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Importance of the Hydration Degree in the Use of Clay−Fungal Biocomposites as Adsorbents for Uranium Uptake

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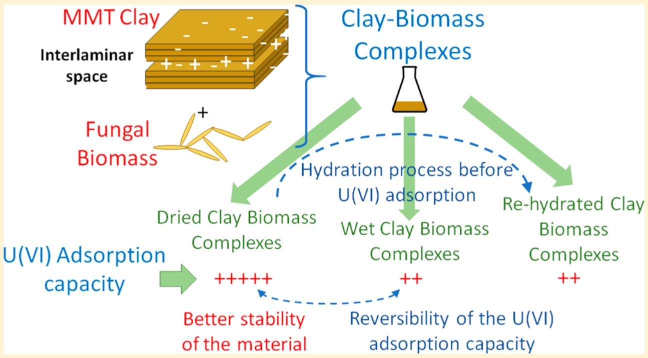
Supporting Information



ABSTRACT: The development of new adsorbent materials is a key factor for applying sorption-based technologies designed to clean effluents. Clay biomass complexes (BMMT) from fungal biomass grown on a raw montmorillonite (MMT) were generated in a previous work and used in a wet state. These samples were examined previously as a material to retain metals and improve separation after adsorption processes. The objective of this study was to characterize the uranium(VI) adsorption of previously dried BMMT, to determine differences from wet BMMT samples, and to understand some of the processes responsible for those differences. The differences between dried and wet BMMT adsorption capacities were verified. Proton exchange of dried BMMT samples was analyzed. Furthermore, X-ray diffraction and ζ-potential measurements of the samples after uranium(VI) uptake were performed. The hydration degree during the adsorption contact time was evaluated. Contact-angle measurement and diffusion experiments by Fourier transform infrared spectroscopy were also conducted. Dried BMMT samples presented a higher uranium(VI) uptake capacity than wet BMMT samples. Biomass played an important role in the behavior of samples evaluated, and the results indicated the importance to specify the hydration degree of adsorbents.

■ INTRODUCTION

Typically, conventional remediation techniques for metal-contaminated water are not suitable because of the large volumes and high costs involved in treating these effluents. Adsorption/sorption using adsorbents of different nature is an efficient technique developed for these effluents, with the advantages of specific affinity, low cost, and simple design, that has been widely used over the years.[1−8] New adsorbent materials and improvement of the adsorption technique are still in continuous development and discussion.[6−8] For our interest, the adsorption of uranium(VI) from model aqueous solutions using biopolymer-based materials,[9−11] biomass,[1,12,13] and minerals[14,15] or mixtures of the latter two,[16] has also been extensively studied. Independent of the adsorbent used, for the development of a process at a greater scale, basic knowledge about the process and parameters affecting sorbate uptake is necessary.

In our former study,[17] we characterized the adsorption of uranium(VI) on matrixes of montmorillonite (MMT) and/or fungal biomass. These matrixes were generated by the growth of fungal biomass over a natural MMT. Such generated samples (clay with fungi) were labeled as BMMTs. BMMTs have some advantages compared to MMT and biomass separately. Especially, improved coagulation properties were found that favor the subsequent separation of the loaded adsorbent from the solution. That study was conducted on samples retained directly from the raw wet matrix without any drying process involved.

However, for handling these samples in technological implementation, in batch and continuous processes, the degree of drying and stability of the matrix are of great importance.

Despite the large number of studies on biosorption, the influence of the hydration state of the matrix before adsorption experiments usually was not evaluated. The authors did an extensive literature survey on heavy-metal adsorption. Over 150

Received: December 22, 2016
Revised: February 17, 2017
Accepted: February 28, 2017
Published: February 28, 2017

DOI: 10.1021/acs.iecr.6b04881
Ind. Eng. Chem. Res. 2017, 56, 2824−2833

adsorption research papers were surveyed (for references, see the Supporting Information), and in most of the studies on adsorption, the description of the experiments did not point out the use of a particular hydration state or the type of drying of the adsorbents. In 129 research papers, authors specified whether the adsorbent was used in dead, alive, or dried form. Among all of the surveyed researches, only 12 papers pointed out having observed differences between dried and hydrated materials used for adsorption and barely discussed the physicochemical phenomena responsible for the reported differences. The state of the adsorbent was not specified in the other nine researches.

As examples, Zhang et al.[18] and Dardenne et al.[19] evaluated the adsorbent hydration degree in the case of minerals or inorganic adsorbents. Zhang et al. studied the effect of the water content on the separation of CO_2/CH_4 with active carbon by an adsorption−hydration hybrid method. They reported that the use of active carbon with different hydration degrees allowed to obtain a CO_2/CH_4 separation with a hybrid method for high water contents was more efficient than the single adsorption method.[18] For the adsorption of lutetium(III), Dardenne et al.[19] indicated that species adsorbed onto ferrihydrite had been characterized and no evidence for surface precipitation or noticeable differences between wet paste and dried powder samples were found.

In the case of the biosorption of metals, some studies described the hydration degree of the biomass used. In a study using algae biomass for chromium(III) and nickel(II) adsorption, the use of dried biomass was specified, but the results from dried biomass were not compared with those for fresh biomass.[20] An interesting comparison was conducted by Solisio et al.,[21] evaluating the copper adsorption capacity of dry and rehydrated biomasses of *Spirulina platensis*, in which they found that the rehydrated biomass presented a higher copper adsorption capacity than the dried biomass.

Gargarello et al.[22] studied uranium(VI) adsorption on a dried fungal biomass and indicated that there were differences in the uranium(VI) adsorption capacities of dried and fresh fungal biomasses. A fungal biomass of *Trichoderma* sp. was also tested, although for the treatment of contaminated groundwater. Again, it was found that dried *Trichoderma* sp. demonstrated higher extraction of cadmium(II), nickel(II), and chromium(III) ions compared to wet *Trichoderma* sp. biomass.[23] However, the nature of those differences was not explained.

