ADSORPTION MECHANISM OF TOXIC METAL IONS BY CLAY (ATTAPULGITE)

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ABSTRACT

A series of adsorption tests were conducted to analyze the sorption capacity of attapulgite. Ions such as cobalt, nickel, lead and cadmium were adsorbed from waste solutions onto attapulgite surface. Adsorption depletion tests were performed as a function of solid to liquid ratio, conditioning time, heavy metal ion concentration, and pH to identify the mode and extent of interactions in the system. Conditioning time data confirm that ion exchange is nearly complete after 30 seconds indicating the fast kinetics of the ion exchange process. Solid to liquid ratio data suggest that optimum ratio is 50g/Liter. The adsorption isotherms constructed as function of heavy metal concentration and pH reveal that adsorption of metal ions increase in the order of Co < Ni < Cd < Pb.

The attapulgite was found to be rather receptive to the adsorption of heavy metal ions, and fairly high amounts of calcium, potassium and magnesium ions were desorbed from the attapulgite into the solution. A quantitative analysis of the adsorption results indicates that a one-to-one ion exchange mechanism is responsible for the incorporation of cations into the structure of attapulgite. The results show that attapulgite, similar to sepiolite, is a potential clay mineral for the removal of toxic metal ions from wastewater streams.

INTRODUCTION

As environmental pollution becomes of greater concern, alternative methods to filter wastewater are being studied. The interest or cheaper and more efficient adsorbents is mounting causing greater amounts of research to be conducted about adsorption. One of these areas of research is focusing upon cation exchange resins, such as clay, to abate wastes from water [1]. Attapulgite and sepiolite, both members of the palygorskite family, are two such clays that adsorb metal cations from solution.

Attapulgite is a crystalline hydrated magnesium aluminum silicate with a unique chain structure that gives it unusual colloidal and sorptive properties. It consists of a double
chain of tetrahedrons of silicon and oxygen (Si₄O₁₁) running parallel to the long axis. A layer of magnesium atoms in six-fold coordination links upper and lower parts of each double chain. The overall structure resembles a channeled wall where every second brick is missing [2]. Attapulgite’s unique structure presents two unusual characteristics. First, the clay cannot swell because the structure consists of three-dimensional chains. Second, an unusual needlelike shape is formed by cleavage parallel to the 110 plane along the Si- O-Si bonds holding the strips together. These needle-like formations generally remain in bundles, similar to haystacks, giving attapulgite products their principle structural feature [3].

The extremely large surface area of attapulgite, approximately 167 m²/g, makes it very sorptive in its natural form. Both external and internal structures contribute to this surface area. The internal bundles, or haystarchs, aid the external surface area in achieving great amounts of adsorption. Attapulgite can take up water to 200% of its own weight. During calcinations, the haystack structure of the clay becomes very porous. Pore volume is about 0.6 ml/g and pore diameter is about 200 Å. The creation of this porous structure is believed to be more important to sorptive capability than the high surface area of attapulgite [4]. Many studies were done on the selective adsorption by attapulgite. The order of sorptivity is suggested to be: water > alcohols > acids > aldehydes > ketones > n-olefins > neutral esters > aromatics > cycloparaffins > paraffins [5].

Attapulgite is very important gel-forming clay. Compared to other clays, it gives stable suspensions of high viscosity at relatively low concentrations. During dispersion disassociation of the bundles of needle-like crystals occurs. Thus a random lattice is formed that entraps liquid to increase the system’s viscosity. Attapulgite can thicken a large variety of liquids, including fresh and salt water. Attapulgite suspensions are thyrotrophic and non-Newtonian at all concentrations. A rapid increase in fluidity is apparent as the shear stress increase. Without sufficient shear force, attapulgite does not disperse well. Therefore, high shear mixers are needed to achieve optimum dispersion.

The viscosities of aqueous dispersions of attapulgite can run as high as 40000 cP and over [2].

1 EXPERIMENTAL

1.1 Materials

The attapulgite sample used in this study has been received from Words Company in Georgia, USA. The chemical analysis of this attapulgite grounded to minus 80 microns, was performed by inductively coupled plasma (ICP). Table 1 presents the impurity accompanying attapulgite. The surface area of attapulgite was found to be 167 m²/g by means of BET method using nitrogen as adsorbent. Three samples of attapulgite were prepared for surface area, and 167 m²/g is an arithmetic average of
these three results. Therefore, the accuracy of the 167 m$^2$/g surface area data was ensured by multiple samples.

