also known as the calcination, would evaporate lattice water molecules, which further induce the reorganization of the clay structure. For example, after calcinations under 450–600 °C, kaolinite will lose its lattice water and reorganize its Al–O network and is transformed into metakaolinite with highly disordered structure [1]. From the perspective of chemical activation, both acid and alkaline treatments are conducted to prepare high sorption capacity as well as affinity sorbents [2]. The advantage of using chemical activation lies in

that it can be carried out under mild conditions, minimizing further separation and regeneration processes. During acidification, the H⁺ attack would induce the leaching of mineral impurities, the disaggregation of clay particles, and the dissolution of the external layers [3]. Also, the H⁺ attack is accompanied with the replacement of exchangeable cations that are originally adsorbed on the clay surface to compensate the negatively charged clay surface. As a result, this replacement produces certain number of acid centers and thus the catalytic property of acid activated clay particles is much different from that of the original clay minerals [4]. For example, the catalytic property of montmorillonite could be greatly altered by replacing the internal Al³⁺ or Fe²⁺ with H⁺ during acidification [5]. On the other hand, the surface areas of acid activated clay particles are greatly increased due to the decomposition of lamellar structure of montmorillonite [3]. During decomposition stage, octahedral aluminum ions are preferentially released from the clay structure, causing the formation of additional Al–OH and Si–OH vibration bonds without much affecting the original mineral structure [6]. With these additional hydroxyl groups the sorption capacity of these activated clay minerals is quietly promoted toward some environmentally hazardous contaminants such as Pb(II) [7], Ni(II),

* Corresponding author at: Institute of Nuclear Engineering and Science, and Department of Engineering and System Science, National Tsing Hua University, Hsinchu 300, Taiwan. Tel.: +886 3 5742670; fax: +886 3 5720724.

E-mail address: spteng@ess.nthu.edu.tw (S.-P. Teng).

Cu(II) ions [8]. The removal of printing and dyeing waste in the wastewater treatment by using acid activated clay minerals is also reported in literature [9].

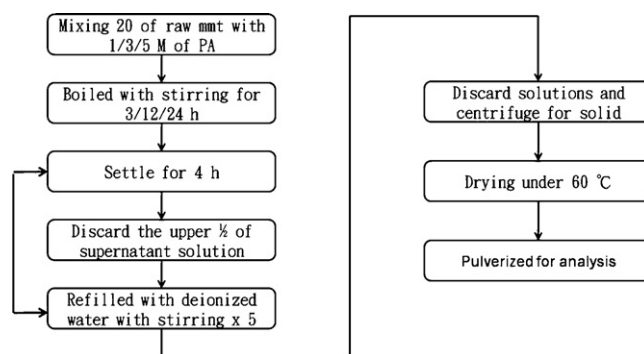
It is widely accepted that the surface charges, surface areas, and the structural integrity of clays would be significantly modified during acid treatment [5], but the extent of such alteration would be strongly correlated to the entity of acid solutions that was used. For example, it is reported that all the silicon and aluminum atoms are removed from the chemical structure of the clay lattice when using HF, HSO₃Cl, or H₂SO₄ solutions whereas only a mild digestion, which increases the laminar distance of the montmorillonite, is observed by using HCl solutions [10]. The magnitude of disorders in lamellar structure by acid activation as a consequence increases the surface area and greatly influences the integrity of acid activated clay particles. The latter entity is the fundamental requirement for hazardous waste repository, especially for the radioactive waste repository. In this case, clay minerals (especially the montmorillonite) are usually applied as buffer material to tightly adsorb released radionuclides, reducing their threat to the biosphere. Due to strong affinity between these clay minerals and radionuclides, these adsorbed radionuclides are generally regarded as immobile. In most cases, the remobilization is not the result of desorption but rather mainly stems from the so-called colloid mediated transport. This is undertaken by the ablation of disruptive fraction on surface of clay particles into aquifer solutions, producing the observed suspension colloids. With suspension colloids, migration of these radionuclides, which adsorbed tightly on suspension colloids, becomes unpredictable, depending upon the hydrological environments of groundwater flow [11,12]. That is, the migration of radionuclides would be far beyond the expected distance when considering only the adsorption between radionuclides and clay minerals.

Although many works have devoted to develop high affinity adsorbent for removal or remediation of hazardous wastes, few studies focused on the integrity of acid activated clay particles. As mentioned above, the integrity of these activated clay particles is important to reduce the probability of colloid mediated transport. Accordingly, phosphoric acid, which exhibits only mild acidity, is applied in this study to activate montmorillonite particles. Also, surface adsorbed phosphate anions, which behave as soft bases compared to sulfate and fluoride anions, are expected to have stronger affinity toward some soft cations such as the transuranium ones. The performance of these phosphoric acid activated montmorillonite (PAmmt) is examined by cesium sorption isotherms, while the integrity of PAmmt samples is evaluated by observing the amount of suspension solid produced during these sorption experiments.

2. Experimental

2.1. Solid and chemicals

The montmorillonite clay (mmt) used here was purchased from Aldrich (cat. 281522) and was used without any further purification. The surface area of montmorillonite clays is 243 m²/g (N₂-BET) and its cation exchangeable capacity (CEC) is 125 meq/100 g. The idealized formula of mmt is Na_{0.2}Ca_{0.1}Al₂Si₄O₁₀(OH)₂(H₂O)₁₀. All chemical reagents including phosphoric acid solutions are of analytical grade purchased from Aldrich. The specific surface area of raw (mmt) and phosphoric acid activated montmorillonite (PAmmt) samples were determined by N₂-BET method, while their CEC was examined by following the method 9081 A (sodium acetate, US EPA). The potentiometric titration was conducted in the mixture of 0.1 g-mmt/PAmmt with 100 mL solution containing 0.1 M NaCl background electrolyte. The 0.01 M of HCl and NaOH solu-



Scheme 1. The flow chart of preparation of phosphoric acid activated montmorillonite (PAmmt).

