Behavior of bentonite in an aqueous electrolytic solution – evaluation of electrolytic aggregation for adsorption capacity of Cd$^{2+}$ ions onto bentonite

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**ABSTRACT**

In this study, we used aqueous solutions containing 1 mg/L of Cd$^{2+}$ for electrolysis while varying the current density (CD), amount of bentonite added and the effective submerged area to investigate the adsorption capacity of Cd$^{2+}$ ions onto bentonite by electrolytic aggregation. The adsorption of Cd$^{2+}$ ions increased with increasing amount of bentonite added to the electrolytic solution. The addition of bentonite also regulated the pH of the electrolytic solution during the electrolysis process in addition to the hydrolysis of water. The maximum adsorption capacities at equilibrium ($q_e$) for current densities of 3.14 and 7.49 mA/cm$^2$ (i.e. for 2 and 1 L electrolytic solutions) with 0.2 g of bentonite were 4.54 and 2.92 mg/g, respectively. The removal of Cd$^{2+}$ ($R_{Cd}$) clearly depended on the pH of the electrolytic solution. Moreover, $q_e$ decreased with increasing amount of bentonite used for electrolytic aggregation. The findings of this study will be useful for understanding the aggregation of clay particles under electrolysis and their adsorption behaviors.

**Key words** | adsorption, aggregated morphology, bentonite, electrolytic aggregation, electrolytic solutions, pH

**ABBREVIATIONS**

Cd-D dietary Cd intake
CD current density
pzc point zero charge
Redox oxidation-reduction
STD standard solutions
zp zeta potential

**INTRODUCTION**

Toxic heavy metals in contaminated water cause various health and environmental problems. The occurrence, origin and mobility of heavy metals can be a result of human intervention or natural processes. Ground and surface water sources may be contaminated with anthropogenic and/or naturally occurring toxic heavy metal ions, whose concentration exceeds the maximum permissible levels for drinking water in certain areas of the world.

Cadmium (Cd) is one of the most toxic elements encountered in industry and contaminated environments. In Japan significant issue of Cd and its effects on human health was reported in the 1960s by the mining activity and consequently by the irrigated water for rice cultivation (Aoshima 2016).

High dietary Cd intake (Cd-D) has been a focus of administrative as well as public concern in Japan for years since the outbreak of Itai-itai disease tragedy (Ikeda et al. 2015), primarily, Cd contents in rice were suspected to be higher in Japan than in neighboring rice-producing areas, whereas rice is a traditional staple food for general populations in Japan (Ministry of Health, Labor and Welfare, Japan 2015). Currently, Cd-D levels are below 20 µg/day. It was reported 600 µg/day for Cd-polluted areas in the 1960s. Replacement of Cd-polluted rice paddy soil with clean soil resulted in substantial reduction in rice-associated Cd-D (Ikeda et al. 2015). Similarly, it is crucial to take preventive measures to achieve the discharge standards for industrial wastewater of the Japanese government to...
maintain the environmental quality parameters (tolerable limit for Cd is 0.03 mg/L by Ministry of Environment, Japan).

Electrocoagulation has been suggested as an effective method for removing various heavy metal pollutants from industrial wastewater (Merzouk et al. 2009; Akbal & Camci 2011; Un & Ocal 2015) and contaminated groundwater (Kumar et al. 2004; Parga et al. 2005; Balasubramanian et al. 2009; Vepsalainen et al. 2012).

Adsorption using clay minerals is also considered as a promising low-cost technique for removing metal ions from contaminated water. Bentonite, which is mainly composed of smectite, has been used as a low-cost adsorbent for the removal of heavy metal ions in single and competitive adsorption systems (Bereket et al. 1997; Kubilay et al. 2007; Karapinar & Donat 2009; Huang et al. 2011; Anna et al. 2015; Boroomand & Shokria 2017).

Electrocoagulation and adsorption onto bentonite are considered as effective methods for the removal of heavy metal ions. The combination of these two methods might be useful for improving water quality at a low cost.

