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# Evaluation of an Organoclay, an Organoclay-Anthracite Blend, Clinoptilolite, and Hydroxy-Apatite as Sorbents for Heavy Metal Removal from Water

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Heavy-metal laden effluents from industrial activities such as manufacturing and mining have caused widespread contamination of soil and water resources. Combined heavy metal and organic contamination may also leach from containment facilities such as landfills or other surface impoundments (Li and Li 2001). Traditional sorbent materials for treating aqueous heavy-metal contamination such as activated carbon and ion-exchange resins are effective, but have high capital and re-generation costs (Banat et al. 2002). Consequently, a need exists to identify low-cost, natural sorbents to treat water contaminated with heavy metals.

Organoclays are effective at removing relatively non-polar organic pollutants such as oil, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, chlorinated solvents, and gasoline hydrocarbons from water (Alther 2002; Smith and Jaffé 1994). However, little is known about the ability of these sorbents to remove heavy metals from solution. In addition, there are relatively little data that quantify the sorption of metals to organoclays, zeolites, and hydroxyl-apatite in flow-through, column reactors (which mimic field treatment systems).

Given the strict regulatory requirements on heavy-metal discharges to the environment, it is important to develop cost-effective sorbents that can treat metal-contaminated waters (or in some cases, water contaminated with both metals and organic pollutants). In this study, we evaluate the suitability of four sorbents (an organoclay, an organoclay/anthracite blend, a zeolite, and hydroxy-apatite) for the removal of heavy metals from water.

## MATERIALS AND METHODS

Four sorbents were evaluated in this study: an organoclay, an organoclay/anthracite blend, clinoptilolite and hydroxy-apatite (bone char). All sorbents were obtained from Biomin, Inc. in Ferndale, Michigan. The organoclay was exchanged with ditallowdihydrogenated-ammonium chloride at 40% of the cation-exchange capacity of the base bentonite. The tallow functional group represents a 16-18 carbon heterogeneous chain. The organoclay/anthracite blend is a mixture of 70% anthracite and 30% organoclay. Clinoptilolite (hydrated

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sodium, potassium aluminosilicate) is a natural zeolite. Hydroxy-apatite is created by the oxidization of animal bones. The mesh sizes and surface area of all sorbents are given in Table 1.

**Table 1.** Sorbent properties.

| Sorbent | Mesh Size | Surface Area ($m^2/g$) |
|---|---|---|
| Organoclay/Anthracite Blend | 8x30 | 0.97 ± 0.05 |
| Organoclay | 8x30 | 1.23 ± 0.69 |
| Clinoptilolite | 8x20 | 6.49 ± 0.70 |
| Hydroxy-Apatite | 10x28 | 83.85 ± 3.1 |

Metal sorption to the four sorbents was quantified using both batch equilibrium sorption isotherms and flow-through column experiments. For all flow-through experiments, a column constructed of 30-inch long (76.2 cm) by 3-inch diameter (7.62 cm) poly-vinyl-chloride (PVC) and fitted with flexible couplings, reducing bushings and NPT thread-to-5/8" hose fittings was used. Two layers of circular type-304 stainless steel woven cloth (20x20 mesh) were placed inside each end-fitting to suspend the sorbent inside the column and prevent sorbent material from entering the tubing. A 55-gallon (208.2 L) self-supporting polyethylene tank was used to prepare and hold the inflow metal solution. A Master-Flex peristaltic pump was used to force the aqueous-metal solution up through the column to displace void-space air and ensure maximum contact with the sorbent material.

Each packed column was back-flushed with clean water several times prior to each experiment in order to remove fines associated with the sorbent. After the fines were removed, the physical properties of each packed column were measured, including porosity, pore volume, sorbent mass, experimental flow rate and water residence time. These values are given in Table 2.

