

Effect of Acidic Conditions on Surface Properties and Metal Binding Capacity of Clay Minerals

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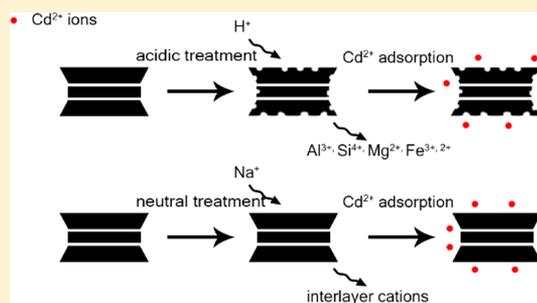
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ABSTRACT: Clays are one of the most abundant minerals on the Earth's surface, and they play a significant role in global trace element cycling because of their ability to adsorb and incorporate a range of metal cations. However, to what extent clay surface reactivities are affected by changes in pH of the surrounding environment remains poorly understood. To address this uncertainty, we investigated three common clay minerals (kaolinite, illite, and montmorillonite) and compared their surface properties and metal binding capacity prior to and after acidic treatment (pH ranges from 0 to 7). We report that (1) the morphologies and crystal structures of the three studied clay minerals do not differ markedly after exposure to an acidic solution, (2) all three clays display increases in surface area after the pH 0 acidic treatment, and (3) cadmium adsorption to all three clays decreased after the pH 0 acidic treatment. Our results suggest that the variation in metal adsorption capacity is related to acidic modification of clay surface properties. Importantly, this work shows the relevance of acidic environments on surface-controlled reactions of trace metals to clay minerals.

KEYWORDS: kaolinite, illite, montmorillonite, acidic treatment, surface properties, cadmium adsorption capacity



1. INTRODUCTION

Clay minerals are layered aluminosilicates that are ubiquitous in soils and sediments, making them an important component of ancient sedimentary rocks.^{1–3} The fine-grain size of clay minerals enables them high chemical reactivity, and as a consequence, they exert a considerable impact on global trace element cycling (e.g., refs 4–17). However, one aspect of clay reactivity that has received less attention is changes in the surface reactivity during variations in solution pH. For instance, at local or regional scales, the environment can receive significant acid input, as might be expected from metal and coal mine abandonment [e.g., acid mine drainage (AMD)] or acidic rain caused by industrial activities.

Solution pH influences the protonation behavior of adsorbents and the aqueous speciation of trace elements.^{18–22} However, in highly acidic environments, clay minerals undergo partial dissolution, during which structural elements, such as Si and Al, leach into solution.^{23–26} The loss of structural elements changes the surface properties of clay minerals, leading to, for example, variations in the crystal structure, morphology, and surface electrostatic field, and, thus, may influence their metal binding capacity.²³ Indeed, clay acidification has been widely used in industrial applications, for example, the removal of dyes, trace metals, and catalyst of chemical synthesis.^{27–31}

Although clay minerals are widely reported to undergo acidic leaching (e.g., refs 32–34), it is still not clear to what extent clay surface reactivity can be modified through this process. Moreover, previous studies focused on the pH impact on metal adsorption onto clay minerals,^{35–40} but there are few studies that have focused on acidification and the structural changes to the clay mineral reactivity. In this regard, our work aimed to assess the surface properties and metal binding capacity of three common clay minerals (kaolinite, illite, and montmorillonite) under acid-washed (hereafter named as “acid-treated clay”) and neutral-washed (hereafter named as “neutral clay”) conditions to mimic conditions that clay minerals experience when exposed to acidic fluids (e.g., AMD) on the Earth's surface. We used Cd²⁺ as a model divalent cation for the following reasons: (1) the aqueous speciation is relatively simple and does not precipitate at our experimental conditions until pH > 8; (2) its use in laboratory settings is not complicated by the precipitation of cadmium carbonate or hydroxide solids; and (3) many previous researchers study

Received: June 7, 2019

Revised: September 5, 2019

Accepted: September 9, 2019

Published: September 9, 2019

Table 1. continued

^aA, acidic treatment; N, neutral treatment; numbers 1, 2, and 3, first time wash, second time wash, and third time wash, respectively; and BD, below detection limit. Our detection limit for ICP–MS analysis is 0.002 ppm.