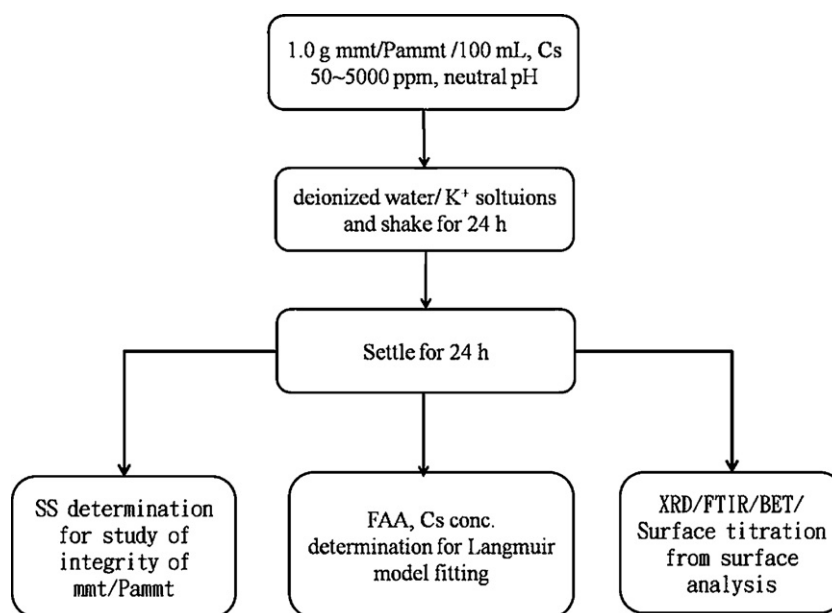
tions were used in the titration experiments. The inert nitrogen gases were simultaneously bubbled throughout the titration experiments to reduce the influence from the dissolved carbon dioxide. After adding certain amount of HCl/NaOH solutions, the corresponding pH was monitored and only the one with a variation less than 0.1 pH unit in 3 min was recorded. The X-ray diffraction (XRD, Shimadzu XRD 6000) analysis of these mmt/PAmmt powders were recorded with the scan range from 2° to 10° (2θ) and the scan rate of 4°/min, with Cu Kα radiation (λ = 0.15406 nm) at 30 kV and 20 mA. The transmission mode of infrared spectra of these montmorillonite samples was obtained by Fourier Transform Infrared Spectroscopy (FTIR, Horiba) in KBr pellets. The FTIR specimen was prepared by mixing 5 mg of mmt/PAmmt powders with 50 mg of KBr salt and then hydraulically pressed to obtain a transparent ingot 2 mm in thickness. The FTIR spectra were recorded with a scan rate of 1.00 cm⁻¹/s and the resolution of 2 cm⁻¹.

2.2. Preparation of phosphoric acid activated montmorillonite

The procedure of preparation of PAmmt was shown in Scheme 1. Briefly, it was obtained by mixing 20 g of raw mmt with 2 L of 1, 3 and 5 M of phosphoric acid, respectively. Mixtures were then refluxed for certain reaction hours (3, 12 and 24 h). The nomenclature of these PAmmt follows the rule of Ax.Yh, where x is the concentration of the mixed phosphoric acid and Y is the reflux time. For example, A3.12 h means the PAmmt samples were obtained from the activation with 3 M of phosphoric acid under 12 h of reflux. The activation was conducted within a 5 L double-necked Pyrex bottle with rigorous stirring throughout the entire reflux process. At the end of reflux, the mixture was placed intact for 4 h. An adequate amount of supernatant solutions was sampled to determine the concentration of released Si and Al ions by the ethylene-air flame atomic absorption spectrometer (FAA, Varian SpectraAA-30). Then most of the supernatant solutions were discarded and then refilled with fresh deionized water (Millipore, 18 MΩ) to volume of 2 L. These new mixtures were vigorously stirred again for 30 min and placed stationary for sediment of PAmmt particles. After repeating the aforementioned washing processes for five times, the “cleaned” PAmmt particles were collected by centrifugation and were dried overnight under 60 °C. These dried PAmmt particles were then pulverized for further physical analysis and for Cs sorption experiments.

2.3. Sorption batch experiments

The Cs ions sorption experiments were carried out in serum bottles at room temperature. In these experiments, 1.0 g of mmt/PAmmt powders were mixed with 100 mL of deionized water with the Cs ions concentration of 50–3000 ppm (mg-Cs/L). The



Scheme 2. The flow chart of sorption experiments.

concentration of Cs ions selected herein was to qualify sorption capacity of raw/activated mmt samples although it is expected that the concentration of accidentally released radiocesium ions is extremely low (<1 ppb) (Karamanis and Assimakopoulos [12]). The purpose of using deionized water is to directly evaluate the amount of suspension solid produced during the sorption experiments since the presence of background electrolyte would decrease the Debye length reducing the repulsion forces between particles and consequently enhances the precipitation. As a result, using deionized water directly is able to avoid an overestimated structure integrity (produce little suspension solids) of PAmmt samples. The pH values in these sorption experiments were adjusted toward neutral environments (pH 7.3–7.5) by adding negligible volume of 0.01 M HCl/NaOH solutions. Mixtures were placed end-to-end in a reciprocal shaker with a continuous shake for 24 h. At the end of shake, mixtures were placed intact for one day to settle PAmmt particles. After one day of settling, appropriate amount of upper supernatants were sampled for suspension solids (SS) and equilibrated Cs concentration determination. For SS determination, 5 mL of upper supernatant was gradually dipped into a glass fiber filter (Whatman 934AH). The wet glass fiber filter was then dried at 105 °C while the increased weight on the filter was interpreted as the weight of suspension solid. To determine the equilibrated Cs concentrations, the supernatant solution was filtered preliminarily through a 0.45 μm Millipore filter cell and then introduced into ethylene-air FAA (Scheme 2). The experimental results were also fitted by Langmuir sorption model to evaluate the maximum sorption capacity namely,

(1) $q = \frac{q_{\max} b C}{1 + b C}$ where q represents the amount of adsorbed Cs per gram of montmorillonite (adsorbed Cs mg/g), q_{\max} is the maximum sorption capacity, C is the concentration of Cs ion in solution (mg Cs/L), and b is the Langmuir constant relevant to the sorption affinity.