In summary, the results show that adsorption is influenced by a lot of factors such as the solute concentration, pH, temperature, and ionic strength but also by the hydration state of the adsorbent. The contact time between the adsorbent and sorbate is of great interest as well (see the references in the Supporting Information), but there is very little information regarding the achievement of the equilibrium state between the sorbate and sorbent. The mentioned factors can also influence parameters like the kinetics or the diffusion of molecules through the adsorbent. Kinetic models are commonly used to identify the possible mechanisms of biosorption processes, and the diffusive solute flux of anions and cations can give information about interface properties, electrostatic interactions in the diffuse double layer at adsorbent surfaces, and interactions in the clay−water-diffusing solute system.[24]

As was stated above, in our previous work, wet BMMTs were generated, characterized, and used for uranium(VI) adsorption.[17] Complexes were defined as “wet BMMT” when they were used directly after being centrifuged and rinsed with water, without any drying step in between. Furthermore, the study of some of their structural properties such as the ζ potential, interlayer spacing, and proton-exchange capacity indicated that clay−biomass complexes have a unique structure that is not the sum of the individual component properties.[17] However, wet BMMT samples have the disadvantage that they cannot be stored for long periods of time. To complete that previous study, some additional adsorption experiments using dried matrixes were conducted and indicated that handling a previously dried BMMT could be much more convenient and efficient for the development of biofilters at a greater scale. For these reasons, it is important to evaluate the differences in the adsorption capacities and material stability of adsorbents, depending on their hydration state, especially for relating this to processes applied at larger scales.

The aim of the present study is to evaluate and characterize the uranium(VI) adsorption using previously dried BMMTs to determine differences from wet BMMT adsorption and to understand some of the processes responsible for the detected differences. To achieve these objectives, structural characterizations by X-ray diffraction (XRD), ζ potential, apparent particle diameter, and proton-exchange capacity of dried BMMTs were performed. Furthermore, uranyl diffusion by attenuated-total-reflectance (ATR) Fourier transform infrared spectroscopy (FTIR) experiments and hydration degree assays were conducted, and the wettability in terms of the contact angle (CA) was characterized.

■ MATERIALS AND METHODS

Biomass−Clay Samples. Biomass−clay samples were synthesized using a montmorillonite (MMT) (sodium montmorillonite) from Rio Negro, Argentina,[25,26] as the mineral support and two different fungal genuses as biomasses:[17] *Aphanocladium* sp. (*Apha* sp.) and *Acremonium* sp. (*Acre* sp.). To generate the samples, the biomass was grown axenically in batch cultures for 5 days, on the MMT in the presence of the culture medium P5 [P5 composition: 1.28 g/L K_2HPO_4; 3 g/L $(NH_4)_2SO_4$; 0.25 g/L $MgSO_4 \cdot 7H_2O$; 10 g/L glucose; 0.1 g/L thiamine; 1% (v/v) cation solution; 1% (v/v) anion solution]. To synthesize the different matrixes, batch cultures contained 1% (w/v) or 5% (w/v) MMT clay and the same amount of initial inocula (pH 5.5, 25 °C).

The following BMMTs and controls were obtained: 1% BMMT(*Apha* sp.), 1% BMMT(*Acre* sp.), 5% BMMT(*Apha* sp.), 5% BMMT(*Acre* sp.), 1% MMT(P5), or 5% MMT(P5). The sample MMT(P5) is the result of incubating the culture medium with MMT without any fungal inoculum, under the same conditions as those of the cultures that contain the fungal inoculum.

The generated BMMTs and controls were recovered by centrifugation (20 min, 2200*g*, 4 °C) and rinsed twice with deionized water.[17] Samples for this study were used in a dried form. For drying of the samples, they were placed in an oven at 60 °C for 24 h, or until a constant weight was reached.

Adsorption Experiments. Adsorption experiments were carried out using uranyl nitrate [analytical grade $UO_2(NO_3)_2$] solutions at pH 3.6. The pH was maintained constant during the adsorption process to keep uranyl in the uranium(VI) state during the experiment. Equilibrium assays for dried BMMTs and controls were performed in order to establish the equilibrium time for the isotherms: BMMT samples (0.01 g), in contact with a 0.21 mM (50 ppm) uranium(VI) solution, were shaken up to 72 h, and samples for uranium quantification in the solution by Arsenaze(III)[27] were taken at different times. The equilibration time was determined to be 3 h (data not shown). Dried BMMT adsorption isotherms were carried out using uranyl nitrate solutions at pH 3.6 containing 0.04, 0.1, 0.21, 0.42, 0.63, 0.84, and 1.05 mM uranium(VI), respectively. The experiments were carried out three times as independent experiments, and each isotherm concentration had four replicates. Biopolymer samples were shaken (0.01 g) in polypropylene tubes with 10 mL aliquots of each solution. After equilibration (3 h), the metal adsorbed (Q) was calculated by the difference between the initial concentration and that of the supernatant in equilibrium. All uranium(VI) adsorption results were expressed in grams of dried sorbent. Q data for wet BMMT in the previous work[17] were also expressed in grams of dried sorbent. After adsorption, BMMT solids were recovered by centrifugation, and pellets with uranium adsorbed were reserved for XRD and ζ-potential analysis.

For the adsorption reversibility studies, adsorption isotherms using rehydrated samples (detailed in the BMMT Hydration Assays part of the Materials and Methods section) were performed. For those samples, the addition and amount of uranyl nitrate solutions, the isotherm data analysis, and the detection of uranium were carried out as described above for the dried BMMT adsorption isotherms.

Characterization Methods. The different samples collected from the dried BMMT adsorption isotherms, and samples without uranium(VI) adsorbed, were analyzed by XRD, electrophoretic mobility, and apparent particle diameter (D_{app}), under the same conditions as those of the wet BMMT samples.[17] Methods are described below in detail.