Uchibori et al. (2008, 2010) concluded that the aggregation of clay particles was promoted by electrochemical treatment, and a significant decrease in residual turbidity was observed at higher mixing intensities. Moreover, Kubilay et al. (2007) described the effect of protonation (i.e., the adsorption of H⁺ ions in a solution) based on the point zero charge (pzc) of a clay surface on enhancing heavy metal adsorption onto bentonite as a result of changes in surface charges. The changes in H⁺ and OH⁻ ion concentrations in the solution caused the protonation or deprotonation of surface functional groups, which regulated the net surface charges of clay particles. They noted that clay samples had a higher affinity for adsorbing metal cations at high pH values.

In this study, we were focusing on enhanced Cd²⁺ ion adsorption onto bentonite by electrolysis, by changing the surface charges of the clay particles and facilitating the aggregation of the bentonite clay particles, ‘electrolytic aggregation’ which was not reported before.

The objective of this study was to investigate the removal efficiency of Cd²⁺ ions through their enhanced adsorption onto bentonite by electrolysis. We evaluated the adsorption capacity of Cd²⁺ ions onto bentonite after electrolytic aggregation. Our findings are expected to be useful for understanding the morphological changes of clay particles during electrolytic aggregation and their adsorption behaviors.

MATERIALS AND METHODS

In this study, preliminary experiments were conducted using 1 mg/L Cd²⁺-containing aqueous solutions, which prepared with pure water (Wako, Pure Chemical Industries Ltd, Japan) and tap water to identify the influence of the competitive typical alkali cations in water such as K⁺, Na⁺, Ca²⁺ and Mg²⁺ as well as the adsorption capacities of Cd²⁺ ions onto bentonite by stirring and electrolytic aggregation.

Based on the results of the preliminary experiments, electrolytic aggregation was effective to enhance the adsorption of Cd²⁺ ions with the availability of other typical ions when compared to the stirring technique for Cd²⁺ adsorption. Thus, we continue other experiments by electrolysis of Cd²⁺-containing aqueous solutions, which prepared using tap water.

Preparation of solutions for electrolytic aggregation Cd²⁺-containing aqueous solutions were prepared using 1,001 g/L Cd standard solution (Cd(NO₃)₂ in 0.1 mol/L HNO₃) by adding tap water. An aqueous solution containing 1 mg/L of Cd²⁺ was used as the electrolytic solution for electrolysis after the dispersion of commercially available bentonite powder, which acted as an adsorbent and also participated in the aggregation process during electrolysis.

Experimental apparatus

A cylindrical acrylic resin cell of 17 cm diameter and 23 cm height was used as the reactor cell for the electrochemical reaction.

The electrode materials, used in the electrochemical process, were selected to increase the efficiency of the process. A nontoxic, inert platinized titanium, Pt-Ti (12 cm diameter, 12 cm height and 0.1 cm thickness) anode and a steel, Fe (14 cm diameter, 17 cm height and 0.1 cm thickness) cathode for electrolyzing Cd²⁺-containing aqueous solution with Bio-Rad power supply (Bio-Rad Power Pac HC, CA, USA) with 250 V output voltage. The steel electrode was cleaned using a commercially available rust removal agent. Then, it was cleaned with detergent and thoroughly washed with tap water before the experiments.

Current densities of electrodes

The current density J (mA/cm²) of the cylindrical electrodes was calculated by dividing the current I (A) by the effective
area $A_e$ (cm$^2$). The effective area of each cylindrical electrode was calculated as follows:

$$A_e = A_o + A_i + (2 \times A_{cs}),$$

where $A_o$, $A_i$ and $A_{cs}$ are the outer, inner and cross-sectional areas of the cylindrical electrodes, respectively. The effective areas and current densities of the anode for 1 and 2 L electrolytic solutions were 267.10 and 653.86 cm$^2$, and 7.49 mA/cm$^2$ and 3.14 mA/cm$^2$, respectively. The radial distribution of the current through the anode was used to calculate the current densities based on the corresponding effective area.