Cd²⁺ adsorption; therefore, we can compare our results to those of previous studies.

2. MATERIALS AND EXPERIMENTAL PROCEDURES

Samples of kaolinite (KGa-2), montmorillonite (SWy-2), and illite (IMt-2) were obtained from the Clay Mineral Society, Source Clays Repository (Purdue University, West Lafayette, IN, U.S.A.). All three clays were ground by an agate mortar and pestle to pass through a 100-mesh sieve. A 0.1 M NaNO₃ [American Chemical Society (ACS) certified, Fisher Scientific] solution was prepared in advance of the clay mineral washing. For all treatments (pH 0, 2, 4, and 7), 4 g of each of the three clays were washed with 30 mL of 0.1 M NaNO₃ solution. The pH of the 0.1 M NaNO₃ solution was adjusted with aliquots of 70% HNO₃ (ACS certified, Fisher Scientific) to pH 0, 2, and 4 for acidic leaching (hereafter “acidic treatment” refers to the pH 0–4 range). We use this range because it encompasses the effluent pH from most acidic mine drainage environments.^{41–44} For the pH 7 treatment (hereafter referred to as “neutral treatment”), the same amount of all three clays were washed with 30 mL of 0.1 M NaNO₃ without adjusting pH (at pH around 7). For both methods, clays were washed 3 times, at time intervals of 1, 2, and 4 h. Between washes, the solid and liquid were separated by centrifugation at 10000g for 10 min. The liquid was collected for inductively coupled plasma (ICP) analysis, and the solid was resuspended, as described above. Total elemental release as a result of washing was calculated by summing the elemental release from all three washes.

Following washing, the pelleted clay samples were stored at –20 °C for 24 h. Once frozen, each clay sample was freeze-dried (Thermo Savant MicroModulyo-115) to remove water molecules from their surface and interlayers. Hereafter, Kao-N is used to indicate neutral kaolinite, while Kao-A0, Kao-A2, and Kao-A4 indicate acidic kaolinite at pH 0, 2, and 4, respectively. The same nomenclature is applied to illite and montmorillonite.

To quantify how acidic treatment changes the surface of each clay, morphological analyses of the clays were conducted using Zeiss Sigma 300 VP-FESEM scanning electron microscopy (SEM). Before SEM imaging, samples were carbon-coated via a Leica EM SCD005 evaporative carbon coater. Crystal structure changes after acidic treatment were determined by X-ray diffraction (XRD) analysis using a Rigaku Powder X-ray diffractometer. XRD data were collected over a 2θ range from 5° to 90° with a scanning speed of 2°/min in continuous mode. The Brunauer–Emmett–Teller (BET) surface areas were determined for raw and treated kaolinite, illite, and montmorillonite samples (Autosorb iQ, Quantachrome Instruments, Boynton Beach, FL, U.S.A.). All samples were degassed at 250 °C for 4 h before analysis. The BET surface area was calculated using multipoint N₂ BET by tagging a P/P₀ range of 0.05–0.30. Triplication analysis was performed on samples to confirm the surface area values of all clay samples.

The supernatants of both acidic and neutral treatments were analyzed for Al, Mg, Si, and Fe concentrations by inductively coupled plasma mass spectrometry (ICP–MS, Agilent 8800). An internal indium standard (20 ppb) was employed to

quantify instrumental drift during measurements. The standard deviation for each element analyzed was less than 3%.

Cadmium adsorption onto both acidic clay and neutral clay was studied as a function of the Cd²⁺ concentration. Batch experiments were performed in a reciprocating shaker with a speed of 50 rpm. In each experiment, 40 mg of clay minerals were suspended in 40 mL of Milli-Q water to make a 1 g/L clay suspension at Cd²⁺ concentrations of 1, 10, 20, 30, and 40 ppm. Sodium nitrate, at a concentration of 0.01M, was used to buffer the ionic strength of the solution. After 12 h, 5 mL of the suspension was taken out and filtered through 0.2 μm nylon membranes, and the supernatant was analyzed by ICP–MS to determine the Cd²⁺ concentration in solution. The Cd²⁺ adsorption experiments were confirmed by duplication, and the analytical uncertainty is <5%.

