

Selective Adsorption of Cadmium Species onto Organic Clay Using Experimental and Geochemical Speciation Modeling Data

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Abstract—The effect of cadmium speciation on cadmium adsorption onto Hexadethyl-trimethyl ammonium (HDTMA) modified montmorillonite was investigated experimentally and using Minteqa2 geochemical speciation model. The results revealed that the increase in cadmium uptake at higher pH values is selective and directly related to the nature of species present and that this increase does not affect the form of cadmium species adsorbed onto the HDTMA modified montmorillonite.

Index Terms—Adsorption, cadmium removal, cadmium speciation.

I. INTRODUCTION

Cadmium is a toxic heavy metal classified as a carcinogen and teratogen of significant environmental and occupational concern [1], [2]. It is present in different wastewater sources such as mining, smelting, electrolyzing, painting, alloying, electroplating, textile processing and printing, to name a few sources. Given the pervasive cadmium contamination and the low treatment standards [3], there is considerable interest in the development of techniques to remove cadmium from contaminated water and wastewater. Traditional methods for the removal and recovery of cadmium from industrial waste water are precipitation, ion exchange, electrolysis, and adsorption on activated carbon [4]-[7].

Adsorption has been developed as an efficient method for the removal of heavy metals from contaminated water and soil. A variety of adsorbents, including clays, zeolites, dried plant parts, agricultural waste biomass, biopolymers, metal oxides, microorganisms, sewage sludge, fly ash and activated carbon, have been used for cadmium removal [1], [8].

However, many techniques that have been used have their drawbacks and shortcomings. Use of large amounts of reagent and creation of second pollution are the flaws of precipitation method, while high cost is the main problem of the ion exchange method, membrane separation method and adsorption method by activated carbon.

Organo-clays have increasingly been used as adsorbents because they are cheaper than other materials such as activated carbon and zeolites. In many cases, organo-clay linings have been used as barriers in landfills to prevent contamination of groundwater and subsoil by leachates containing metals [9]. Bentonite and montmorillonite clays

are usually chosen to avoid pollutant release into the environment as adsorbents due to their high specific surface areas, low cost and common presence in most soils [10].

Organo-clays are natural ion exchangers and adsorbents. They have a structure containing an excess of fixed negative or positive charge and take up ions from solution as needed to neutralize the charge. They can preferentially adsorb some types of ions relative to other ions; therefore the ratio between different counter-ions on an ion exchanger is usually not the same as the ratio between those ions in solution [11].

The type of clay is significant as its ability of clay to accumulate metals decreases, as seen in the following order: montmorillonite > vermiculite > illite > chlorite > kaolinite > [12]. In general it may be said that the greater the ability of clay to expand and effectively increase its surface area, the more metals it can accumulate. Clays can therefore contain considerable quantities of metals both on the surface and in between layers.

In an earlier paper [7] montmorillonite was modified with HDTMA to increase its surface area and pore size and hence its adsorptive capacity. The results revealed increased adsorption capacity of the modified montmorillonite for cadmium complexes in general and at higher pH values. Although this is advantageous for cadmium removal from contaminated water and wastewater, cadmium exists as a free divalent cation under common environmental conditions dominated by pH values up to 8 [7], [13]. Furthermore, in our previous investigations the adsorption isotherms were found to follow both Freundlich and Langmuir very well and showed slightly better fit with the latter isotherm [7].

These observations led to the identification of chemical reduction and surface precipitation as the limiting mechanisms for cadmium adsorption onto HDTMA modified montmorillonite.

In this paper, the limitations posed by cadmium speciation and the role speciation plays in cadmium adsorption onto the HDTMA modified montmorillonite are investigated using experimental results and geochemical equilibrium modeling.

II. METHODOLOGY

A. Experimental Methods

HDTMA modified montmorillonite was prepared by adding HDTMA to the full Cation Exchange Capacity (CEC) of the clay using the methodology described elsewhere [7].