XRD was performed on oriented samples, prepared by spreading the sample suspension on glass slides, and dried at room temperature overnight with relative humidity control (rh = 0.47) to allow an accurate peak analysis. Analyses were performed using a Philips PW 1710 diffractometer (Madison, WI) with Cu Kα radiation at 40 kV and 30 mA, 1° divergence and detector slits, 0.02° (2θ) step size, counting time 10 s/step, and patterns collected from 3° to 14° (2θ). The d(001) reflection peaks from U-BMMT were decomposed using the *Origin Pro 7.0* software (fitting the wizard method) using Gaussian functions. The fit quality was controlled by the R^2 value (>0.98).

The ζ potential and apparent particle diameter were determined with a Brookhaven 90 Plus/Bi-MAS equipment (New York, NY), in the respective mode, operating at $\lambda = 635$ nm, 15 mW solid-state laser, scattering angle 90°, and temperature 25 °C and using 10^{-3} M KCl as an inert electrolyte.

BMMT Hydration Assays. BMMT samples (0.01 g) were shaken for 3 h [equilibrium time for uranium(VI) adsorption] or 24 h (to determine differences at longer hydration times) in polypropylene tubes with 10 mL of deionized water. After the hydration time, each tube was centrifuged (2200g, 10 min). Solid samples were weighted before and after drying and dried at 60 °C until a constant weight, and the percentages of water content were calculated by weight differences.

Hydrated Samples. BMMT samples (0.01 g) were shaken for 3 h (according to the previous equilibrium assays) in polypropylene tubes with 10 mL of deionized water. After the hydration time (3 h), each tube was centrifuged (5000g, 10 min), the water was discarded, and the pellets were used for the reversibility studies detailed in the Adsorption Experiments part of the Materials and Methods section.

Biomass Content. The content of organic matter was determined by the weight difference before and after thermal treatment of the samples at 600 °C for 3 h. All BMMT samples used for wet or dried BMMT experiments were analyzed. Both dried and wet BMMTs were dried at 60 °C until constant weight before thermal treatment. For dried and wet BMMTs, the values of the biomass content are expressed as dried biomass per gram of dried BMMTs after water elimination.

Total Proton Exchange. The total proton exchange was determined on suspensions of 0.13% (w/v) of each sample by potentiometric titrations.[17] The amount of 0.02 M HNO_3 consumed by the suspension to reach pH 2.8 was determined. The experiments were performed in duplicate.

Wettability and Apparent Diffusion Experiments. The wettability was determined by CA measurement with the sessile drop method, using a charge-coupled device equipped a contact-angle microscope (OCA 15, DataPhysics, Filderstadt, Germany) as described in detail by Goebel et al.[28] The sample was fixed on a glass slide with double-sided adhesive tape as ideally a one-grain layer by sprinkling and pressing. Placement of a drop of water was recorded by the video camera and the initial CA (33 ms after placement) evaluated by automated drop-shape analysis (ellipsoidal fit) and the fitting of two tangents on the left and right sides of the drop using the software *SCA20* (Data Physics, Filderstadt, Germany). The CA is given as the mean of the left and right sides of the drop. Per sample, at least six drops were placed.

Through diffusion experiments, the following samples were performed: dried 1% BMMT(*Apha* sp.) and rehydrated 1% BMMT(*Apha* sp.) as described in detail by Schampera and Dultz.[29]

The experiments were conducted in a diffusion cell attached on top of a single-reflection ATR unit (MIRacle, PIKE Technologies, Madison, WI) of a FTIR spectrometer (TENSOR 27, Bruker, Karlsruhe, Germany) with a resolution of 4 cm^{-1}. For each uranyl nitrate [25 ppm uranium(VI) → D_2O] experiment, 10 mg of D_2O-saturated samples was compacted to 1 mm height in a Teflon cylinder with an inner diameter of 2.5 mm. The diffusion coefficients were calculated from the temporal evolution of measured peaks using the spectroscopic range 930−670 cm^{-1} corresponding to the $\nu_{\mathrm{as}+\nu s}$ O−U−O stretching−vibration.[30] Details regarding the experimental setting and calculations of the diffusion coefficients are described by Schampera and Dultz[29] and additional details of the adsorption influence on the apparent diffusion by Schampera et al.[24]

Intraparticle Diffusion. For determination of the intraparticle diffusion coefficient, kinetic experiments were performed using wet and dried 1% BMMT(*Apha* sp.). BMMT samples (0.01 g), in contact with a 50 ppm uranium(VI) solution, were shaken up to 4.5 h (longer than the adsorption equilibrium time, in order to include a longer time interval), and samples for uranium quantification[27] were taken at different times (every 10 min up to minute 30; every 15 min up to minute 120; every 30 min up to minute 270). Intraparticle diffusion modeling was performed following the model described by Srivastava et al.,[31] where adsorption data (Q) over time (t) can be plotted as in eq 1. K_{id} is the coefficient of intraparticle diffusion rate, and c is related to the thickness of the boundary layer.