**Table 2.** Physical properties of packed columns.

| Sorbent | Mass (kg) | Porosity | Flowrate (mL/min) | Residence Time (min) |
|---|---|---|---|---|
| Organoclay/Anthracite | 2.90 | 0.37 | 158.30 | 8.20 |
| Organoclay | 2.94 | 0.36 | 156.02 | 8.00 |
| Clinoptilolite | 3.50 | 0.33 | 142.64 | 8.00 |
| Hydroxy-Apatite | 2.63 | 0.42 | 71.79 | 20.20 |

The aqueous-metal inflow solution was prepared using dry-reagent compounds. A solution containing 60 mg/L Cadmium, 150 mg/L Chromium, 120 mg/L Copper, 60 mg/L Nickel and 60 mg/L Zinc was pumped through columns containing the sorbents to be studied. In each experiment, samples were collected at times ranging from 15 minutes to several hours at the outflow of the column in 50-mL graduated polypropylene tubes and capped. Samples were analyzed for aqueous-metal species using Acetylene-Air Flame/Atomic Adsorption (Perkin-Elmer Model 5100PC) with single-element hollow cathode lamps. Two-point calibration curves were prepared from the stock solution for each element. Samples collected at the column outflow were diluted with water to bring the concentration within the linear range of the instrument. Check samples were used periodically throughout sample analysis to ensure quality control.

Batch isotherm experiments were performed by combining sorbent, the aqueous metal solution described above, and distilled deionized water in 50-mL polypropylene tubes. Sorbent masses used in each isotherm experiment were: 0.25 g hydroxy-apatite, 0.5 g clinoptilolite, 5 g organoclay, and 6 g organoclay/anthracite blend. The aqueous multi-metal solution was mixed with deionized (DI) water prior to contacting the sorbent materials in the following ratios: 100% (v/v) metal solution; 80% metal solution/20% DI water; 50% metal solution/50% DI water; and 20% metal solution/80% DI water. The tubes were capped and shaken for 5 days to ensure equilibrium was reached prior to sampling. After reaching equilibrium, the supernatant was removed and analyzed for the aqueous metal species using Acetylene-Air Flame/Atomic Adsorption (Perkin Elmer Model 5100PC) as described above. Tubes containing the diluted metal solution and no sorbent were carried through the experiment and analyzed to determine the initial concentration of each metal prior to contacting the sorbent. The difference in mass between the initial metal concentration and the concentration measured in the aqueous phase at equilibrium was considered to be sorbed to the solid phase.

The surface area of the sorbents was measured using a multipoint BET method (Gemini 2360 surface area analyzer, Micromeritics) with $N_2$ as the adsorbate. Surface area measurements were performed in triplicate.

## RESULTS AND DISCUSSION

Figure 1 (plots A-D) presents the breakthrough curves for each of the four sorbents. The vertical axis is relative concentration, defined as the ratio of the inflow concentration to the outflow concentration. In all cases, the breakthrough curves are approximately S-shaped (or are approaching an S-shape), which is characteristic of advective/dispersive transport through a water-saturated porous medium. The time for complete breakthrough varies with both metal type and sorbent, indicating that some metals are sorbing to a greater extent than others. In the absence of sorption, the relative solute concentration (defined as the influent concentration divided by the effluent concentration) is expected to equal 1 at 1 pore volume of flow. For all experiments, the number of pore volumes corresponding to a relative concentration of 0.5 (retardation factor) is greater than 1, indicating that there is measurable sorption of every metal to every sorbent. These results are presented in Table 3.

Competitive batch isotherm data are presented in Figure 2 (plots A-D). For sorption of all five metals onto each sorbent, sorption is non-linear, indicating the mechanism of metal uptake may be adsorption to reactive sites on the sorbent surface (McLean and Bledsoe 1992). Isotherm data were fit with a Langmuir isotherm:

$$C_s = \frac{bC_e N_{\max}}{1+bC_e} \quad (1)$$

where $C_s$ = amount of solute sorbed, $b$ and $N_{max}$ are isotherm parameters, and $C_e$ is the equilibrium aqueous solute concentration. Isotherm parameters and model fits are given in Table 4. Competitive sorption of Ni to all sorbents was very weak at all levels of aqueous metal concentration compared to the other metals in solution, and as a result, the Langmuir model was not used to describe these data.