3. Results and discussion

3.1. Cs sorption studies

It must be emphasized that all the sorption experiments were conducted under the neutral (pH 7.2–7.5) conditions since the

Cs sorption behavior is strongly affected by the environmental pH. Fig. 1 shows the amount of suspension solid produced in the sorption experiments with 5 M of phosphoric acid activated mmt samples for various Cs concentrations. The increased amount of suspension solid indicates that these PAmmt particles will be unsuitable for use in the radioactive waste repository because they would produce more colloids during the sorption although they exhibit higher sorption capacity. It is noteworthy that even with the most severe acidification conditions (5 M of phosphoric acid), these PAmmt particles only produce at most 1.75 wt.% of suspension solid. In addition, the amount of suspension solid increases as the activation time increases but is independent of Cs loadings. The PAmmt samples with 3 h of activation produce similar suspension solid as the original mmt samples do, while the A5_24 h samples produce about 1.75 wt.% of suspension solid during Cs sorption experiments. This implies the structural integrity of these PAmmt particles, showing their potential application to the radioactive waste repository because they could minimize the occurrence of colloid transport.

Besides few colloids that are produced, these PAmmt samples also possess high sorption capacity toward Cs ions as indicated in the isotherm experiments (Fig. 2). After fitting with Langmuir

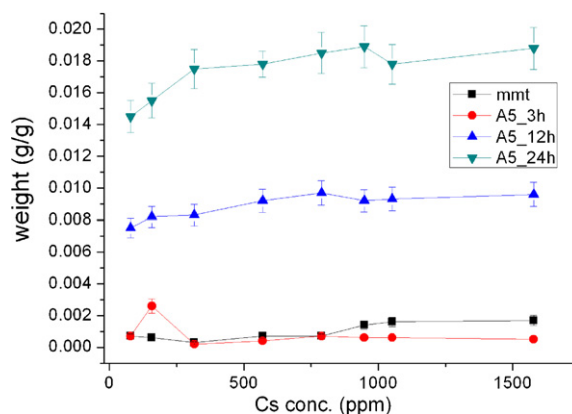


Fig. 1. The amount of suspension solid produced in these sorption experiments with 5 M of phosphoric acid activated mmt samples in various Cs concentrations.

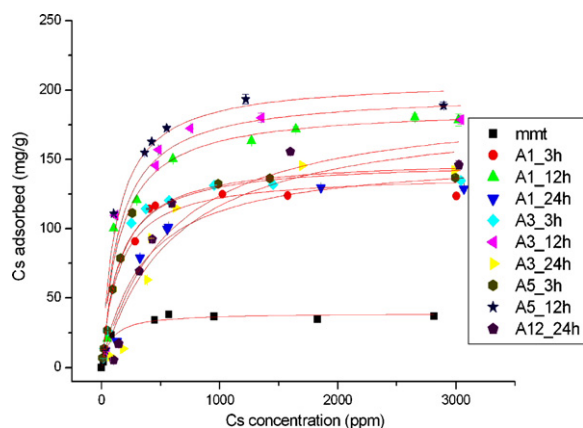


Fig. 2. The sorption isotherms of Cs ions to original and phosphoric acid activated montmorillonite.

model, the maximum sorption capacity is derived and listed in Table 1. It is obvious that activation by phosphoric acid greatly increases the Cs sorption capacity by 3–5 times. Moreover, PAmmt samples show similar sorption capacity to that of aluminum-pillared montmorillonite (AlPmmt), demonstrating the effect of activation by using phosphoric acid. The slight difference between results from PAmmt and AlPmmt might be attributed to the incomplete cation exchange capacity restoration or the strong binding of hydromium toward PAmmt surfaces [12]. These PAmmt samples also demonstrate superior sorption selectivity toward Cs ions even in saline solutions with 0.5, 1.0, and 3.0 wt.% of potassium ions, respectively, which are analogous with the average salinity of observed groundwater and seawater. Fig. 3 shows the normalized sorption capacity, which is determined by comparing the sorption capacity (by Langmuir fitting) of these PAmmt samples in saline solutions to that in deionized waters. Generally speaking, the Cs uptake of PAmmt samples is higher in 0.5 wt.% salinity than in 3 wt.% ones, regardless of the activation time that was applied. This observation is in good agreement with literature, indicating potassium cations, which have low hydration energy together with relatively similar hydrated ion radius, pronouncedly compete with Cs ions for limited sorption sites on clay surface [13]. It is worth mentioning that the PAmmt samples subjected with 5 M of phosphoric acid demonstrate the higher selectivity than those obtained from 3 and 1 M phosphoric acid solutions with 3 and 12 h of activation. However, after 24 h of activation these PAmmt samples seem to have relatively similar selectivity regardless of the concentration of phosphoric acid. This difference is probably due to the magnitude of H^+ exchanged and the modification happened on the surface and the structure of these PAmmt samples.

Table 1
Results fitted by Langmuir model applied on Cs ions sorption of original and phosphoric acid activated montmorillonite.

Samples	q_{max}	Std	b	Std	R^2
mnt	39.2304	±1.3902	0.0130	±0.0014	0.9795
A1_3h	139.5358	±6.6513	0.0070	±0.0016	0.9758
A1_12h	187.7384	±9.5374	0.0067	±0.0017	0.9375
A1_24h	152.4432	±13.2079	0.0028	±0.0008	0.9520
A3_3h	148.8517	±6.4953	0.0069	±0.0014	0.9801
A3_12h	197.9683	±15.9969	0.0068	±0.0025	0.9130
A3_24h	186.7109	±29.9738	0.0017	±0.0007	0.8971
A5_3h	150.7481	±6.2279	0.0068	±0.0010	0.9807
A5_12h	208.0341	±13.5484	0.0080	±0.0024	0.9443
A5_24h	192.7714	±28.4619	0.0018	±0.0007	0.9065

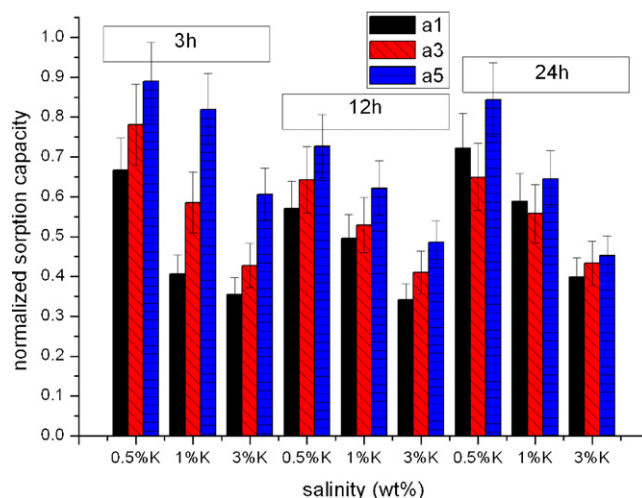


Fig. 3. The selectivity toward Cs ions of original and phosphoric acid activated montmorillonite in the presence of 0.5 and 1 wt.% of K ions with 3, 12, and 24 h of activation.