$$Q_t = K_{\mathrm{id}} t^{1/2} + c \qquad (1)$$

DOI: 10.1021/acs.iecr.6b04881
Ind. Eng. Chem. Res. 2017, 56, 2824−2833

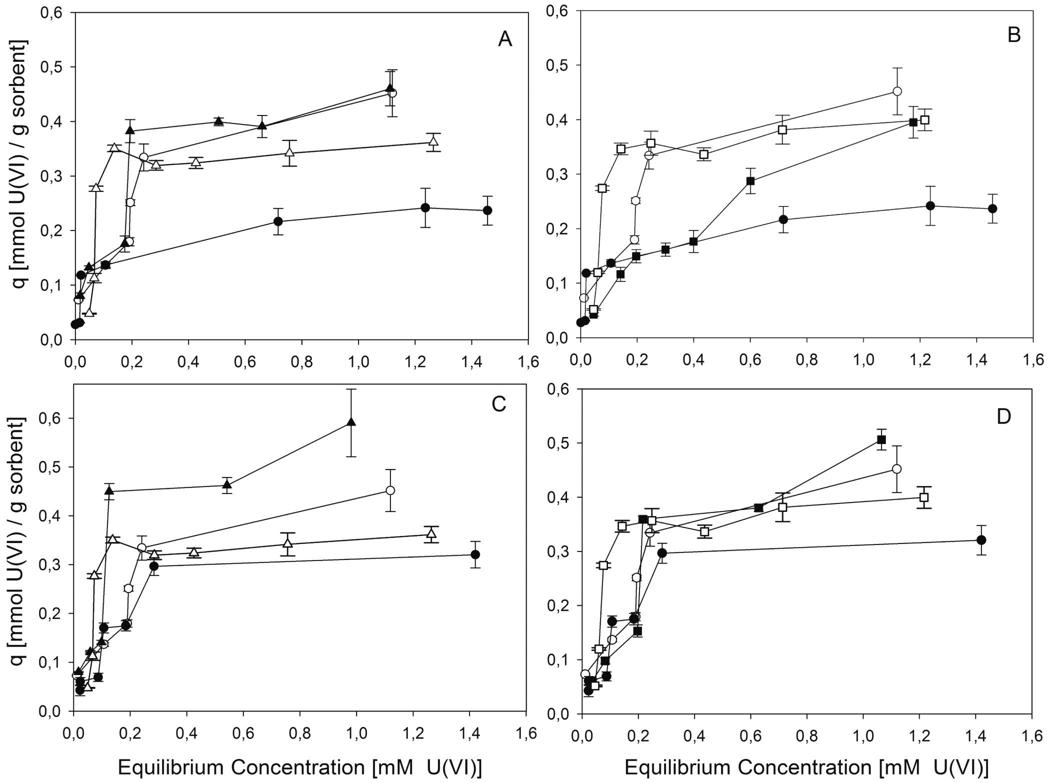


Figure 1. Adsorption isotherms of uranium(VI) on dried BMMTs and the respective controls: (A and B) BMMTs in 1% (w/v); (C and D) BMMTs in 5% (w/v). Symbols: (○) MMT; (●) MMT(P5); (▲) BMM (*Apha* sp.); (△) *Apha* sp.; (■) BMMT(*Acre* sp.); (□), *Acre* sp.

Table 1. Maximum Adsorption Capacity (Q_{max}) of Dried (Q_{dried}) and Wet (Q_{wet}) BMMTs, Biomass Content of Dried and Wet BMMTs, and Total Proton Exchange of Samples

sample	Q_{dried}[a] (mmol/g)	Q_{wet}[a] (mmol/g)	ratio Q_{dried}/Q_{wet}	dried BMMT biomass content (mg of biomass/g of BMMT)	wet BMMT biomass content (mg of biomass/g of BMMT)	total proton exchange (H^+_{dried}/H^+_{wet})	ratio H^+/ratio Q_{max}
1% BMMT(*Apha* sp.)	0.42 ± 0.03	0.18 ± 0.02	2.3	283 ± 12	257 ± 14	4.81	2.09
1% BMMT(*Acre* sp.)	0.41 ± 0.03	0.28 ± 0.02	1.5	252 ± 15	237 ± 12	4.43	2.95
5% BMMT(*Apha* sp.)	0.53 ± 0.07	0.21 ± 0.02	2.5	63 ± 5	73 ± 3	4.80	1.92
5% BMMT(*Acre* sp.)	0.44 ± 0.02	0.22 ± 0.01	2.0	71 ± 6	57 ± 8	4.43	2.22
1% MMT(P5)	0.24 ± 0.03	0.17 ± 0.01	1.4			0.87	0.62
5% MMT(P5)	0.32 ± 0.01	0.18 ± 0.01	1.8			0.97	0.54
MMT	0.46 ± 0.05	0.18 ± 0.02	2.5			1.35	0.54
Acre sp.	0.36 ± 0.02	0.05 ± 0.01	6.8			8.44	1.24
Apha sp.	0.34 ± 0.02	0.05 ± 0.01	7.2			7.03	0.98

[a] Results are expressed as mmol of uranium(VI) adsorbed per gram of dried sorbent. In the case of wet BMMT, values are normalized to the amount of dry sorbent contained in 0.1 g of wet BMMT.

■ RESULTS AND DISCUSSION

Hydration Degree. The water content in wet samples varied between about 70 and 90% (data are shown in Table S1 in the Supporting Information). This value represents the difference between wet and dry samples. The water content in dry samples is very low (<1%) and was considered negligible compared to wet samples.

Uranium Uptake by Dried Matrixes. Figure 1 presents uranium(VI) adsorption isotherms using dried MMT, MMT-(P5), and BMMT samples. All dried BMMT isotherms presented a higher maximum adsorption capacity (Q_{max}) than those found for wet BMMTs in a previous work (Table 1). These dried BMMT adsorption values were similar to the uranium adsorption capacities found for other biosorbents.[13,32] Furthermore, for instance, proton exchange for dried samples was higher than that found for wet material. These differences and other results of both types of samples will be discussed further in this work.

The adsorption behavior of dried BMMTs (Figure 1) with respect to the controls [MMT and MMT(P5)] was similar to that found for wet BMMTs.[17] As reported before for the wet BMMT isotherms, dried BMMTs as well presented sigmoidal-

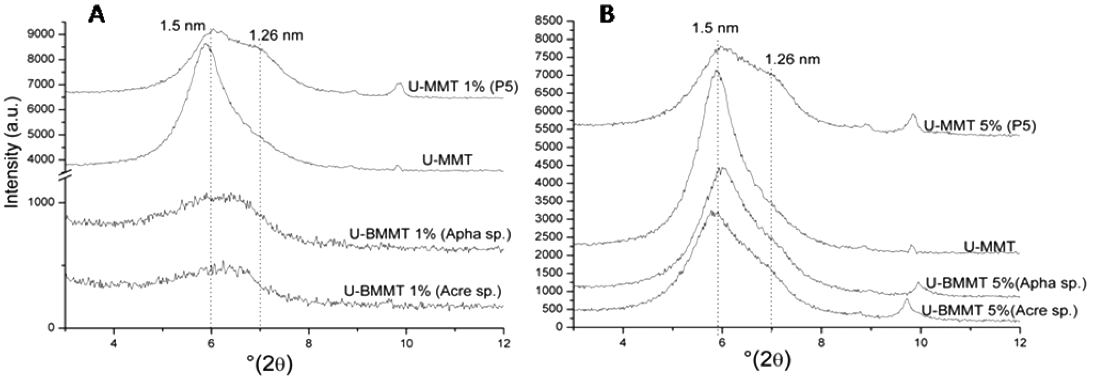


Figure 2. XRD patterns of BMMT dried samples with Uranium adsorbed: (A) 1% BMMT; (B) 5% BMMT.