3. RESULTS AND DISCUSSION

3.1. Release of Elements during Neutral and Acidic Treatments. The major elements released into solution during neutral and acidic treatments of kaolinite are Al and Si, with lesser amounts of Mg and Fe (Table 1). This is possibly because kaolinite [Al₂Si₂O₅(OH)₄] has less isomorphous substitution by Mg and Fe in its structure.¹ In comparison to Kao-N, Kao-A2 released approximately 10 times more Al and 4 times more Si into solution, and the elemental release of Kao-A4 and Kao-N shows little difference with less than 10 ppm of each element released. Interestingly, Al and Si release from Kao-A0 is less than that of Kao-A2, which could be attributed to the generation of a leached layer and secondary precipitation of the released elements.^{45,46}

The neutral wash of illite [(Al,Mg,Fe)₂(Si,Al)₄O₁₀(OH)₂·K] released considerable amounts of Mg and smaller amounts of Si, while Al and Fe were also leached at acidic conditions (Table 1). Magnesium in the structure of illite mainly exists as a result of isomorphous substitution on the octahedral sheet, and the release of Mg at neutral pH indicated the instability of it, which could easily be released into solution. Acidic treatment (pH 0, 2, and 4) of illite releases more ions than the neutral treatment, and decreasing pH leads to the release of higher elemental concentrations. At pH 0 treatment, illite released more than 1000 times Al, 2 times Mg, 20 times Si, and 1000 times Fe than the neutral treatment. The treatment of illite at pH 4 resulted in only slight increases in elemental release compared to pH 7, while significant amounts of Al release were observed for pH < 2 treatment. In comparison to kaolinite, illite has more isomorphous substitution in both the tetrahedral Si sheets and octahedral Al sheets,^{1,47} and as a consequence, these substituted elements (for example, Al, Mg, and Fe) are more easily extracted during acidic treatment.

Magnesium and Si are the main elements mobilized during both acidic and neutral treatment of montmorillonite [(Al,Mg)₂(Si,Al)₄O₁₀(OH)₂·nH₂O(Na)_{0.33}], while the release of Al under pH > 2 treatment was negligible (Table 1). This is likely the consequence that the substituted ions (Al and Mg replace Si and Al in tetrahedral and octahedral layers, respectively) in the clay structure are more liable to be leached during acidic exposure. Aluminum substitution of Si in the tetrahedral layer of montmorillonite is minor (0.025%)