**Batch experimental procedure for investigating Cd$^{2+}$ ion adsorption onto bentonite**

The adsorption of Cd$^{2+}$ ions onto bentonite was examined using a batch experimental procedure at room temperature. Bentonite powder was dispersed in a Cd$^{2+}$-containing aqueous solution by magnetic stirring at a constant speed of 1,500 rpm. Then, the solution was used for electrolysis and the adsorption of Cd$^{2+}$ onto bentonite in the aqueous solution was evaluated.

First, the adsorption capacity of bentonite in the aqueous electrolytic solution was evaluated for current densities of 1.57, 2.36, 3.14 and 3.93 mA/cm$^2$ at a pH of 1.0, 1.5, 2.0 and 2.5 A in a 2 L solution. The area of electrodes in the Cd$^{2+}$-containing aqueous solution, that is the submerged area was considered as the effective area for the flow of electrical charges. The second experiment was conducted to examine the effects of the submerged area using 1 and 2 L electrolytic solutions. The third experiment was performed to identify the effect of the mass of bentonite on the adsorption of Cd$^{2+}$ ions. The mass of bentonite added to the 2 L electrolytic solution was 0.2, 0.4, 1.0 or 2.0 g, and 0.2, 0.4, 0.8, 1.0 or 1.5 g of bentonite was added to the 1 L electrolytic solution. A 10 mL sample aliquot was taken after the electrolytic solution before the start of the electrolysis. An unfiltered 5 mL sample aliquot was used to measure pH and EC, while a 5 mL sample filtered with a 0.45 µm pore size was used to measure the Cd$^{2+}$ concentration using an inductively coupled plasma-optical emission spectrometer (ICP-OES; Optima 5300DV, PerkinElmer, Shelton, CT, USA) at each retention time. A 1% HNO$_3$ matrix was used to prepare a blank solution, standard solutions (STD) and samples. All the experiments were conducted in duplicates or triplicates. Triplicate samples were analyzed for the Cd$^{2+}$ adsorption. The standard deviation (SD), %relative standard deviation (%RSD) values were tested. The %RSD values of adsorption data for measured ions (i.e. Cd$^{2+}$, Fe$^{3+}$, K$^+$, Na$^+$, Ca$^{2+}$ and Mg$^{2+}$ ions) were <5%.

**Analysis of zeta potential values to understand the aggregation behavior based on the pH of the electrolytic solution**

Samples were selected considering pH at the equilibrium after the electrolytic aggregation experiments. Triplicate samples were analyzed for each pH value using zeta potential and particle size analyzer (ELSZ-2000S, Otsuka Electronics Co., Ltd, Tokyo, Japan).

**Evaluation of Cd$^{2+}$ ion adsorption onto bentonite**

The removal percentage $R_{Cd}$ (%) and adsorption capacity $q_{e}$ (mg/g) of Cd$^{2+}$ ions were calculated using the following formulae (Kubilay et al. 2007; Karapinar & Donat 2009):

$$R_{Cd} = \frac{C_0 - C_e}{C_0} \times 100\%$$

$$q_{e} = \frac{(C_0 - C_e)V}{m}$$

where $C_0$ and $C_e$ are the initial and equilibrium concentrations of Cd$^{2+}$ (mg/L), respectively. $V$ is the volume of the solution (L) and $m$ is the weight of bentonite used as the adsorbent (mg).
RESULTS AND DISCUSSION

Electrochemical processes of electrolysis

Oxidation-reduction (redox) reactions occurred during the electrolysis of bentonite-dispersed Cd\textsuperscript{2+}-containing aqueous solutions. The Pt-Ti anode was an inert electrode and was not involved in the chemical reactions. However, the hydrolysis of water occurred resulting in the evolution of H\textsubscript{2} and O\textsubscript{2} by the oxidation of OH\textsuperscript{-} ions on the anode and the reduction of H\textsuperscript{+} ions on the cathode. Further, rust formed on the surface of the steel cathode.