shaped isotherms. The fitting parameters of the sigmoidal and Langmuir models are resumed in Table S2 (Supporting Information). These parameters were used to obtain the maximum adsorption values (Q_{max}) for dried BMMTs to be compared to those obtained for wet BMMTs.[17]

Comparison of Uranium(VI) Adsorption by Wet and Dried BMMT Samples. The uranium(VI) adsorption capacities from previously dried BMMT and BMMT samples without any drying step (wet BMMTs) are compared in Table 1.

Table 1 indicates Q_{max} for both wet and dried materials and their respective contents of biomass. The Q_{max} value for dried samples was higher than that for wet samples in all cases.

The Q_{max} value for dried BMMT samples increased about 2 times compared to that for wet samples. The increase in maximum adsorption compared to a single biomass was even 6−8 times higher. The Q_{max} increase of dried MMT with respect to wet MMT was only 2.5 times, and that of dried MMT (P5) compared to wet MMT(P5) was around 1.5 times (Table 1).

Despite the high values obtained for the Q_{dry}/Q_{wet} ratio for dried/wet biomass ($a \sim 7$), the Q_{dry}/Q_{wet} ratios of BMMTs were similar to those obtained for the MMT samples ($a \sim 2$). This evidence indicated that the presence of biomass was not affecting the Q_{dry}/Q_{wet} ratio in BMMTs.

Even though the values for the biomass content of 1% BMMT and 5% BMMT were different, only small differences in the Q_{dry}/Q_{wet} ratio were observed.

Comparable changes in the uranium(VI) adsorption capacities of *Apha* sp. and *Acre* sp. dried biomasses as the adsorbent compared to the wet samples were also observed by Gargarello et al.[22]

According to these observations, the results can be interpreted as follows:

In order to take into account the importance of exchangeable sites, changes in the proton exchange of wet and dry systems were compared. In a previous work,[17] proton exchange of wet BMMT indicated that in wet BMMT samples the proton exchange attributed to biomass in the BMMT structure was increased when the proportion of biomass in the BMMT sample was lower because of a more even distribution of the biomass. Table 1 provides the ratio between the total proton exchange from dried and wet BMMTs. Data showed that the amount of sites to exchange protons in dried BMMT samples were close to 5 times higher than those found for wet BMMT samples. The increase in the $H^{+}_{dried}/H^{+}_{wet}$ ratio was even higher for raw biomass (close to 8), but hardly any differences were found for the ratios of MMT and MMT(P5). These results led to the assumption that the presence of biomass caused a higher increase in the proton-exchange capacity of BMMTs when a drying step is included during preparation.

Although the ratio $H^{+}_{dried}/H^{+}_{wet}$ indicated that the presence of biomass in the dried BMMT could explain the increase in the proton-exchange capacity, the presence of biomass alone could not explain the increase in uranium(VI) adsorption of dried BMMT samples because the Q_{dried}/Q_{wet} ratios obtained for BMMTs and MMT or MMT(P5) were similar. In summary, it can be stated that the increase in uranium(VI) adsorption cannot be explained only by the increase of the amount of proton-exchange capacity. The uranium(VI) uptake increased at the same rate as the proton-exchange capacity for dried/wet biomass, but in the case of BMMTs (1 and 5%), the increase in the ratios Q_{dried}/Q_{wet} and $H^{+}_{dried}/H^{+}_{wet}$ was independent of the amount of biomass. On the basis of the differences, it can be suggested that the biomass hydration degree played an important role in the amount of exchange sites, as observed from the proton-exchange capacity data. In contrast, the hydration degree of the "clay component" of BMMTs and the hydration degree of MMT itself was responsible for the observed differences in uranium(VI) uptake by dry or wet sorbent. Therefore, the increase in the uranium(VI) adsorption capacities could be due to a stoichiometric as well as to a kinetic phenomenon caused by diffusional processes, as will be explained later.

XRD. XRD of dried BMMT was performed to achieve a more complete understanding of the adsorption process by studying changes in the clay interlayer space of the dried BMMTs after uranium(VI) adsorption. Figure 2 shows the oriented XRD patterns of dried BMMT samples in the presence of uranium(VI). These samples were pellets recovered from the uranium adsorption of C_i = 1.05 mM (the highest concentration used for the isotherm performance).

Similar to the patterns obtained for wet BMMTs,[17] samples with uranium(VI) adsorbed presented *d*(001) values of 1.50 nm (Figure 2). The increase of the *d*(001) value (1.50 nm) of samples with uranyl adsorbed compared to that found for samples without uranium(VI)[17] (1.26 nm) indicated the entrance of the uranyl cation into the clay interlayer. In addition, there is evidence that the entrance of the uranyl cation is heterogeneous, as described in other studies,[33,34] because of the not sharp and broad peaks. The peaks can be deconvoluted into subpeaks as described below.

Comparable interlayer space values after the uranium(VI) addition were obtained for wet[17] and dried samples (Figure 2).