3.2. The surface properties of the acid activated montmorillonite

The increased sorption capacity of the PAmmt samples is believed to be closely related to the increased specific surface area (Fig. 4a). It is noteworthy that a local maximum of specific surface area is reached with 12 h of activation and then the specific surface area decreases gradually along with the activation time. After 24 h of activation, the specific surface area of the PAmmt samples resembles that of the original mmt samples. This corresponds to the observation that the highest sorption capacity was

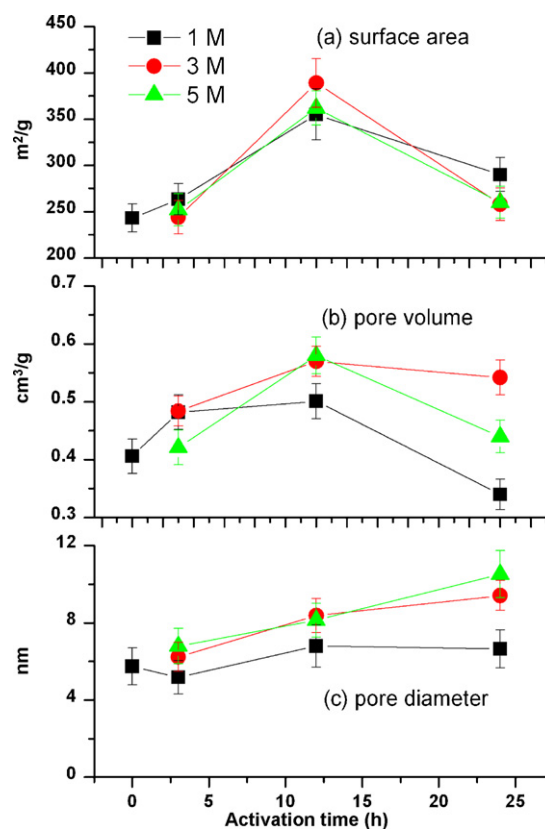


Fig. 4. The (a) specific surface area; (b) pore volume; and (c) pore diameter of original and phosphoric acid activated montmorillonite.

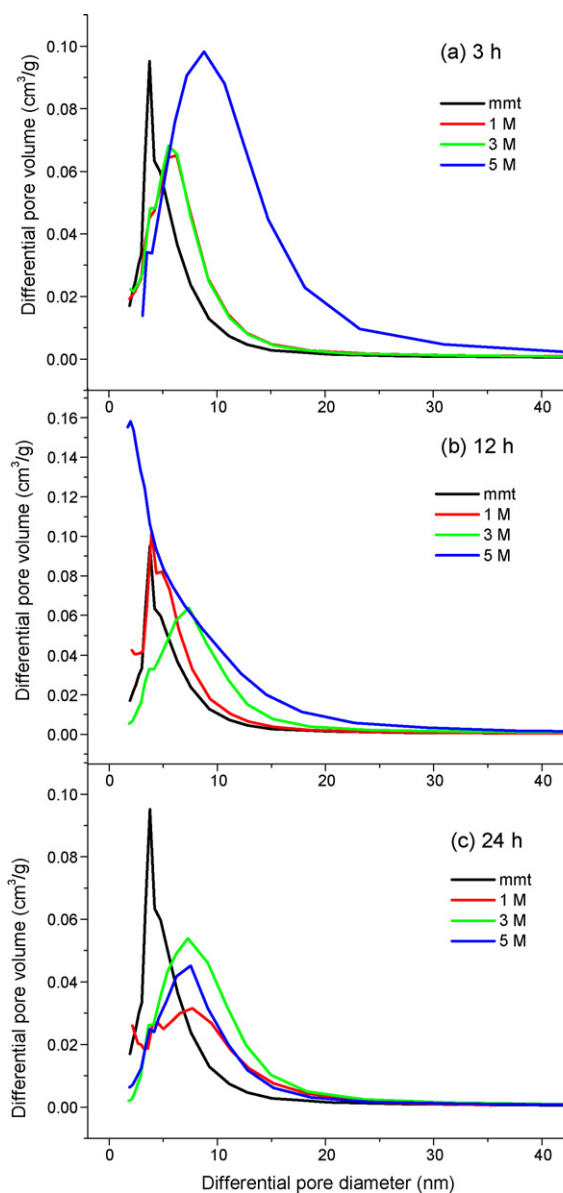


Fig. 5. The pore size distribution of original and phosphoric acid activated montmorillonite.

obtained in A1_12, A3_12, A5_12 h samples, respectively. Similarly, the pore volume shows a local maximum with 12 h of reaction and afterwards the pore volume slightly decreases (Fig. 4b). While activating under 1 M of phosphoric acid solutions the pore diameters are relatively unaffected by the activation time, whereas under 3 and 5 M of phosphoric acid solutions, the pore diameter responds positively to the increase of activation times (Fig. 4c). In addition, the porosity transformation could be observed by deriving the N_2 adsorption/desorption isotherm with the BJH (Barrett-Joyner-Halenda) method [14]. As indicated in Fig. 5, the original mmt particles are with mesoporous texture containing the major pore diameter distribution at 3.77 nm and the minor fraction at 4.77 nm. After 3 h of activation, the surface porosity transforms to a mesopore distribution with diameter around 5.54–6.27 nm under 1 and 3 M of phosphoric acid solutions. While under severe acid condition (5 M) a broad mesopore distribution centered at 8.79 nm was observed. This entity implies that more mesopores are generated during the acid activation. After 12 h of activation, A1_12 h samples present the similar mesoporous texture as that of the original mmt samples, whereas the A3_12 h samples show a wide pore distribu-