Effect of current density on adsorption and desorption properties

The batch experimental procedure was conducted for different current densities (i.e. for different input currents in A). Figure 1(a) shows the Cd\textsuperscript{2+} ion concentration as a function of retention time for different current densities. The changes in the pH during the electrolysis process for different current densities are illustrated in Figure 1(b). The adsorbed Cd\textsuperscript{2+} ions were released into the electrolytic solution when a current was applied. The maximum desorption (\(d_{\text{max}}\)) occurred after a short retention time for a current density of 3.93 mA/cm\textsuperscript{2}, labeled as CD\textsubscript{4} in Figure 1(a), and \(d_{\text{max}}\) decreased gradually with decreasing current density (CD\textsubscript{4} to CD\textsubscript{1}). Even though the desorption rate was different for different current densities, the Cd\textsuperscript{2+} ion concentration and pH of the electrolytic solution at equilibrium were almost the same. After a retention time of 90 min, the four electrolytic solutions exhibited 96.4–97.4% Cd\textsuperscript{2+} ion removal, confirming that there is no effect of the current density (at low current densities) in the range of 1.57–3.93 mA/cm\textsuperscript{2} on the removal of Cd\textsuperscript{2+} ions from the aqueous electrolytic solution. The results of the experiments revealed that the selected low current densities did not affect the adsorption of Cd\textsuperscript{2+} ions onto bentonite after a retention time of 90 min.

Results of the experiment can be explained as below; when a current is applied, electrons flow in the opposite direction (steel cathode to Pt-Ti anode) to the current. Inside the electrolytic solution, the Cd\textsuperscript{2+} ions are attracted to the negatively charged faces of thin clay particle sheets by weak van der Waals forces. When a current is applied, the forces bonding the Cd\textsuperscript{2+} ions may be affected, allowing Cd\textsuperscript{2+} ions to move into the electrolytic solution. \(d_{\text{max}}\) increased with increasing CD owing to the increased flow of negatively charged electrons into the solution. This may increase the kinetic energy between the weak van der Waals bonding forces, increasing the frequency of the desorption process. Moreover, during the electrolysis, the hydrolysis of water occurs, resulting in the evolution of H\textsubscript{2} and O\textsubscript{2}. After the stabilization of the system, Cd\textsuperscript{2+} ions are readorsed onto the negatively charged faces.

Effect of amount of bentonite on adsorption of Cd\textsuperscript{2+} ions

To evaluate the effect of the amount of bentonite on the adsorption of Cd\textsuperscript{2+} ions, the results of the batch experiment using 1 L of aqueous electrolytic solution are illustrated in Figure 2(a) and 2(b).
The \( \text{Cd}^{2+} \) ion concentration decreased with increasing retention time. At the beginning of the electrolysis, desorption occurred (see Figure 2(a) after 0 min). Moreover, adsorption proceeded after the stabilization of the chemical bonding of bentonite particles. The adsorption increased with increasing amount of bentonite added to the electrolytic solution. Moreover, the \( \text{Cd}^{2+} \) ion concentrations of the electrolyzed solutions with 1.0 and 1.5 g of bentonite added were almost the same after a retention time of 90 min. The final electrolytic solutions were moderately acidic (3.13 and 4.59) or slightly acidic (5.27) in the case of using 0.2, 0.4 and 0.8 g of bentonite, respectively. On the other hand, the final solution was neutral (pH 7.14) for 1.0 g of bentonite. The results of the experiment suggest that the amount of bentonite, which is added as an adsorbent to accelerate the removal of \( \text{Cd}^{2+} \) ions in the electrolysis process, regulates the properties of the final solution. Further treatment is necessary before the treated solution is used as a drinking water source or released into the environment. The opportunity cost of bentonite addition or the cost of pH adjustment should be considered when selecting a suitable amount of bentonite as an adsorbent.