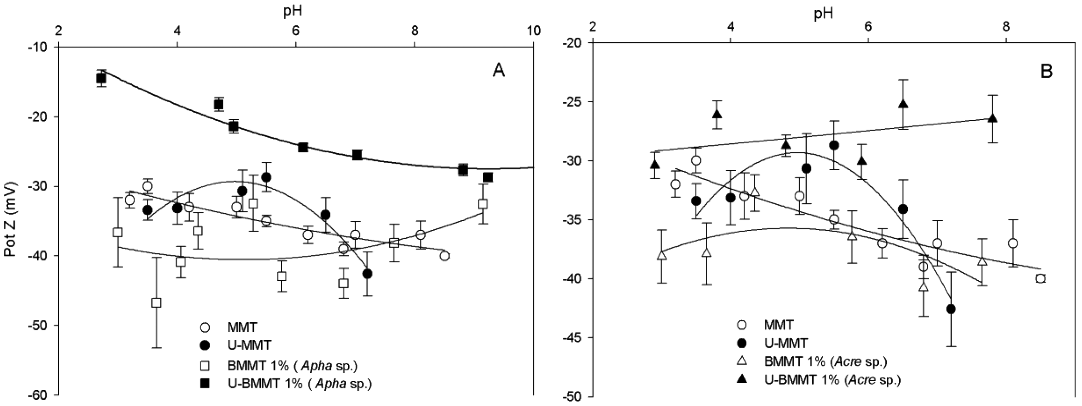


Figure 3. ζ-potential curves for dried MMT, (A) 1% BMMT(*Apha* sp.) and (B) 1% BMMT(*Acre* sp.) samples, with and without uranium adsorbed.

To study differences between the dried and wet BMMTs, mathematical deconvolution of the $d(001)$ reflection peaks into two subpeaks (X1 and X2) was performed, and the results are resumed in Table S3 (Supporting Information).

Deconvolution of the $d(001)$ peak for dried samples indicated that fewer areas were occupied by uranyl ions in dried (this work) than in wet 1% U-BMMT(*Acre* sp.) and -(*Apha* sp.) samples.[17] The uranium(VI) adsorption into the interlayer of dried BMMTs with 5% of MMT resulted in greater areas of $d(001)$ reflection peaks compared to BMMT with 1% of MMT samples (Table S3 in the Supporting Information). This behavior correlated with the amount of MMT in the composition of BMMT, indicating an active participation of the MMT interlayer during uranium(VI) adsorption due to cation exchange. However, deconvolution analysis of the different samples indicated that this effect could not be correlated to uranium(VI) adsorption capacities of all samples.

The differences observed in analysis of the mathematical $d(001)$ reflection peak deconvolution did not explain the higher uranyl adsorption capacities found for dried BMMT samples. This can be assigned to the fact that XRD analysis of the $d(001)$ reflection peak can only provide information on the entrance of the uranium(VI) cations to the clay interlayer, and it cannot account for the differences in uranium(VI) adsorption due to the biomass component of the dried or wet BMMT. This suggested that, in addition, other factors like, e.g., the hydration states of the biomass/adsorbent were important for uranium(VI) adsorption in BMMTs.

Electrophoretic Mobility. ζ Potential. ζ-potential determinations from the electrophoretic mobility of dried BMMTs before and after uranium(VI) adsorption were obtained in order to study changes in the surface charge of the samples.

Figure 3 shows the ζ potential of dried MMT, 1% BMMT(*Apha* sp.), and 1% BMMT(*Acre* sp.) samples, with and without uranium(VI) adsorbed (C_i = 1.05 mM).

Particularly, the comparison of ζ-potential curves for dry U-BMMT(*Apha* sp.) and -(*Acre* sp.) samples (Figure 3) with respect to samples in the wet state[17] did not show differences in the negative surface charge value. Furthermore, the similar decrease of the negative surface charge found in dried (Figure 3) and wet BMMT samples,[17] due to uranium(VI) adsorption, indicated that differences in the adsorption capacities between dried and wet samples could not be explained by surface charge analysis.

Apparent Particle Diameters. D_{app} values for all samples were measured. For samples containing uranium, solids were recovered from the adsorption point C_i = 1.05 mM of the isotherms performed with wet or dried BMMTs. The results are shown in Table 2

Table 2. Apparent Particle Diameter Values (D_{app}) Obtained for Wet or Dried BMMT, MMT, or Biomass Samples in the Presence or Absence of Uranium(VI)

sample	D_{app} (nm)
MMT	880 ± 80
U-MMT	880 ± 10
dried MMT	800 ± 100
dried U-MMT	840 ± 90
Apha sp.	10000 ± 1000
U-*Apha*	21000 ± 1000
dried *Apha* sp.	11000 ± 2000
dried U-*Apha* sp.	14000 ± 3000
1% BMMT(*Apha* sp.)	1300 ± 700
1% U-BMMT(*Apha* sp.)	1400 ± 200
1% dried BMMT(*Apha* sp.)	8000 ± 1000
1% dried U-BMMT(*Apha* sp.)	14000 ± −4000

The D_{app} values for BMMT(*Apha* sp.) and BMMT(*Acre* sp.) (data not shown) were similar.

Only small differences were observed between dry and wet D_{app} values for raw biomass and MMT samples. However, the D_{app} value obtained for dried BMMT(*Apha* sp.) was around 6 times higher than that obtained for wet BMMT(*Apha* sp.). This indicated that BMMTs had a higher agglomeration tendency after the drying process. The increase in D_{app} of dry BMMTs was even more pronounced after uranium(VI) adsorption.

However, the increase in D_{app} of dried BMMTs compared to wet BMMTs could not be correlated with the uranium adsorption capacity of dried BMMTs.

Hydration Experiments. In the case of swelling clays, water uptake or solute adsorption is an interlayer phenomenon where water and solute movement occurs during water absorption.[35,36] Accordingly, water and solute entrance into the samples was evaluated in order to explain the differences observed between dried and wet BMMTs.

To achieve this, BMMT hydration experiments and uranium adsorption isotherms with rehydrated BMMTs were performed.

For the hydration experiments, analysis regarding the amount of water retained in different samples was done and related to the uranium(VI) adsorption capacity of each sample, using the 1.05 mM uranium(VI) solution. Table 3 shows the results from water retention in percentages after 3 h of hydration time and water mass per gram of dried sample. Because there were no differences between retained water percentages at 3 or 24 h, data from the 3 h hydration time were used because this was the time to achieve isotherm equilibrium.