Adsorption experiments were then conducted with cadmium using 200-ml flasks. Stock solution of cadmium

was prepared and added to the desired initial concentrations. Cadmium concentrations were measured before and after each pH adjustment. In the case of controlled pH experiments, the pH was periodically checked during the adsorption process and adjusted using buffer solutions; a minimal headspace was allowed to insure good mixing throughout the adsorption experiment. The flasks were shaken in a Gyrotory shaker model G33-B positive rotary motion shaker (250 rpm) for about 18 to 24 h. Following the reaction period, the flasks were allowed to settle and samples were taken for analysis of residual aqueous concentrations. Phase separation was achieved by filtration using 0.45- μm membrane filters.

Samples were analyzed for cadmium concentration using a multiple ion meter (pX meter) model 925 (Fisher Scientific), which measures pH, voltage, temperature and ion concentration. The electrode used was an Orion combination electrode (sure-flow combination electrode model 9648), pH changes were accounted for with regard to the electrode potential behavior versus pH and limits of detection.

Prior to the measurement of concentrations, the samples were prepared in 50-ml beakers after being filtered and adjusted for ionic strength. The ionic strength adjustment was done after the pH measurement, this is because the electrode performance depends solely on the use of ionic strength adjuster (5M NaNO_3 , model 940011).

B. Geochemical Modeling

A geochemical equilibrium model (MINTEQA2) [14] was used to study the speciation of cadmium (30 mg/l) solution leaving pH free and fixing the pH as desired.

III. RESULTS AND DISCUSSION

Organo-clays consist of composite layers of tetrahedrally and octahedrally coordinated cations. Layers of silica-oxygen tetrahedra are connected by cation-hydroxyl layers, the most common cations being aluminium ion and magnesium ion. Water molecules are also often found in between the layers [15].

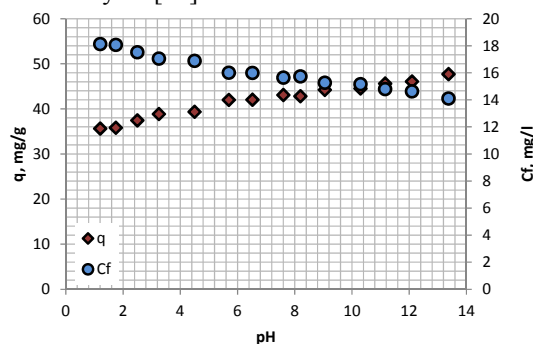


Fig. 1. Adsorption of cadmium onto modified montmorillonite as a function of pH.

The clay minerals differ in their cation exchange properties according to the nature of their interlayer cations and residual surface charges. In clays, Si, Mg and Al are often replaced by other cations with similar sizes but different charges. Thus, the surface of the clay can become negatively charged, which attracts more metal ions [16].

Adsorption of metals onto clays is influenced both by the number of free bonding sites on the clay surface and by the

proportion of atoms replaced with others of different valencies in the clay. The pH, the charge and the hydration of the metal species also influence adsorption.

Upon fully exchanging HDTMA the montmorillonite interlayer structure changes and its pores becomes larger enabling a larger surface area and ability to accommodate larger metal molecules [17].

Fig. 1 shows an increased uptake of cadmium species as a function of pH and increased removal efficiency. This enhancement of adsorption at higher pH values indicates favorable adsorption of hydroxo-complexed cadmium ions for reasons related to the nature of adsorption process whether thermodynamic or chemical. This phenomenon is clear from the Minteqa 2 geochemical modeling results shown in Fig. 2.

(q) is the solid phase concentration and (C_f) is the final cadmium concentration plotted on the secondary axis.