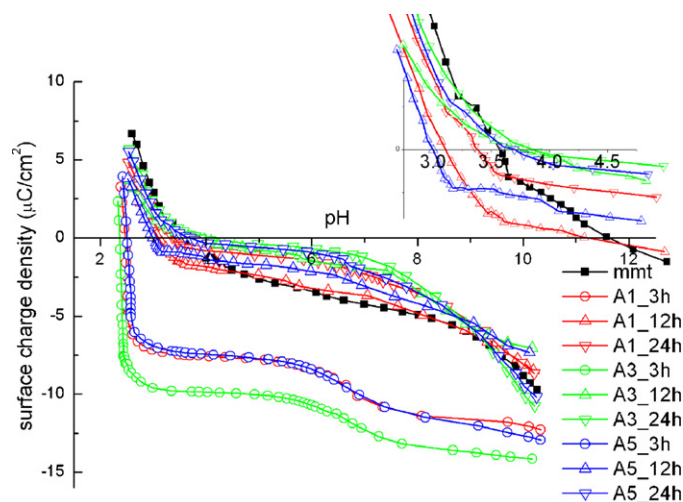


Fig. 6. The surface titration of original and phosphoric acid activated montmorillonite.

tion centered at 7.37 nm, which is very close to that of the A5_3 h samples. Notably, a large number of micropore is produced after 12 h of activation with 5 M of phosphoric acid solutions. With 24 h of activation, the PAmmt particles demonstrate resembling mesoporous texture centered at about 7.28–7.69 nm, regardless of the concentration of phosphoric acid.

The observed positive response to the increase of specific surface area with reaction time is the result of H^+ substituted octahedron and tetrahedron spaces that are originally occupied by the leached Mg^{2+} , Fe^{3+} and Al^{3+} ions within montmorillonite. With the progress of activation, these sites transformed from the micropores to mesopores. Finally, with the decomposition of lattice structure at these locations, some of the mesopores disappear, leading to a drop in specific surface area [3].

Besides the increase in surface area, the promoted selectivity of the PAmmt samples could also be related to the increased surface charge density as demonstrated by the surface titration experiments (Fig. 6). The surface charge density is calculated from the potentiometric titration curves according to the relationship:

$$(2)\sigma_H = F(C_a - C_b + [OH^-] - [H^+])/mS$$

where σ_H is the surface charge density ($C m^{-2}$), F is the Faraday constant ($C mol^{-1}$), C_a and C_b are the concentrations ($mol L^{-1}$) of the acid and the base added to the suspension solutions, $[OH^-]$ and $[H^+]$ the concentration of OH^- and H^+ measured from the pH of the solutions respectively, m is the mass of the PAmmt/mmt samples in the solution ($g L^{-1}$), and S is the specific surface area of the sample ($m^2 g^{-1}$).

Although it is expected that high concentration and long reaction time will result in a highly charged surface, our findings showed a different behavior. With 3 h of acid activation, it is noted that the PAmmt samples (A1_3 h, A3_3 h, A5_3 h) possess the most negative surface charge density compared to that of the starting mmt samples. This entity corresponds to the highest selectivity as shown in Fig. 3, especially for the A5_3 h samples, which possesses stronger negative surface charge density and demonstrates better selectivity even in the most severe K^+ solutions (Fig. 3). Furthermore, the main difference between these PAmmt systems is the difference in pH_0 value where σ_H becomes zero (the isoelectric point). The isoelectric point is the pH at which the particle surface carries zero net electrical charge. The surface charge of montmorillonite is mainly stemmed from the edge surfaces and from the structural charge sites. The structural charge sites, which usually represent the regular sorption sites that locate on the basal plane (regular plane) of the mmt particles, are the permanent negative charges due to isomorphous substitutions taking place in the

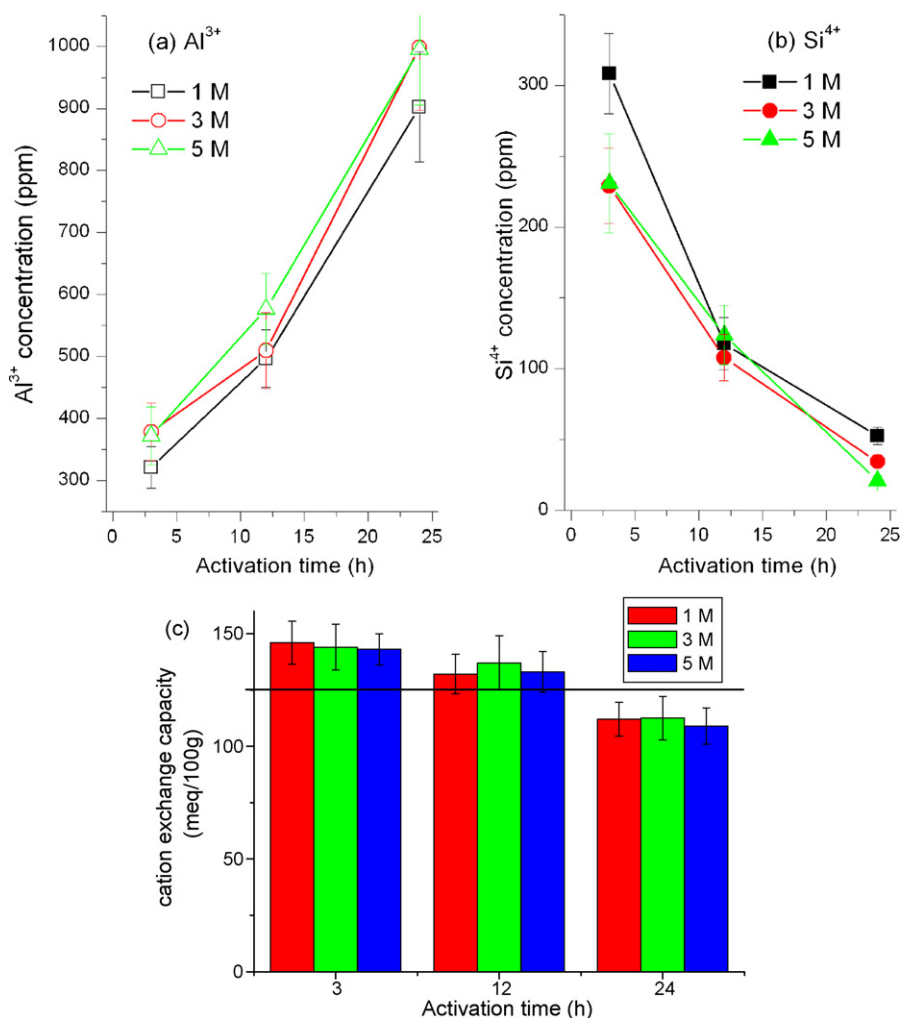


Fig. 7. The amount of leached Al^{3+} (a) and Si^{4+} (b) during the phosphoric acid activation and (c) the cation exchange capacity of these PAMmt particles.

tetrahedral layers (Si^{4+} substituted by Al^{3+}) and in the octahedral layers (Al^{3+} substituted by either Mg^{2+} or Fe^{2+}); whereas the edge surface charge comes from the proton adsorption at the hydroxyl groups ($-\text{Si}-\text{OH}$ at tetrahedral layers, $-\text{Al}-\text{OH}_2$ at octahedral layers) [15]. Generally speaking, proton uptake on the structural charge sites happens generally under low pH and low ionic strength environments via cation exchange reactions and consequently the resultant potentiometric titration is reasonably contributed by the edge surface sites [16].