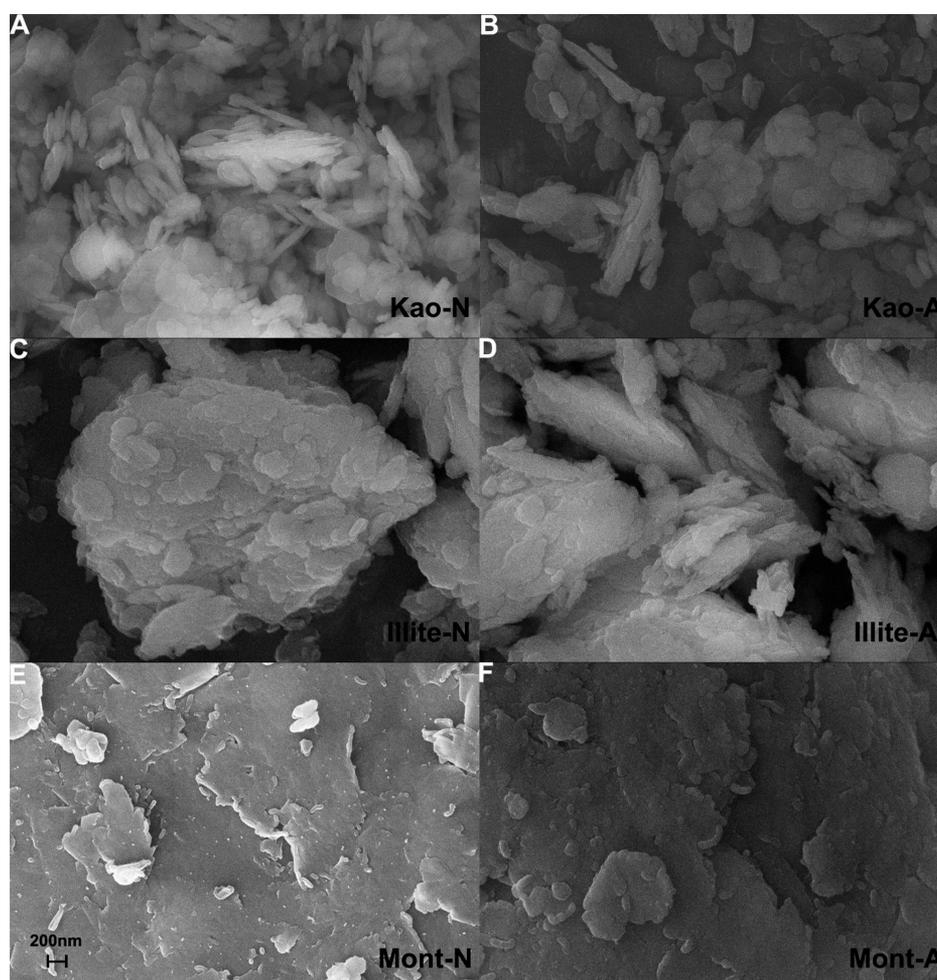


Figure 1. SEM images of neutral- and acid-treated clay minerals (A, Kao-N; B, Kao-A; C, Illite-N; D, Illite-A; E, Mont-N; and F, Mont-A).

compared to illite (15.38%), which explains why illite releases more Al compared to montmorillonite during acidic treatment. However, the pH 0 treatment of montmorillonite releases a greater amount of Al (344.8 ppm in total), which could be explained as stoichiometric dissolution because the elemental release ratio is around 1.5:1:1.5:1 for Al/Mg/Si/Fe.^{45,46} This result is also consistent with Si release (tetrahedral layer dissolution), which is significant for the pH 0 treatment. Interestingly, Mg release from montmorillonite shows little difference for the pH 2, 4, and 7 treatments (approximately 100 ppm released in total), indicating that isomorphically substituted ions are more liable to release, a result also observed for illite.

Once structural elements, such as Si, Mg, Fe, and Al, are released from a clay mineral into solution post-acidification, the resulting vacancy in the octahedral or tetrahedral sheet can be replaced by dissolved cations from the external milieu. In natural environments, the most abundant cations (e.g., Ca^{2+} and Na^+) could potentially replace these structural cations. This process is similar to isomorphic substitution of higher valent cations (for example, Al^{3+} and Si^{4+}) by lower valent cations (Mg^{2+} and Fe^{2+}) that occur extensively in clay structures.^{48–50} Consequently, excess structural charge will be generated, which leads to a greater negatively charged surface electric field and increased electrostatic attraction metal cations.

Pentrak et al. studied the dissolution of 2:1 clay minerals and found that those with higher degrees of isomorphic substitution are more easily dissolved in HCl.⁵¹ Our study shows similar findings, with montmorillonite and illite having more isomorphic substitution than kaolinite, and thus, the former has a higher degree of elemental release, particularly at lower pH.⁵¹ Interestingly, kaolinite, a 1:1 clay mineral, released more Al than either montmorillonite and illite at the pH 2 condition.⁵² This might be attributed to the property that Al octahedral sheets in 1:1 clay minerals are more exposed to solution (i.e., acid attack) versus 2:1 clays, where the Al octahedral are sandwiched between two Si tetrahedral sheets.