Table 3. BMMT Hydration Percentages (H%) and Water Mass Entrance (m_{H_2O})

sample	H%	m_{H_2O} (g of H_2O/g of dried sample)	α (mmol of U/g of dried sample)	ΔQ (Q_{dried} − Q_{wet})
1% BMMT(*Apha* sp.)	67.03	2.034	0.003	0.239
1% BMMT(*Acre* sp.)	79.02	3.774	0.006	0.126
5% BMMT(*Apha* sp.)	88.35	7.638	0.011	0.324
5% BMMT(*Acre* sp.)	88.17	7.469	0.011	0.222
1% MMT(P5)	90.21	9.233	0.013	0.064
5% MMT(P5)	91.01	10.219	0.015	0.138
MMT	94.73	12.137	0.018	0.280
Acre sp.	77.72	3.488	0.005	0.307
Apha sp.	75.21	3.035	0.004	0.293

Analysis of the results from water retention reveals that the MMT sample had the highest water retention percentage, whereas biomass had the lowest value and BMMT samples presented water retention values between clay and biomass or a little lower (Table 3). These results indicated that hydration was not restricted to the intercalation of water in the swelling clay but was also the result of a balance between the retention of water by the clay and biomass.

Considering a uranium(VI) solution density of 1.00 g cm^{-3} (equal to the density of water) and the amount of retained water (g of H_2O/g of dried sample; Table 3), the parameter α was calculated. The parameter α represents the amount of uranium(VI) that could adsorb to the samples due to hydration during the contact time between the uranium(VI) solution and dried adsorbent.

ΔQ (Table 3) represents the difference between the uranium(VI) adsorption capacities of dried and wet samples indicated in Table 1, respectively. If this difference was caused by the absorption of uranium(VI) during the hydration process, then α should be equal to ΔQ. Indeed, according to the MMT water retention value, MMT should have presented the highest uranium(VI) adsorption capacity. Additionally, α should be equal to ΔQ for all samples if the increase in uranium(VI) retention observed for dried systems was a consequence of the entrance of solute with water molecules during the hydration process. However, for all samples (Table 3), α was much lower than ΔQ (1−2 orders of magnitude).

Therefore, uranium(VI) entered, was absorbed, into dried BMMTs with water molecules during the hydration process. However, the amount of uranium(VI) that entered by this mechanism was too little to explain uranium(VI) adsorption differences observed between dried and wet BMMT samples (calculated parameter α; Table 3). The results from this experiment allowed one to conclude that the main increase of the uranium adsorption capacity of dried samples was not related to the hydration process of dried BMMT samples during contact with the uranium(VI) solutions.

To study the reversibility of the increase in uranium(VI) adsorption, uranium(VI) adsorption isotherms were performed using samples of different hydration degrees. Because BMMT-(*Apha* sp.) and BMMT(*Acre* sp.) samples did not show differences in the uranium sorption capacity, hydration during the performance of the isotherms was tested on BMMT(*Apha* sp.) and MMT samples. The uranium(VI) adsorption isotherms were performed for the following samples: dried BMMT(*Apha* sp.) and dried MMT samples that had been previously hydrated (as performed in hydration assays) before being used; dried BMMT(*Apha* sp.) and MMT samples; wet BMMT(*Apha* sp.) and MMT samples. The results of the adsorption isotherms are displayed in Figure 4.

The uranium(VI) adsorption capacity of dried BMMT samples that were previously hydrated was similar to that found for wet BMMT samples (Figure 4; this was the condition under which BMMT samples were used for isotherms in Figure 1). In contrast, both adsorption values were significantly smaller than those obtained for dried BMMT samples without any prior hydration. These results indicated that the increase in the adsorption capacity of dried samples was reversible when these samples were hydrated previously. Pretests evaluating the uptake kinetics were performed, and they showed that adsorption equilibrium was reached after 3 h (data not shown).

As was indicated previously by other researchers, wet or hydrated clay matrixes can exhibit an approximate gel-like conformation,[37,38] which affects molecule diffusion through the materials.[39,40]

To evaluate the diffusion of uranium(VI) in dried and rehydrated samples, determination of the apparent diffusion coefficients (D_a) for UO_2^{2+} cations in dried 1% BMMT(*Apha*

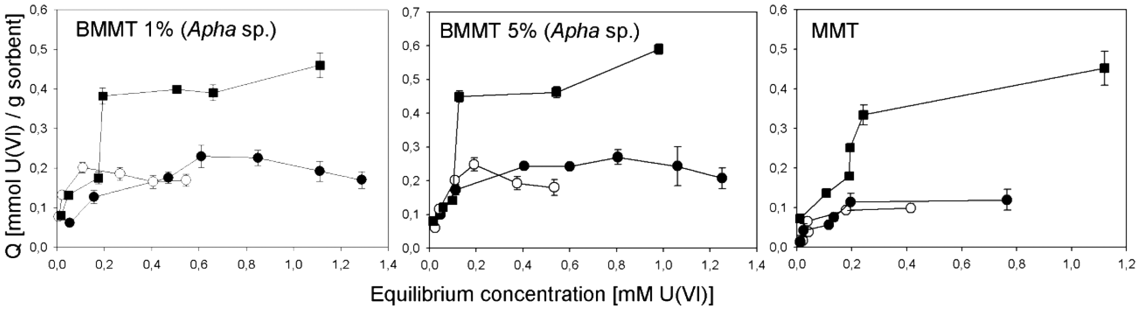


Figure 4. Uranium(VI) adsorbed on BMMT(*Apha* sp.) and MMT. Isotherms performed with wet samples (○), dried samples (■), or dried and rehydrated samples (●).