For mmt particles with 3 h of activation the isoelectric point appears at pH 2.3–2.5, which is close to the isoelectric point of SiO_2 (pH < 4) [15]. When the pH exceeds the isoelectric point the PAMmt particles carry the net negative charge, which provides a favorable environment for adsorbing the positively charged Cs ions as indicated by Fig. 3. Except those PAMmt samples with 3 h of activation, the rest of PAMmt samples show similar pH_0 to those of the starting mmt particles (the inserted panel of Fig. 6). This reveals that higher selectivity of PAMmt particles (with activation more than 3 h) is accounted to the larger surface areas. That is, although these PAMmt particles exhibit similar surface charge densities to those of the starting mmt particles, their larger surface areas provide more available sorption sites for Cs ions and thus they perform higher sorption selectivity toward Cs ions even in highest saline solutions (3 wt.% of K^+ solutions). In addition to the variation occurs at the edge surface sites, their structural charge sites would also be altered during the acid activation at the same time [17]. The

variation in structural charge sites would not directly affect the proton uptake behavior at the edge surface sites but will possibly cause the spillover of their electric double layer to the hidden electric double layer at the edges [15]. This would consequently redistribute the charge density at the edge sites, however, it is difficult to observe in our potentiometric titrations because in this work, experiments were performed with background electrolyte for only one concentration. In other words, the potentiometric titrations were conducted for only a single salinity (0.1 M NaCl). However, differences in structural charge sites (the variation on the regular plane) could be revealed by further surface and structural analyses such as chemical analysis results, XRD and IR spectra stated in the next paragraph.

3.3. The structural properties of the acid activated montmorillonite

As mentioned above, structural charge sites were altered during the acid activation. One substantial evidence is that the amount of leached Al^{3+} increases from approximately 300–400 ppm after 3 h of activation to circa 850–1000 ppm after 24 h of activation (Fig. 7a), whereas the aqueous Si^{4+} gradually decreases from 220–320 ppm (3 h) to less than 50 ppm after 24 h of activation (Fig. 7b). This corresponds to the variation in the specific surface areas where the unoccupied sites after the leaching of tetrahedral Al^{3+} ions that increases the specific surface areas of these PAMmt particles are

preserved. With the progress of activation, the decomposition of crystal structure takes place at these locations, leading to a drop in specific surface area [3]. The decomposition is accompanied with the precipitation of SiO_2 species at the mouth of the lamellae. It not only impedes the clay structure to further H^+ attack but also induces the transformation in porosity as indicated by N_2 -BET measurement [18]. Despite the significant leaching of Al^{3+} from mmt particles and the precipitating of Si^{4+} from acid solutions along with the activation time, only the PAMmt samples with 24 h of activation show a lower cation exchange capacity (CEC). The rest PAMmt particles have a relatively higher CEC compared to the starting mmt particles (the straight line in Fig. 7c). This might be related to the entity that phosphoric acid is not a strong acid source as sulfuric acid or hydrochloric acid is. It has been reported that activation by using strong sulfuric acid the silicon and aluminum atoms were significantly removed from mmt lattice and then to be physisorbed or dispersed in the interstices of clay lattice, while treating with HCl led to a mild digestion on mmt structure [10]. This explains why the phosphoric acid, which is a relatively weak acid source, would only modify the mmt structure to a less level than the strong acid sources do. Accordingly, a relatively minor variation in the CEC value was observed. Furthermore, the precipitating Si^{4+} as indicated in Fig. 7b passivates the mmt particles resisting against further acid attack. This enables the PAMmt samples to keep the lattice structure as intact as their parent particles do [18]. Effect of passivation might also be also related to the different findings in our observations of surface charge density (Fig. 6). That is, passivation suppresses further H^+ attack on mmt surface and thus limits the surface charge density change with the activation time.

In addition to chemical analysis results, the XRD and FTIR analyses also provide substantial evidences on the structural variation. Herein, the PAMmt particles refluxed with 1 M of phosphoric acid solutions is taken as an example of all similar XRD and FTIR patterns observed. It is noted that PAMmt samples keep the same lattice structures as the original mmt particles do but the intensity of the diffraction peaks is proportionally reduced with the increase of activation time (Fig. 8a). This indicates that the H^+ exchange procedure in phosphoric acid does not significantly alter the lattice structure of montmorillonite materials in comparison with those under sulfuric acid or other superacid conditions [10]. In the case of 24 h activation, the A1_24h samples show very blurred diffraction peaks, and in particular the (100) diffraction peak is almost invisible compared to other mmt/PAMmt particles. The (100) plane is one of the crystalline planes that contribute to the edge plane of mmt particles [16]. Accordingly, the relative disappearance of the (100) diffraction peak indicates that H^+ attacks preferentially on the edge surface than on the regular plane surface during activation. The protonated edge surface is then gradually dissolved after the H^+ attack, leaving a destructed edge surface corresponding to a blurred diffraction peak shown in XRD patterns. Meanwhile, a hump appears between 9.0° and 17.5° (2θ) in the XRD pattern of A1_24h samples, which might result from the precipitation of porous silica amorphous phase [2].