### Table 1. Chemical composition of attapulgite

<table>
<thead>
<tr>
<th>Compound</th>
<th>% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>70.77</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>5.04</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.05</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.01</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.69</td>
</tr>
<tr>
<td>FeO</td>
<td>1.87</td>
</tr>
<tr>
<td>MgO</td>
<td>5.34</td>
</tr>
<tr>
<td>CaO</td>
<td>1.55</td>
</tr>
<tr>
<td>L.O.I</td>
<td>12.69</td>
</tr>
</tbody>
</table>

Adsorption experiments were conducted using attapulgite clay mineral and the heavy metal ions of Co$^{+2}$, Ni$^{+2}$, Pb$^{+}$ and Cd$^{+2}$. The heavy metal stock solution (10$^{-2}$ M) was prepared by dissolving CoCl$_2$, NiCl$_2$, CdCl$_2$ and Pb(NO$_3$)$_2$ (Fisher Grade) in deionizer water. For this study, the air-dried attapulgite was not subjected to any further pretreatment procedures. All experiments were conducted at room temperature. Solid to liquid ratio, conditioning time, effect of solution pH, and effect of heavy metal ions concentration on adsorption and desorption densities of these Mg$^{2+}$, Ca$^{2+}$ and K$^{+1}$ ions concentration were studied.

## 2 RESULTS AND DISCUSSION

### 2.1 Solid to Liquid Ratio

In order to perform accurate M$^{2+}$ adsorption /desorption experiments, the proper ratio of attapulgite weight to M$^{2+}$ ions must be determined. To determine this ratio, separate samples of dry attapulgite powder ranging in weight from 0.4-8.0 g were weighted and placed in 60 ml polyethylene bottles containing distilled water.

For the solid to liquid ratio study, attapulgite was added to each 10$^{-3}$ M Co$^{+2}$, Ni$^{+2}$, Pb$^{+2}$ and Cd$^{+2}$ solutions to obtain the appropriate solid to liquid ratio. For this experiment, the five solid to liquid ratios studied were 0.1, 0.2, 0.5, 1, and 2 in 10 cc solution, respectively.

Three samples of the 0.5/10 cc solid to liquid ratio were prepared because this has been the preferred ratio in past experiments. Therefore, the accuracy of the 0.5/10 cc solid to liquid ratio data was ensured by multiple samples. Once the samples were prepared, each was covered and stirred for six hours at a rate of 180 strokes per
minute. After stirring, the samples were centrifuged at 10,000 rpm for 15 minutes and the clear supernatants were collected in vials for analysis.

The presence of residual Co\(^{2+}\), Ni\(^{2+}\), Pb\(^{2+}\) and Cd\(^{2+}\) adsorb and Mg\(^{2+}\), Ca\(^{2+}\) and K\(^{+}\) desorb ions in the supernatant was determined using ICP.

The adsorption of M\(^{2+}\) onto attapulgite versus solid to liquid ratio is presented in Figure 1 and desorption density of exchangeable ions Mg\(^{2+}\), Ca\(^{2+}\) and K\(^{+}\) is presented in Figure 2.

Adsorption density decreases with increasing solid concentration at about 50 mg/ml then decreases after this level. The initial M\(^{2+}\) concentration for these experiments is 10\(^{-3}\) M (Co\(^{2+}\) = 58.98, Ni\(^{2+}\) = 58.70, Pb\(^{2+}\) = 207.0 and Cd\(^{2+}\) = 112.41 ppm) and the residual M\(^{2+}\) ions concentration are Co\(^{2+}\) = 0.27, Ni\(^{2+}\) = 0.52, Pb\(^{2+}\) = 0.31 and Cd\(^{2+}\) = 0.56 ppm. It appears that approximately 50 g/L solid to liquid ratio which provides over 99% of M\(^{2+}\) is adsorbed [9].

![Graph](Figure 1: Effect of solid to liquid ratio on adsorption of Pb\(^{2+}\), Cd\(^{2+}\), Co\(^{2+}\), and Ni\(^{2+}\) onto attapulgite. (Conditioning time of six hours, heavy metal ions initial concentration 10\(^{-3}\) M, Temperature 20°C, and pH 5-8)
2.2 Adsorption Equilibrium Time

The effect of conditioning time on adsorption density of M\textsuperscript{2+} ions onto attapulgite is presented in Figure 3 and adsorption density of exchangeable ions is presented in Figure 4.

These experiments were performed in order to quantify the time required for complete adsorption of M\textsuperscript{2+} ions onto the ion exchange sites of attapulgite. 50g/L solid to liquid suspension were prepared and sufficient M\textsuperscript{2+} ions were added to the suspension to produce 10\textsuperscript{-3} M heavy metal solutions. The total volume of the mixture was adjusted to 40 ml. After a period of time ranging from 30 s to 24 h, the suspension was centrifuged at 10,000 rpm for 15 min. The supernatant was determined by ICP (Perkin-Elmer Model 3800). After subtracting the residual M\textsuperscript{2+} ions concentration from initial, the adsorption density has been calculated. These experiments showed that M\textsuperscript{2+} ions adsorption onto attapulgite was a fast process. Over 87% of heavy metal ions adsorption is completed in the first 5 min. Also, desorption densities of Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, and K\textsuperscript{+1} reach maximum level in 5 min, too. Therefore, the equilibrium time before 5 min is needed to be studied. Figures 5 and 6 present the effect of equilibrium time from 30 s to 5 min on adsorption/desorption onto attapulgite.
Figure 3: Effect of equilibrium time on adsorption density of Co$^{2+}$ onto attapulgite. (Solid to liquid ratio 50 g/L, initial Co$^{2+}$ concentration 58.98 ppm ($10^{-3}$ M), temperature 20°C and pH 7.5 ± 0.2)