**Dependence of adsorption on submerged area**

The amount of adsorption in different amounts of electrolytic solutions (i.e. for different submerged areas) and the changes in pH during the electrolysis process were evaluated (Figures 2 and 3). We used 1.0 and 2.0 L electrolytic solutions with different amounts of bentonite. Figure 2(a) and 2(b) show the adsorption behavior and changes in pH for different amounts of bentonite during the electrolysis of 1 L electrolytic solutions. The submerged area for the 1 L solutions was 267.10 cm\(^2\), which resulted in CD of 7.49 mA/cm\(^2\) during electrolysis. The same experiment was conducted for 2 L electrolytic solutions while varying the amount of bentonite. The submerged area for the 2 L solutions was 635.86 cm\(^2\), which resulted in CD of 3.14 mA/cm\(^2\) (see Figure 3(a) and 3(b)). Interestingly, when the amount of bentonite was increased, the amount of \( \text{Cd}^{2+} \) removal increased accordingly. The maximum removal of \( \text{Cd}^{2+} \) ions was 97.3%, which occurred when 2.0 g of bentonite (i.e., 1.0 g/1 L) was added.

The electrolytic solutions with different amounts of added bentonite were neutral to alkaline. The equilibrium pH values of the 2 L electrolytic solutions with 0.2, 0.4, 1.0 and 2.0 g of bentonite were 7.08, 6.67, 8.26, and 8.93, respectively, after a retention time of 90 min.

The pH of the electrolytic solution was regulated by the amount or frequency of the hydrolysis of water, resulting in the evolution of \( \text{H}_2 \) and \( \text{O}_2 \), the amount of negatively charged electrons introduced into the solution by the applied current, and the amount of \( \text{H}^+ \) ions attracted onto the negatively charged faces of the bentonite particles. The 1 L electrolytic solutions remained strongly acidic when 0.2 and 0.4 g of bentonite were added. Thus, it is crucial to determine an appropriate submerged area when designing a treatment system for electrolysis.

Moreover, the results of the experiments for different submerged areas suggest that the adsorption of \( \text{Cd}^{2+} \) ions onto bentonite in an electrolytic solution is highly regulated by the pH of the solution. The pH of the electrolytic solution
varies with the amount of bentonite and the submerged area (resulting different current densities) of the electrodes.

pH dependence of adsorption of Cd\(^{2+}\) ions onto bentonite in aqueous electrolytic solution

The aqueous electrolytic solutions were initially neutral. The pH of the aqueous electrolytic solutions during the electrolysis changed with the amount of bentonite and the retention time. During the electrolysis, hydrolysis occurred, introducing H\(^+\) and OH\(^-\) ions into the electrolytic solution. This process regulated the adsorption of Cd\(^{2+}\) ions onto bentonite, resulting in the limited adsorption of Cd\(^{2+}\) ions.

In the aqueous solution, the positive cations are attracted to the surface of the bentonite particles. Because natural montmorillonite (bentonite) is composed of sheets of tetrahedra, Si\(^{4+}\) ions might be partially replaced by Al\(^{3+}\) ions, and in sheets of octahedra, Al\(^{3+}\) ions might be replaced by Mg\(^{2+}\), Fe\(^{2+}\), Zn\(^{2+}\) or another ion with a lower-valence. The replacement of Si\(^{4+}\) and Al\(^{3+}\) ions with lower-valence ions resulted excess negative charges (i.e. isomorphic substitution) (Briaud 2013; Prasad & Nardo 2015). As a result of isomorphic substitution, the surface of bentonite particles is negatively charged except at their ends, where positive charges may appear owing to the broken bonds. Thus, the particles can attract or repel each other. Moreover, the attraction of the particles influences the structure of the bentonite as it develops (i.e. flocculated or dispersed) (Briaud 2013). Wilkinson et al. (2017) and Preocanin et al. (2016) discussed the morphological changes of bentonite and other clay minerals in terms of the pH of the aqueous solution.

According to the pH dependent morphological description of Wilkinson et al. (2017), individual bentonite clay particles, described as thin sheets or flakes, can self-interact in three different ways: edge–edge, face–face and edge–face. Edge–edge interactions lead to chainlike morphologies, whereas face–face interactions lead to dense stacks. Edge–face interactions produce very open and random morphologies. According to their findings, at pH 4, bentonite aggregates exhibit open edge–face– and edge–edge-dominated structures, whereas at pH 8.5, bentonite aggregates exhibit a dense face–face-dominated structure.