Other substantial evidences are presented in FTIR spectra shown in Fig. 8b. Obviously, signals of PAMmt samples at 532 and 918 cm^{-1} disappear and that at 1035 cm^{-1} shift to 1100 cm^{-1} after acid activation in comparison with those of the original mmt samples; while signals at 471 and 801 cm^{-1} seem unaffected by the acid activation. Since signal at 532 cm^{-1} is resulted from Si–O–Al bending and the one at 918 cm^{-1} represents Al–Al–OH bending in the octahedral layers [6], the disappearance of these two signals directly indicates that the octahedral layer is significantly modified. This corresponds to the continuous dissolution of Al^{3+} during the acid activation (Fig. 7a). At the same time, the tetrahedral Si-bearing species are also affected since the Si–O vibrations (1035 cm^{-1}) disappeared. Simultaneously, the Si-bearing species are transformed into amor-

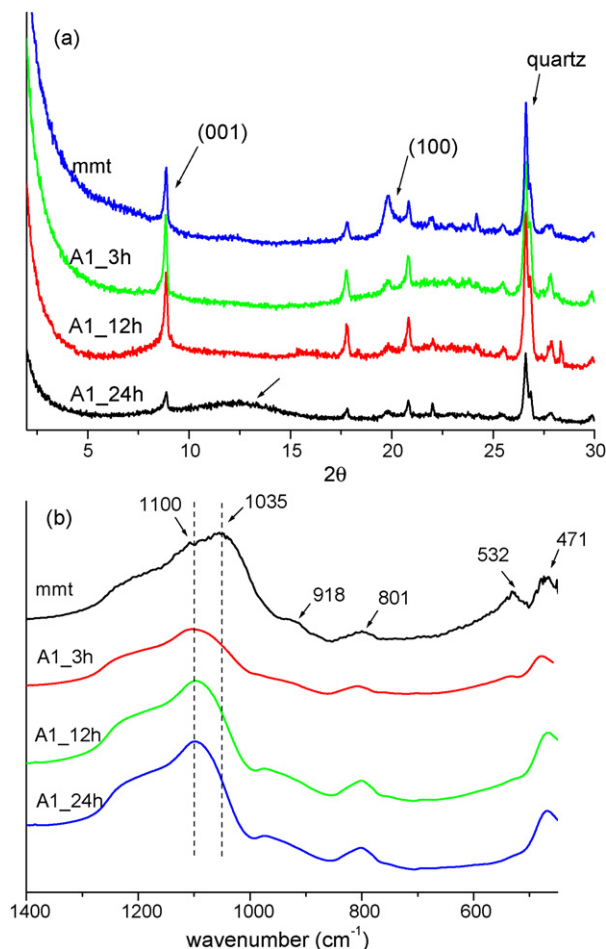


Fig. 8. The XRD (a); and FTIR (b) of original and phosphoric acid activated montmorillonite.

phous silica with three-dimensional framework as suggested by the emergence of IR signal at 1100 cm^{-1} , which is consistent with the Si precipitation observed in Fig. 7a.

It was reported that during acid attack, the octahedral Al^{3+} ions are preferentially released from the clay structure, leading to the formation of additional Al–OH and Si–OH bonds without changing significantly the original mineral structure [6]. At the same time, the relatively large decrease in the intensity of the basal (001) peak together with the partial conservation of the other reflections in XRD patterns indicate a loss of periodicity along the c direction, probably due to a partial delamination of clay structure [2]. Accordingly, the mechanism behind the acid activation on mmt particles should follow the proposed pathway as shown in Fig. 9. When contacted with acid solutions, the cations (Na^+ in this case), which compensate the negatively charged surface of mmt particles, are gradually replaced by the abundant H^+ in solutions. The octahedral Al–OH groups are simultaneously protonated especially those situated at edge surface of the mmt particle. These protonated Al–OH $_2^+$ groups are highly unstable, resulting in the dissolution of octahedral Al^{3+} . This is evidenced by the increase of Al^{3+} concentration in phosphoric acid solutions (Fig. 7a) and the disappearance of Si–O–Al and Al–Al–OH bending in FTIR spectra (Fig. 8b). The vacancy of released octahedral Al^{3+} grants H^+ access to attack further Al species located deeper in mmt particles. Then, the surface porosity is modified by creating more micro/meso pores, which is accounted for the greater surface area of acid activated clay particles (Fig. 4). Greater surface area implies more available sorption sites and hence it leads the way to the higher sorption

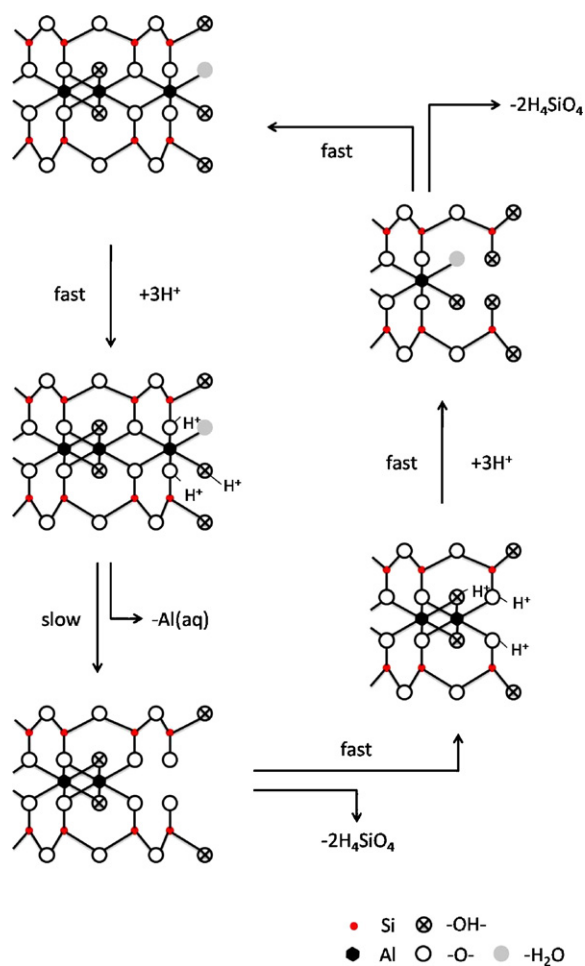


Fig. 9. The scheme of activation mechanism.

capacity as well as better sorption selectivity (Fig. 3). The extent of the dissolution of octahedral Al³⁺ depends mainly on the strength of acid applied. That is, using the superacid solution would produce a completely disruptive clay structure while treated with mild acid solution such as phosphoric acid in this study could produce activated particles that still conserve the lattice structure of the starting materials [2,10]. Some Si⁴⁺ ions would also be released during the acid activation but they would eventually precipitate as three-dimensional amorphous silica (Fig. 8b), which passivate the reactivity of activated particles against further H⁺ attack [18]. This accounts for the observation that the increased surface area of acid activated mmt particles does not proportionally respond to the concentration of acid solution and the activation time. Most importantly, by using phosphoric acid the lattice structure of PAmmt samples are relatively intact. This implies that less colloid due to the ablation at the surface of activated particles would be produced. Therefore, it greatly reduces the occurrence of colloidal transport when these materials are used in the radioactive waste repository.