Fig. 2 shows the distribution of cadmium species with pH. In the base case, the equilibrium pH was about 6.8, and cadmium mostly exists as a free ion. When the pH was fixed at 12, the speciation contained only hydroxyl species (59% CdOH_2^0 and 40% CdOH_3^-) and no solids precipitated, and therefore at such low cadmium concentrations precipitation is not a removal mechanism [7]. Fig. 2 can be used to infer upon the quantities of hydroxocomplexes adsorbed and the nature of the adsorption process. At pHs up to 8 cadmium exists solely as a free ion, and the increase in adsorption capacity is attributed to clay behavior while at higher pHs (10, 12) the formation of cadmium hydroxocomplexes increases significantly and surface reaction with clay may be the sole mechanism of adsorption as in the case of pH 12.

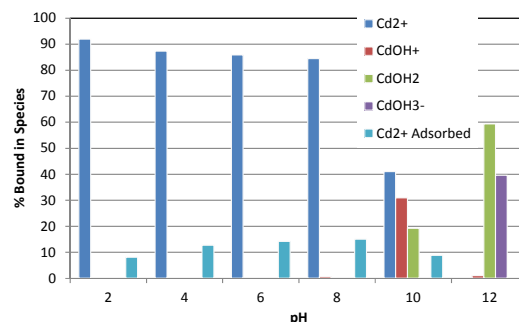


Fig. 2. Minteqa2 speciation results of 150 ml of 30 mg/l Cd and 50 mg modified clay.

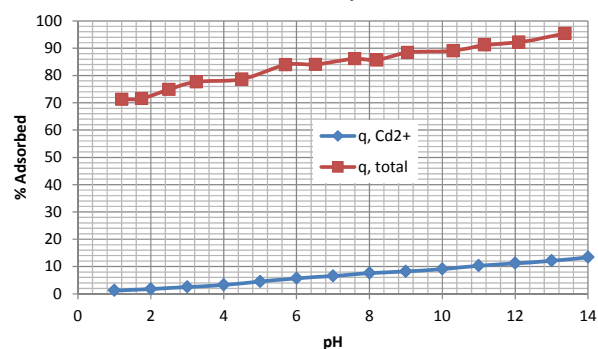


Fig. 3. Experimental percentage of total cadmium uptake from solution versus pH and the Minteqa2 predicted divalent cadmium cation uptake percentage.

Fig. 3 reports the experimental total cadmium species adsorbed versus pH compared to the Minteqa 2 predicted

adsorbed divalent cadmium ion. Although Minteqa 2 under predicted the adsorbed divalent free cadmium ion (as can be clearly seen from Fig. 2), it is also clear that the modified montmorillonite adsorption capacity increases with pH for all ions. Notwithstanding, the increase in capacity for both the free divalent ion and the total cadmium is equal as can be seen in Fig. 3. These phenomena suggest that the uptake of cadmium onto modified montmorillonite is mostly thermodynamic and the final form of cadmium within the clay is the free divalent cation.

Due to the isomorphous substitutions in the aluminosilicate layers of the montmorillonite, it usually has a net negative charge, which is balanced by alkali metal and alkaline earth metal cations such as Na^+ and Ca^{2+} . The strong hydration of these inorganic cations creates a hydrophilic environment on the surface and in the interlayer region of natural montmorillonite.

When these cations are replaced by organic cations, producing an organoclay structure, the montmorillonite clay becomes hydrophobic in character and can be used to remove hydrophilic and hydrophobic contaminants from water. The substitution of Na^+ or Ca^{2+} by quaternary ammonium cations (such as HDTMA) at the exchangeable sites of natural montmorillonite results in organoclay derivatives with organophilic properties that can act as sorbent for different contaminants.

It can be observed from the results that the adsorption of cadmium increases with increase in the pH of the solution. This is true regardless of the concentration of the solution investigated. Organo-clays are known to possess a negative surface charge in solution. As pH changes, surface charge also changes, and the sorption of charged species are affected (attraction between the positively charged metal ion and the negatively charged clay surface). It is conceivable that at low pH values, where there is an excess of H^+ ions in solution, a competition exists between the positively charged hydrogen ions and metal ions for the available adsorption sites on the negatively charged clay surface. As the pH increases and the balance between H^+ and OH^- are more equal, more of the positively charged metal ions in solution are adsorbed onto the negative clay surface and thus the percentage removal of the metal ions increases.