3.2. Changes in Morphology and Crystal Structures of the Studied Clay Minerals. The changes in clay particle morphology and crystal structure between the acidic and neutral treatments are shown by SEM and XRD (Figures 1 and 2). We chose pH 2 and 7 as examples, because pH 2 represents a moderately acidic environment and pH 7 is the lone neutral treatment. All three clay minerals exhibit a planar structure in the SEM images, with clay platelets both stacked on and perpendicular to each other. In all cases, the comparison between acid-treated clay and neutral-treated clay shows that the acidic treatment had a negligible influence on the morphology of the studied clay minerals. Figure 2 shows the comparison of XRD patterns of the three clay minerals after both acidic and neutral treatments. To better visualize the differences, the patterns of Kao-A, Illite-A, and Mont-A were

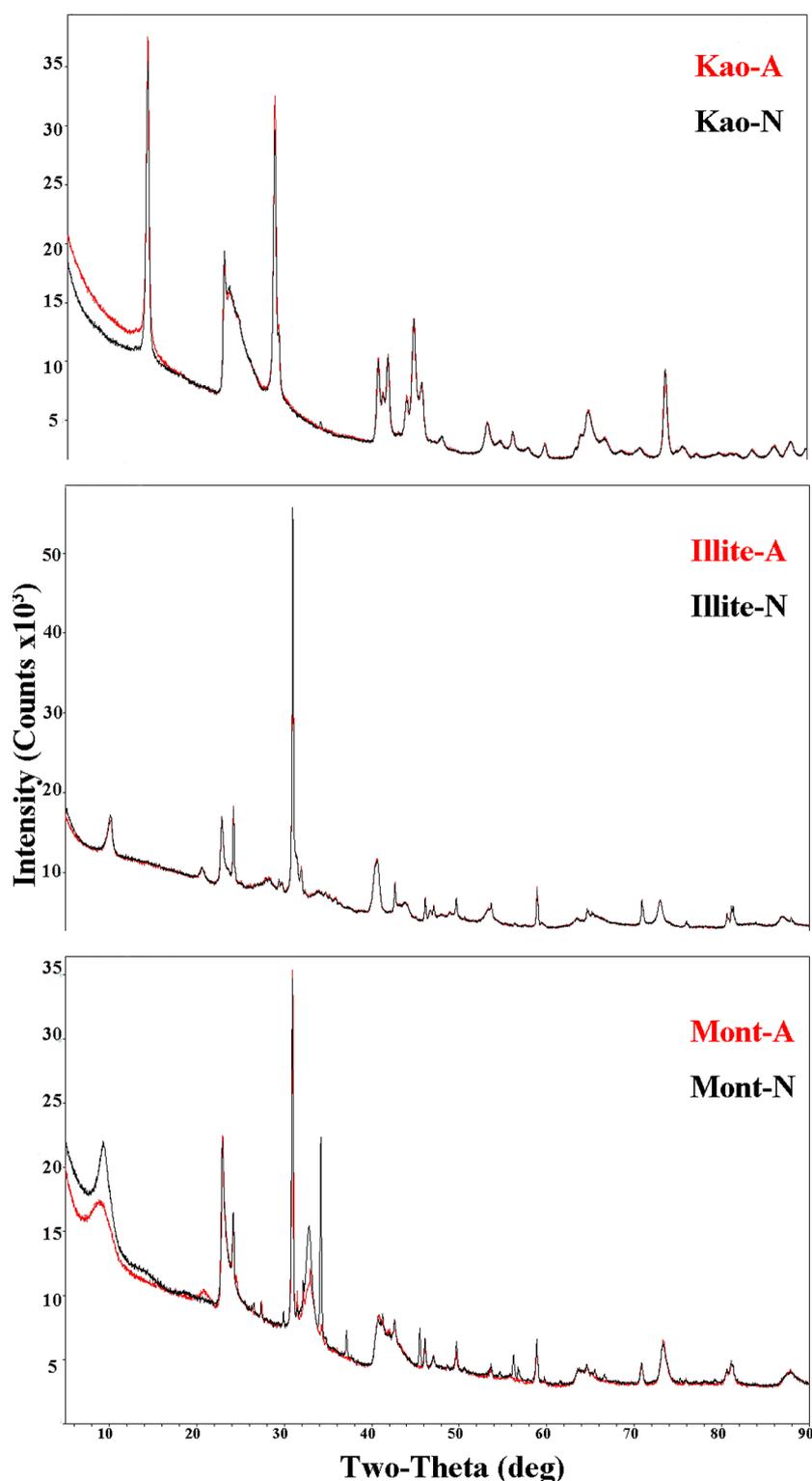


Figure 2. XRD data of the three studied clays under acidic and neutral treatments of acid-treated (A, red) and neutral-treated (N, black) diffraction patterns.