4. Conclusion

In this study, montmorillonite K-10 (mmt) was subjected to acid treatment by using phosphoric acid to obtain phosphoric acid activated mmt (PAmmt) samples. The performance of PAmmt samples was evaluated by Cs isotherm experiments. Our results showed that very limited suspension solids were produced during Cs sorption experiments. Also, PAmmt samples possess a high sorption

capacity together with high sorption selectivity. These promising properties demonstrate their prospective application to radioactive waste repository sites. During the acid activation, the octahedral Al³⁺ of mmt is preferentially released. Then, the vacancy of Al³⁺ sites will suffer further H⁺ attack and lead to the porous surface of mmt particles. Followed by redistribution of tetrahedral Si species and precipitation of partially dissolved Si⁴⁺, the acid activation produces a greater surface area of PAmmt samples, which is accounted for the higher sorption capacity and selectivity. Although some octahedral layer has been modified as indicated by the disappearance of Al-bearing vibration modes in FTIR spectra, the lattice structure of PAmmt remained relatively undamaged based on the XRD observations. This manner explained the low suspension solid produced during the sorption experiments. Based upon our results acid activation procedure with 3 M of phosphoric acid and 3 h of reflux was recommended to prepare PAmmt samples for the buffer materials in radioactive waste repository.

Acknowledgement

The authors are grateful to National Science Council of the Republic of China (NSC 97-2221-E-007-006-MY3) for supporting this study.

References

- [1] G. Kakali, T. Perraki, S. Tsivilis, E. Badogiannis, Thermal treatment of kalin: the effect of mineralogy on the pozzalanic activity, *Appl. Clay Sci.* 20 (2001) 73–80.
- [2] C. Bisio, G. Gatti, E. Boccaleri, L. Marchese, L. Bertinetti, S. Coluccia, On the acidity of saponite materials: a combined HRTEM, FTIR, and solid-state NMR study, *Langmuir* 24 (2008) 2808–2819.
- [3] H. Babaki, A. Salem, A. Jafarizad, Kinetic model for the isothermal activation of bentonite by sulfuric acid, *Mater. Chem. Phys.* 108 (2008) 263–268.
- [4] P.J. Wallis, W.P. Gates, A.F. Patti, J.L. Scott, E. Teoh, Assessing and improving the catalytic activity of K-10 montmorillonite, *Green Chem.* 9 (2007) 980–986.
- [5] P. Liu, L.-X. Zhang, Adsorption of dyes from aqueous solutions or suspensions with clay nano-adsorbents, *Sep. Purif. Technol.* 58 (2007) 32–39.
- [6] K.G. Bhattacharyya, S. Sen Gupta, Influence of acid activation of kaolinite and montmorillonite on adsorptive removal of Cd(II) from water, *Ind. Eng. Chem. Res.* 46 (2007) 3734–3742.
- [7] I. Chaari, E. Fakhfakh, K. Chakroun, J. Bouzid, N. Boujelben, M. Feki, F. Rocha, F. Jamoussi, Lead removal from aqueous solution by a Tunisian smectitic clay, *J. Hazard. Mater.* 156 (2008) 545–551.
- [8] K.G. Bhattacharyya, S. Sen Gupta, Influence of acid activation on adsorption of kaolinite and montmorillonite: kinetic and thermodynamic study, *Chem. Eng. J.* 136 (2008) 1–13.
- [9] X.-L. Guo, Y.-D. Yao, G.-F. Yin, Y.-Q. Kang, Y. Luo, L. Zhuo, Preparation of decolorizing ceramics for printing and dyeing wastewater with acid and base treated clay, *Appl. Clay Sci.* 40 (2008) 20–26.
- [10] Y.M.V. Rodriguez, H.I. Beltran, E. Vazquez-Labastida, C. Linares-Lopez, M. Salmon, Synthesis and characterization of montmorillonite clays with modifiable porosity induced with acids and superacids, *J. Mater. Res.* 22 (2007) 788–800.
- [11] A. Delos, C. Walther, T. Schafer, S. Buchner, Size dispersion and colloid mediated radionuclide transport in a synthetic porous media, *J. Colloid Interface Sci.* 324 (2008) 212–215.
- [12] D. Karamanis, P.A. Assimakopoulos, Efficiency of aluminum-pillared montmorillonite on the removal of cesium and copper from aqueous solutions, *Water Res.* 41 (2007) 1897–1906.
- [13] J.M. Zachara, S.C. Smith, C.-X. Liu, J.P. McKinley, R.J. Serne, P.L. Gassman, Sorption of Cs+ to micaceous subsurface sediments from the Hanford site USA, *Geochim. Cosmochim. Acta* 66 (2002) 193–211.
- [14] F. Rouquerol, J. Rouquerol, K.S.W. Sing, *Adsorption by Powders and Porous Solids: Principles, Methodology and Applications*, Academic Press, 1999.
- [15] E. Tombacz, M. Szekers, Colloidal behavior of aqueous montmorillonite suspensions: the specific role of pH in the presence of indifferent electrolytes, *Appl. Clay Sci.* 27 (2004) 75–94.
- [16] I.C. Bourg, G. Sposito, A.C.M. Bourg, Modeling the acid-base surface chemistry of montmorillonite, *J. Colloid Interface Sci.* 312 (2007) 297–310.
- [17] E. Eren, B. Afsin, An investigation of Cu(II) adsorption by raw and acid-activated bentonite: a combined potentiometric, thermodynamic, XRD, IR, DTA study, *J. Hazard. Mater.* 151 (2008) 682–691.
- [18] C. Pesquera, F. Gonzalez, I. Benito, C. Blanco, S. Mendioroz, J. Pajares, Passivation of a montmorillonite by the silica created in acid activation, *J. Mater. Chem.* 2 (1992) 907–911.