sp.) and rehydrated 1% BMMT(*Apha* sp.) samples was performed. A lower D_a value was found for the rehydrated matrix than for the dried variant (6.2×10^{-11} and 1×10^{-10} m^2 s^{-1}, respectively). The D_a results indicated that diffusion of the UO_2^{2+} cation was somehow retarded inside the rehydrated samples. The diffusion velocity is controlled by material surface properties. Thus, changing the wetting properties (in terms of the CA) should be related to the observed differences. Molecule diffusion and uranyl adsorption are surface related processes. Therefore, CA measurements on BMMT samples were carried out, in addition. With a CA of 129°, dried 1% BMMT(*Apha* sp.) was distinctly hydrophobic (i.e., CA ≥ 90°), while rehydrated BMMT(*Apha* sp.) with a CA of 89° was at the threshold between subcritically water-repellent (i.e., CA > 0° and CA < 90°) and hydrophobic. The results of the sample wettability indicated that the preparation of the rehydrated variant had a measurable effect on the surface wetting properties. In hydrophobic materials, diffusion of water molecules can be higher because of the existence of repulsive forces, which decrease the interaction of H_2O molecules with the material surface, particularly in clays.[29]

Intraparticle diffusion modeling[31] (Figure S1 in the Supporting Information) was performed for wet and dried 1% BMMT(*Apha* sp.) samples by kinetic experiments. The diffusion coefficient values (K_{id}) were 0.295 and 0.416 mg g^{-1} min^{-1}, respectively. These results were in agreement with those obtained from apparent diffusion coefficient (D_a) calculations, where rehydrated 1% BMMT(*Apha* sp.) presented a lower D_a value than dried 1% BMMT(*Apha* sp.), indicating a better intraparticle diffusion in dried samples. This also was in accordance with the results from CA analysis, where smaller CA values were found for the rehydrated variant.

Thus, diffusion coefficients suggested that differences in the adsorption capacities of wet and dry BMMTs could be caused by kinetic effects. Some studies indicate, e.g., that for MMT the Na^+ cation diffusion equilibrium is only attained after longer contact times, taking into account cation-exchange processes at the clay surface.[33] For *Trichoderma* sp. biomass, differences in the adsorption capacities between wet and dried samples were equated after 76 h of contact time for cadmium(II), nickel(II), and chromium(III) adsorption.[23] In order to evaluate the influence of the contact time and to assay whether wet BMMTs could reach the adsorption capacity of dried BMMTs, uranium(VI) adsorption on wet BMMT samples was conducted over more than 72 h. The results indicated that uranium(VI) adsorption capacities for wet BMMTs remained almost constant and did not reach the uranyl adsorption values obtained for dried BMMTs (data not shown).

Because these reaction times are not transferable to technological applications of adsorption techniques, a state of pseudoequilibrium should be achieved, which offered the best compromise between the adsorption performance and hydration time. For practical purposes, the dry BMMT variants promised a more efficient uranium(VI) adsorption performance.

On the basis of our results, uranium(VI) adsorption increases with the BMMT particle size (differences between dried and rehydrated samples). Additionally, the lower diffusion velocity for the rehydrated samples and the intraparticle diffusion modeling indicated kinetic effects. Furthermore, it was shown that more exchange sites were available in dried samples, indicating a higher probability for uranium(VI) adsorption.

Regarding the wettability of the samples, it is not so easy to forecast movement in the hydrophobic samples. Diffusion might be increased because of the repellent surface when the samples are hydrophobic, but when the bulk density increases, diffusion might even be decreased because the accessible pore space is too small and ion movement might be hindered for sterical reasons. Sterical hindrance caused by agglomeration in dried samples might be an explanation for retaining higher amounts of uranium(VI) within the BMMT agglomerates also (the cation might be trapped within the agglomerates).

Correlation of the hydration experiments with D_a values and the wetting properties indicated that, in previously dried samples (more hydrophobic), water molecules are not occupying binding sites that then will be available for the interaction of UO_2^{2+} cations with the adsorbent. In the case of rehydrated samples, the reversibility of the UO_2^{2+} adsorption capacity could be given by water molecules that were already interacting with binding sites, thus preventing the interaction of UO_2^{2+} cations with BMMTs.

Another technological advantage of dried BMMTs in contrast to dried MMT or wet BMMT samples was that dried BMMTs could be used for the development of macroscale adsorption techniques as in adsorption columns.[41] Dried pellets made from MMT samples did not allow a continuous flow through columns, while BMMT dried pellets did (Figure S2 in the Supporting Information). This was due to changes in the structure and stability of the material caused by the fungal biomass growth on the MMT surface. Also, utilization of a previously dried material for adsorption allowed the recovery of solids for reuse.[41]

■ CONCLUSIONS

In this study, the uranium(VI) adsorption capacity of previously dried BMMTs samples was characterized and compared to data obtained for wet BMMTs. Analysis of the uranium(VI) adsorption capacity results indicated that previously dried BMMTs presented a higher uranium(VI) adsorption capacity than wet BMMT samples. This phenomenon was reversible when dried BMMTs were rehydrated before uranium(VI) adsorption.

The results from XRD studies and analysis of exchangeable sites suggested that the hydration degree of both the clay and biomass components of BMMT samples played an important role in the uranium uptake, as observed by the differences between the dry and wet adsorbents. Further, the D_{app} values obtained indicated participation of the biomass component in the increase of the uranium(VI) uptake after the drying process.

Additionally, while electrophoretic mobility studies did not explain differences in the adsorption capacities, data obtained from the hydration experiments and apparent diffusion coefficient analysis evidenced diffusion and kinetic effects on the increase of uranium(VI) adsorption by dried BMMT samples.

This study helps to highlight the importance of the hydration state of the adsorbent used and the high uranium(VI) adsorption capacity shown by BMMTs in its dry form. It can lay the background for application of the adsorption process on a larger scale.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.6b04881.

Specific constants for adsorption models and mathematical decomposition of the *d*(001) XRD reflection peak for BMMT samples, bibliography revision, BMMT water contents, intraparticle diffusion modeling, and photograph of adsorption columns using BMMT pellets containing different amounts of MMT (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the Ministerio de Ciencia y Técnica, Agencia Nacional de Promoción Científica y Tecnológica, MINCyT−ANPCyT−FONARSEC through FS-Nano 008, CONICET PIO 2013, and Deutsche Forschungsgemeinschaft (German Research Foundation), SCHA 1732/1-1, for financial support. G.A.C. and R.M.T.S. are members of CONICET, and M.S.O. acknowledges a CONICET fellowship and a DAAD grant.

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