overlapped with Kao-N, Illite-N, and Mont-N, respectively. Acidic treatment changed diffraction peaks between $2\theta = 5^\circ$ and 15° for kaolinite and montmorillonite, while for illite, there is no difference across the whole 2θ range. Diffraction peaks in Mont-A have a lower intensity compared to Mont-N, while those in Kao-A have a higher intensity than Kao-N at 2θ values below 10° . The comparison of XRD spectra between acidic

clay and neutral clay indicates that the crystal structure of clay minerals displays little difference after acidic treatment.

Although the acidic modification of clay minerals leads to the release of structural elements into solution, this influence cannot be detected by traditional mineral characterization methods, such as SEM and XRD (Figures 1 and 2). A simple calculation was performed, summing all of the elements that

were lost during washing (the total elemental loss) to estimate the total mass of elemental release, which is 0.80, 5.49, 3.39, 4.32, 1.74, and 5.08 mg for Kao-N, Kao-A2, Mont-N, Mont-A2, Illite-N, and Illite-A2, respectively. This accounts for only 0.02, 0.14, 0.08, 0.11, 0.04, and 0.13% of the total clay mass, respectively. It is also possible that secondary precipitation could occur on the clay surfaces that may not be detected by XRD and SEM, because the amount of elemental release is negligible compared to the mass of clay. Kumar et al. and Jozefaciuk and Bowanko treated montmorillonite and kaolinite using various concentrations of acid and found that the XRD spectra of acid-activated montmorillonite varies primarily between 2θ of 0° and 20° .^{53,54} These findings correlate well with our clay XRD spectra that show that the major peak differences are within $2\theta < 20^\circ$. Collectively, acid-treated clays show little difference in the crystal structure compared to neutral-treated clays.

Wang et al. studied morphological modifications of kaolinite after both alkali and acid leaching.⁵⁵ Their results showed significant changes in morphology among untreated kaolinite, alkali-leached kaolinite, and acid-leached kaolinite. The authors found that following an initial alkali leaching of kaolinite, most of Si in the mineral was released into solution (more than 60%), and this led to the morphological changes observed. Although our results also indicate that Si is leached, the amount of Si released is negligible relative to that observed by Wang et al.⁵⁵ in their alkali treatment. This likely explains why the morphology change in our samples is undetectable.

3.3. Variations in the Surface Area of the Studied Clay Minerals. The surface area of kaolinite shows no difference for the $\text{pH} > 2$ treatment (within the analysis uncertainty of $\pm 2 \text{ m}^2/\text{g}$), except for Kao-A0, which has a surface area of $25 \text{ m}^2/\text{g}$, indicating that strong acidic treatment can increase its surface area (Table 2). The same trend is

Table 2. Surface Area Summary of the Three Studied Clay Minerals

BET surface area (m^2/g) (uncertainties of $\pm 2 \text{ m}^2/\text{g}$)					
Kao-A0	25	Mont-A0	115	Illite-A0	30
Kao-A2	21	Mont-A2	24	Illite-A2	22
Kao-A4	21	Mont-A4	7	Illite-A4	23
Kao-N	18	Mont-N	5	Illite-N	19

found for illite, which shows little variation in surface area for the $\text{pH} 2, 4,$ and 7 treatments. Montmorillonite experienced a significant surface area increase for $\text{pH} 0$ ($115 \text{ m}^2/\text{g}$) and 2 ($24 \text{ m}^2/\text{g}$) treatments compared to $\text{pH} 4$ and 7 treatments, implying that the montmorillonite surface area is significantly affected by acidic treatment relative to illite and kaolinite. It should be noted that the surface areas of Mont-N, Mont-A4, and Mont-A2 are lower than for raw montmorillonite, which has a surface area of $32 \text{ m}^2/\text{g}$ (data from the Clay Minerals Society). This could be attributed to the flocculation of clay montmorillonite at the higher solution electrolyte concentration (0.1 M NaNO_3).