The Cd\(^{2+}\) removal (%) for different amounts of bentonite (g) and the changes in pH during the electrolysis are plotted in Figure 4. There was no significant removal of Cd\(^{2+}\) ions \(R_{\text{Cd}}\) for 0.2, 0.4 and 0.8 g of bentonite. However,
the equilibrium electrolytic solution changed from moderately acidic to slightly acidic with increasing amount of bentonite. $R_{Cd}$ for the cases of 1.0 and 1.5 g of bentonite was 77 and 80%, respectively, while the solution remained neutral. There is a significant difference between $R_{Cd}$ in the ranges of 0.2–0.8 g and 1.0–1.5 g of bentonite, while the solution changes from acidic to neutral with increasing amount of bentonite. The significant increase in the removal of Cd$^{2+}$ ions from 0.8 to 1.0 g of bentonite suggests that the pH of the electrolytic solution at equilibrium significantly regulates the adsorption. This behavior might be due to the morphological changes in the bentonite by changing from acidic to neutral. The adsorption at 0.2, 0.4 and 0.8 g remains limited owing to the similar surface charges of the bentonite surface under acidic conditions. Under acidic conditions, positively charged edges are attracted by negatively charged faces to form an edge-face-dominated structure. This may limit the adsorption of cations in the electrolytic solution. In the cases of 1.0 and 1.5 g of bentonite in a neutral solution, bentonite clay particles aggregate to form a face-face-dominated structure. Positively charged cations might be attracted to both faces in the face-face-dominated structure. Kubilay et al. (2007) and Preocanin et al. (2016) discussed the effect of the solution pH on the surface charge of bentonite and other clay minerals. According to Kubilay et al. (2007), in the case of heavy metal adsorption onto bentonite in a single-metal system, adsorption increased with the initial pH. Their findings suggest that when the measured pH of a colloidal system is less than the point of zero charge (pzc), there is competition from H$^+$ ions for the surface complexation sites on clay surfaces, resulting in the surfaces having a positive net charge. In contrast, if the pH is higher than pzc, the net change is negative. Thus, surfaces with negative charges attract metal cations in the solution.

**Limited adsorption of Cd$^{2+}$ ions in aqueous electrolytic solution**

The limited adsorption of Cd$^{2+}$ ions onto bentonite is next discussed on the basis of the results of the electrolysis experiment. The maximum adsorption capacities at equilibrium (i.e. 90 min retention time) for different amounts of bentonite are plotted for 1 L (submerged area 267.10 cm$^2$) and 2 L (submerged area 635.86 cm$^2$) electrolytic solutions in Figure 5. The adsorption capacity decreased nonlinearly with increasing amount of bentonite added to the electrolytic solution. The adsorption capacities for 0.8, 1.0 and 1.5 g of bentonite were 0.78, 0.69 and 0.57 mg/g, respectively. These results suggest that the adsorption capacity is limited by the changes in the surface charges of bentonite in the aqueous electrolytic solution.

According to the t-test results, there was no significant effect of adsorption capacity of 1 L and 2 L of Cd$^{2+}$-containing aqueous solutions by adding different dosage of bentonite. However, it highly regulated the pH of the electrolytic solution at the equilibrium, after 90 min (i.e. for 1 L 0.2–1.0 g of bentonite, pH vary from acidic (3.13) to neutral (7.34) while for 2 L 0.2–2.0 g of bentonite, pH remained >7 (neutral to slightly alkaline) for all tested solutions.

Olu-Owolabi et al. (2010) studied the removal of Cu$^{2+}$ and Cd$^{2+}$ from an aqueous solution by bentonite clay modified with a binary mixture of goethite and humic acid. They investigated the equilibrium adsorption capacity of bentonite for Cu$^{2+}$ and Cd$^{2+}$ decreases with increasing adsorbent dose from 0.2 to 2.0 g in a 200 mg/L metal ion solution.