Figure 4: Effect of equilibrium time on desorption density of Mg$^{2+}$, Co$^{2+}$, and K$^{+1}$ onto attapulgite in the Co$^{2+}$ solution. (Solid to liquid ratio 50 g/L, initial Co$^{2+}$ concentration 58.98 ppm ($10^{-3}$ M), temperature 20°C and pH 7.5 ± 0.2)
**Figure 5:** Effect of equilibrium time on adsorption density of Co$^{2+}$, Ni$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$ onto attapulgite. (Solid to liquid ratio 50 g/L, initial M$^{2+}$ concentration ($10^{-3}$ M), temperature 20°C)

**Figure 6:** Effect of equilibrium time on desorption density of Mg$^{2+}$, Ca$^{2+}$, and K$^{+}$ onto attapulgite in the Co$^{2+}$ solution. (Solid to liquid ratio 50 g/L, initial Co$^{2+}$ concentration 58.98 ppm ($10^{-3}$ M), temperature 20°C, and pH 7.5 ± 0.2)
2.3. Effect of Solution pH on Heavy Metal Ions Adsorption

The effect of solution pH on M$^{2+}$ ions adsorption was determined for the pH range of 2.0 - 11.0 which would normally be found for example, in an electro kinetic soil reclamation process [8]. For this set of experiments, 11 samples of 0.05 solid to liquid ratio were prepared with 40 ml of total solution’s amount. The samples were shaken for 2 h at 400 rpm. Sufficient M$^{2+}$ salt was added to the suspension in order to make a $10^{-3}$ M M$^{2+}$ ions solution. 1 n NaOH and HCl were added to adjust the solution pH of each sample to a specific value between 2.0 and 11.0. The residual M$^{2+}$ concentration in solution was then determined by centrifugation and ICP analysis of supernatants. Significant amount of M$^{2+}$ ions adsorption in the pH range of 4.5 – 6.0 was found with over 99% adsorption at a solution pH > 8.

The adsorption and desorption densities as a function of pH are plotted in Figures 7 and 8, respectively. The experiment of heavy metal ion uptake by adsorbants showed a marked trend as follows: Pb$^{2+}$ > Cd$^{2+}$ > Co$^{2+}$ ≥ Ni$^{2+}$. It reveals that the absorbability by attapulgite independent on pH. The exchange of Ca$^{2+}$, Mg$^{2+}$, and K$^{1+}$ from attapulgite indicates the adsorption mechanism of heavy metal ions is governed mainly by ion exchange mechanism.

The double-layer theory predicts qualitatively correctly that the affinity of the exchanger for bivalent ions is larger than monovalent ions and that this selectivity for ions of higher valence decreases with increasing ionic strength of the solution. However, according to the Gouty theory there should be no ionic selectivity of the exchanger between different equally charged ions [10].

![Adsorption Isotherm of Heavy Metal Ions vs. pH](image)

**Figure 7:** Effect of solution pH on adsorption density of Co$^{2+}$, Ni$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$ onto attapulgite. (Solid to liquid ratio 50 g/L, initial M$^{2+}$ concentration $2 \times 10^{-3}$ M, temperature 20°C, and conditioning time 2 h for all samples)
2.4. Effect of Heavy Metal Ions on Adsorption onto Attapulgite

For the concentration study, 10 separate $2 \times 10^{-3}$ M heavy metal ions samples were prepared in the same manner described at page 8. Each sample had a 50 g/L solid to liquid ratio. Each sample was stirred at 180 strokes per minute for a different amount of heavy metal concentration: $5 \times 10^{-4}$, $10^{-3}$, $2.5 \times 10^{-3}$, $2.5 \times 10^{-2}$, $10^{-2}$, $2.5 \times 10^{-2}$, and $5 \times 10^{-2}$, respectively. After being stirred for its designed concentration, the samples were collected in vials for analysis.

The presence of heavy metal ions concentration and $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, and $\text{K}^{+}$ ions in the supernatant was determined using ICP.
Figure 9: Effect of heavy metal concentration on adsorption density of Co$^{2+}$, Ni$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$, onto attapulgite. (Solid to liquid ratio 50 g/L, temperature 20°C, conditioning time 2 h, and pH 4.80-7.60)

Figure 10: Effect of heavy metal concentration on adsorption densities of Mg$^{2+}$, Ca$^{2+}$, and K$^{+}$, onto attapulgite in the Pb$^{2+}$. (Solid to liquid ratio 50 g/L, temperature 20°C, and pH 6 ± 1.50).
Figures 9 and 10 illustrate the adsorption of heavy metal ions as a function of residual concentration onto attapulgite.

The adsorption isotherms in Figure 9 illustrate two distinct regions each characterized by different adsorption rates and mechanisms. In the first stage, adsorption takes place at a lower rate and is governed by ion exchange process. In the second stage, the adsorption is mainly characterized by chain-chain interaction through Van der Waals forces. However, the ion exchange process still continues to take place in a similar rate as the ion exchangeable ions release continues even in the plateau region.

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REFERENCES