At our experimental conditions, insignificant changes in the surface areas of kaolinite and illite were observed after acidic treatment (Table 2, except for montmorillonite). This contradicts previous studies showing that the surface area of clay minerals increased dramatically after acidic activation.^{31,53,56–58} One clear difference between those studies and ours is that the former applied intensive acid attack to clay

minerals, with acid concentrations up to 8 M , at temperatures over 70°C , and with extended reaction times of as much as 71 h . These experiments aim to modify clay minerals through acidic treatment but, in our opinion, are not relevant to natural conditions. Thus, although structural elements were leached out during the acidic treatment, we observed that there is no significant change in the surface area of kaolinite and illite, especially at conditions that simulate short-term Earth surface acidic drainage exposure (less than 7 h and $\text{pH} 0, 2,$ and 4). However, after decades to centuries of exposure to acidic weathering, large degrees of alteration might be expected.⁵⁹

3.4. Cd^{2+} Adsorption Capacity. The Cd^{2+} adsorption isotherms for the three studied clay minerals are shown in Figures 3–5. Kaolinite basically shows no difference in Cd^{2+}

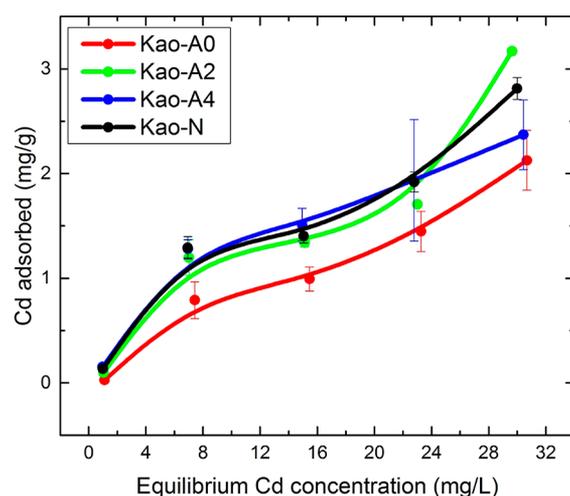


Figure 3. Adsorption isotherms of Cd^{2+} onto kaolinite.

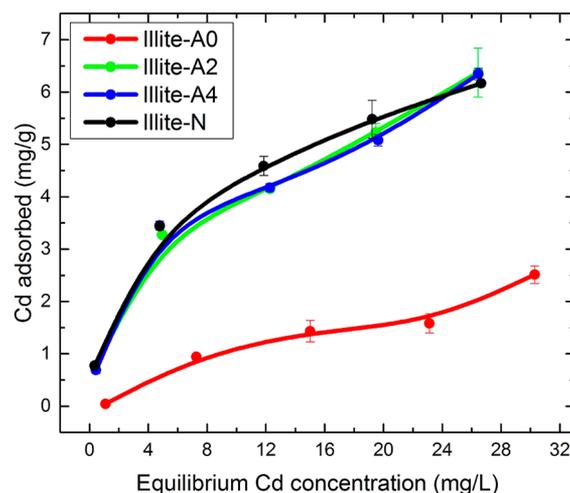


Figure 4. Adsorption isotherms of Cd^{2+} onto illite.

adsorption capacity for the $\text{pH} 2, 4,$ and 7 treatments. However, Cd^{2+} adsorption for the $\text{pH} 0$ treatment of kaolinite markedly decreases compared to the other treatments (around $0.5\text{--}1 \text{ mg/g}$ difference). The $\text{pH} 0$ treatment of illite decreased its Cd^{2+} adsorption capacity by approximately $4\text{--}5 \text{ mg/g}$, more than that of kaolinite. The acidic treatment of montmorillonite illustrates a steadily decrease of Cd^{2+} adsorption with increasing acidity, with only around 2 mg/g maximum