The results of our study are also in agreement with those of Olu-Owolabi et al. (2010), suggesting that the decreased equilibrium adsorption capacity $q_e$ of metal ions by bentonite as its amount was increased can be attributed to the reduced total surface area of the adsorbent resulting from the aggregation of bentonite particles. This reconfirms that the limited adsorption capacity is due to the pH of the equilibrium electrolytic solution, which causes the morphological changes in bentonite (see Figure 6). The equilibrium solution changes from slightly acidic to neutral with increasing amount of bentonite from 0.8 to 1.5 g, resulting in the formation of aggregated bentonite particles. This leads to the limited adsorption capacity.
Wilkinson et al. (2017) supports the findings of our study. They discussed the pH dependences of the bentonite aggregate size and morphology on polymer clay flocculation. The zeta potentials (zp) of the aqueous bentonite solutions varied from $-73$ to $-106$ mV, in the pH range of 3 to 11 resulting in average particle sizes of bentonite ranging from 2.0 to 4.5 µm.

Moreover, several studies investigated the aggregation behavior of clay minerals such as bentonite and kaolinite on the basis of the pH and zp of the clay suspension solution (Yukselen & Kaya 2003; Mekhamer 2011; Au & Leong 2013). The zp of the clay mineral suspension increased with increasing pH of the suspension. The results of our study also accord with their findings.

At a low pH the negative zeta potential becomes smaller in magnitude owing to the permanent surface charges formed by the isomorphic substitution of lower-valence metal ions in the clay crystal structure being progressively neutralized by the pH-dependent positive edge charges (explained by the edge–face-dominant structure in Figure 4), which becomes more important with decreasing pH (Au & Leong 2013). These positive edge charges are not sufficient to completely neutralize all the permanent negative charges even at a low pH. Further, the transformation of surface charges can be explained by the hydroxyl group functionalization at the edges of bentonite sheets.

At a low pH, the surfaces become positively charged (protonation), while at a high pH the surfaces become negatively charged. Overall, the changes in the concentrations of $H^+$ and $OH^-$ ions in the solution cause the surface functional groups and clay minerals to protonate and deprotonate by the adsorption of $H^+$ or $OH^-$ ions (Kubilay et al. 2007; Wilkinson et al. 2017).

According to the Figure 6(b), in an alkaline solution, the $OH^-$ ions are closer to the Stern layer of the electrical double layer, resulting in an increased zp magnitude. On the other hand, the decrease in the zp magnitude at a low pH is attributed to the adsorption of $H^+$ ions on the surface of bentonite and the increased ionic strength. Clay particles tend to aggregate when the negative ions of the electrical
double layer are close to the surface. The particles become stable with increasing distance from the surface. This creates an open structure for competitive ions and enables surface neutralization by negatively charged edges. In conclusion, the H\(^+\) and OH\(^-\) ions regulate the morphology of aggregates of clay particles, which governs the adsorption of cations onto negatively charged surfaces.

**CONCLUSIONS**

The adsorption of Cd\(^{2+}\) onto bentonite was discussed on the basis of the pH changes of the tested electrolytic solutions. There was no effect of the current density at low values (i.e., 1.57–3.95 mA/cm\(^2\)) on the removal of Cd\(^{2+}\) ions.

The maximum adsorption capacities at equilibrium for current densities of 3.14 and 7.49 mA/cm\(^2\) (i.e. for 2 and 1 L electrolytic solutions) with 0.2 g of bentonite were 4.54 and 2.92 mg/g, respectively. The pH values of the corresponding electrolyzed clay suspensions were 7.08 and 3.13. This result confirmed that the adsorption is regulated by the pH of the electrolytic solution and not by the current density. Moreover, the higher current density of 7.49 mA/cm\(^2\) accelerated the hydrolysis process, resulting in a more acidic solution with a pH of 3.13 at equilibrium, limiting the adsorption capacity. The amount of bentonite, which was added as an adsorbent to accelerate the Cd\(^{2+}\) ion removal in the electrolysis process, regulated the properties of the final solution.

Overall, the H\(^+\) and OH\(^-\) ion concentrations and the pzc of clay particles regulate the morphology of aggregated clay particles, which governs the adsorption of cations onto the negatively charged surfaces.

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