This is in agreement with work by other authors [18]. On the other hand, precipitation of metal hydroxides may also occur as the pH in solution increases, which will lead to a corresponding decrease in the amount of metal ions adsorbed onto the clay but an increase in the overall removal efficiency. Our results are in agreement with these broad outlines.

In order to understand the adsorption mechanisms of cadmium species in relation to pH, it is necessary to improve the knowledge of their behavior in the clay-solution system. The most important processes regulating the free concentration of heavy metals in natural media, such as the adsorption and release (desorption) by solid surfaces, highly depend on interfacial chemical reactions.

Generally, montmorillonite removes metals in a variety of ways [19]:

- Cation-exchange when the exchangeable sites are available or when metal ions present in the clay are exchanged for metals in the solution.
- When the clays have high surface area it allows them to bind to a large number of metal species present in the solution.

- Organic matter in the clay can form complexes with metal species in the clay.

In all of these removal mechanisms the pH of the solution is an important variable which controls the removal process and eventually the adsorption of the metal ion at the montmorillonite-solution interface.

Adsorption of heavy metals at montmorillonite-water interface can be described as surface complexation mechanism [21]. The uptake of heavy metals by clay minerals is obviously more complicated. The chemical nature of the metal-clay interaction changes with increasing pH: at low pH values cation exchange is the dominating process [20], [22], whereas at high pH values, the uptake of heavy metal ions is accompanied by a release of hydrogen ions, and seems to be more specific than the uptake at low pH values. Thus, the classical ion exchange model does not cover the whole range of adsorption phenomena and a part of heavy metal adsorption occurs at sites created by displacement of protons from surface hydroxyls (i.e. surface complexation) [23].

Yan *et al.* [24] suggested that the effect of pH may be interpreted on the basis of availability of binding sites present at the clay surface and that the adsorption of free cadmium ion (Cd^{2+}) can be described by utilization of both ion-exchange sites and specific adsorption sites. At low pH, Cd^{2+} is predominantly adsorbed on the permanent charge sites of Na^+ montmorillonite while a substantial portion of Cd^{2+} was probably adsorbed on the edge surfaces at higher pH [25]. This may explain the increase of total cadmium adsorption at higher pH values in tandem with the increased interlayer spacing of the clay [26].

This is in agreement with Barbier *et al.* proposal that the uptake of heavy metal ions by montmorillonite from solution, from acidic to basic conditions can be described by a model assuming two kinds of binding sites [27]:

- Ion exchange sites, XNa;
- Specific adsorption sites, surface hydroxyl groups $\text{Al}(\text{OH})(\text{OH}_2)$, which are amphoteric.

Ion exchange seems to be the main sorption phenomenon depending on the exchanged cation exchange capacity of the montmorillonite, but at low pH values, competition with protons is very important. Also, it appears that the HDTMA has higher ability to sorb cadmium oxyanion through exchange at the HDTMA positive charge sites.

Overall we can conclude that the increase in adsorption capacity of the modified montmorillonite is attributed to surface reaction with the cadmium species at the modified montmorillonite-solution interface. Additionally the free cadmium ion adsorption at higher pH values could be the result of ion-exchange process at the inner clay pores where ion-exchange sites have not been accessed and fully exchanged by the HDTMA.

IV. CONCLUSIONS

The conclusions of this preliminary investigation are as follows:

- 1) Cadmium uptake onto HDTMA modified montmorillonite is pH dependent.
- 2) The mechanisms of uptake are of thermodynamic nature as the increase in uptake at higher pH values is related to

the domination of different species than those at lower pH values.

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