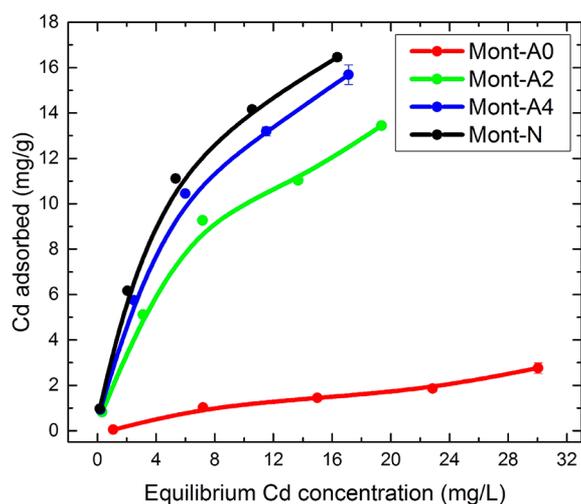


Figure 5. Adsorption isotherms of Cd^{2+} onto montmorillonite.

adsorption for Mont-A0 compared to approximately 17 mg/g for Mont-7.

While it is generally accepted that acidic clay minerals have higher metal adsorption capacity than neutral clays,^{60,61} our experimental results show that the Cd^{2+} adsorption capacity variation is little for treatments of pH 2 and above, while it decreased significantly for the pH 0 treatment (Figures 1–3). This result is different with a previous study that considered Cu(II) and Ni(II) adsorption onto acid-treated clays by applying 0.25 M H_2SO_4 at 110 °C treatment, which results in a higher Cu(II) and Ni(II) adsorption capacity after acidification.³¹ The high-temperature treatment likely activated the clays, creating surface sites for metal adsorption. In our study, the acidic treatment increases the surface area of the three clay minerals but decreases the Cd^{2+} adsorption. This is possibly because strong acidic treatment leads to the dissolution of clay, which creates a leached layer that is enriched in certain elements, ultimately leading to the formation of secondary precipitates on the clay mineral surfaces.^{45,46} The precipitation of secondary minerals, most likely amorphous silica, could explain the increase of the BET surface area. However, it could simultaneously cover the exposed clay surface functional groups and inhibit Cd^{2+} adsorption.⁴⁵ Also, the adsorption of Cd^{2+} onto amorphous Si is significantly lower than that onto clay minerals.⁶² Secondary precipitation of amorphous silica could scarcely form under a high temperature because its solubility increases with the temperature,⁶³ which could explain the literature results that clays treated by acid under a high temperature have higher metal adsorption capacity than normal clays.³¹

Our results show that the variation of Cd^{2+} adsorption capacity and surface area of the clays is negligible for pH 2, 4, and 7, which represents a wide range of environments on the Earth's surface. However, we found that highly acidic conditions (pH 0) may result in a considerable decline in Cd^{2+} adsorption capacity. Our experimental results demonstrate conclusively that acidic treatment has little impact on the morphology and crystal structure of clay minerals but could lead to the release of structural elements and changes in surface area, thus influencing the overall Cd^{2+} adsorption capacity.

4. CONCLUSIONS AND IMPLICATIONS

Our results indicated that the exposure of clay minerals to acidic conditions will extract structural elements, which leads to a measurable variation of Cd^{2+} binding capacity and surface area, although this effect showed no discernible variation in terms of clay morphology and crystal structure. The partial dissolution of clay minerals by acid has several implications for their surface reactivity and potential transport from land to oceans. For instance, in mining operations, the oxidation of pyrite, a mineral constituent of both metal ores and coal bodies, can lead to the acidification of the proximal environment (see ref 64 for details). When clay minerals that are present in the soils become eroded by the AMD or acidic rain (pH 0), their surface properties change, and according to our results, there should be a variation of trace metal adsorption compared to the natural clays. This could be of environmental concern because AMD also carries with it a number of toxic metals in solution, and thus, the soils surrounding the mine might become metal-enriched.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) Discovery Grants (RGPIN-165831) to Kurt O. Konhauser and Daniel S. Alessi. The authors thank Nathan Gerein and Diane Caird of the Department of Earth and Atmospheric Sciences, University of Alberta, for their help in interpretation of SEM and XRD data. Weiduo Hao gratefully acknowledges the support from the China Scholarship Council (CSC, 201506420044). Teruhiko Kashiwabara and Weiduo Hao gratefully acknowledge the support of the Japan Society for the Promotion of Science (JSPS) Grant-in-Aid for Scientific Research JP17H06455.

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