**Table 3.** Experimental retardation factors[a] measured in four column experiments.

| Metal | Organoclay/Anthracite | Organoclay | Clinoptilolite | Hydroxy-Apatite |
|---|---|---|---|---|
| Cd | 1.75 | 1.5 | 18.5 | 151 |
| Cr | 2.25 | 3.25 | 20.0 | 166[b] |
| Cu | 2.25 | 3.0 | 47.0 | 177[b] |
| Ni | 1.75 | 1.25 | 11.5 | 50 |
| Zn | 1.75 | 1.75 | 27.5 | 106 |

[a] Retardation factor is number of pore volumes corresponding to 50% breakthrough.

[b] Estimated by extrapolation of available data.

Based on the results of the batch and column experiments, several important trends can be identified. For the organoclay/anthracite blend, it appears that sorption of all five metals is similar and relatively weak. Sorption increases for the pure organoclay, with percent sorbed descending in the following order for the batch experiments: Cr > Cu > Cd > Zn > Ni. The greater sorption of the metals to the organoclay compared to the organoclay/anthracite blend suggests that the organoclay is a better metal sorbent than the anthracite. Replacing the anthracite in the blend with organoclay results in a better sorbent for the metals. Sorption of the metals is further increased when the sorbent is changed to clinoptilolite, with percent sorbed descending in the following order: Cu > Cr > Cd > Zn > Ni. Unlike organoclays or anthracite, zeolites like clinoptilolite have polar (charged) surfaces that can effectively sorb metals or charged metal-hydroxides, and this feature of the sorbent likely explains its improved performance relative to the organoclay or organoclay/anthracite blend. Other zeolites, such as chabazite, may have a higher removal capacity than clinoptilolite, but these zeolites are more expensive and therefore may not be of practical use. The best metal removal from solution was observed for the hydroxy-apatite, with percent sorbed descending in the following order: Cr > Cu > Cd > Zn > Ni. The strong performance of this sorbent may be attributable to its relatively large internal porosity and correspondingly polar surface area. In general, the order of increasing sorptive capacity for all sorbents corresponded to an increase in measured surface area.

**Table 4**. Langmuir parameters for batch data and sorption capacity from column data.

| | | Column | Batch | | |
|---|---|---|---|---|---|
| Sorbent | Metal | Ultimate Mass Sorbed/Mass Sorbent (mg/kg) | $N_{max}$ (mg/kg) | b (L/mg) | $R^2$ |
| Organoclay/Anthracite | Cd | 51 | 87 | 0.21 | 0.75 |
| | Cr | 162 | 303 | 0.19 | 0.87 |
| | Cu | 131 | 303 | 5.50 | 0.98 |
| | Ni | 45 | N/A | N/A | N/A |
| | Zn | 48 | 44 | 2.60 | 0.88 |
| Organoclay | Cd | 61 | 270 | 0.01 | 0.96 |
| | Cr | 352 | 1,111 | 3.00 | 0.96 |
| | Cu | 212 | 833 | 6.00 | 0.99 |
| | Ni | 46 | N/A | N/A | N/A |
| | Zn | 60 | 200 | 6.30 | 0.95 |
| Clinoptilolite | Cd | 675 | 1,428 | 0.70 | 0.99 |
| | Cr | 1,187 | 3,333 | 1.50 | 0.96 |
| | Cu | 2,348 | 5,000 | 0.30 | 0.98 |
| | Ni | 219 | N/A | N/A | N/A |
| | Zn | 843 | 2,000 | 0.83 | 0.98 |
| Hydroxy-Apatite | Cd | 4,612 | 10,000 | 1.00 | 0.99 |
| | Cr | 13,231 | 25,000 | 0.40 | 0.97 |
| | Cu | 14,131 | 20,000 | 0.71 | 0.99 |
| | Ni | 1,603 | N/A | N/A | N/A |
| | Zn | 3,685 | 5,000 | 2.50 | 0.99 |

Although the organoclay and organoclay/anthracite blend did not perform as well for metal removal as the clinoptilolite or the hydroxy-apatite, it should be noted that these sorbents may still be well suited for waste streams that contain significant amounts of oil and grease (or other dissolved, nonpolar organic pollutants) and relatively small amounts of metals. The organoclay or organoclay/anthracite blend will effectively remove the organic contamination and still be able to remove small amounts of heavy metals. The authors do not know of other comparable dual-purpose sorbents that can effectively treat a mixed-contaminant wastewater stream.

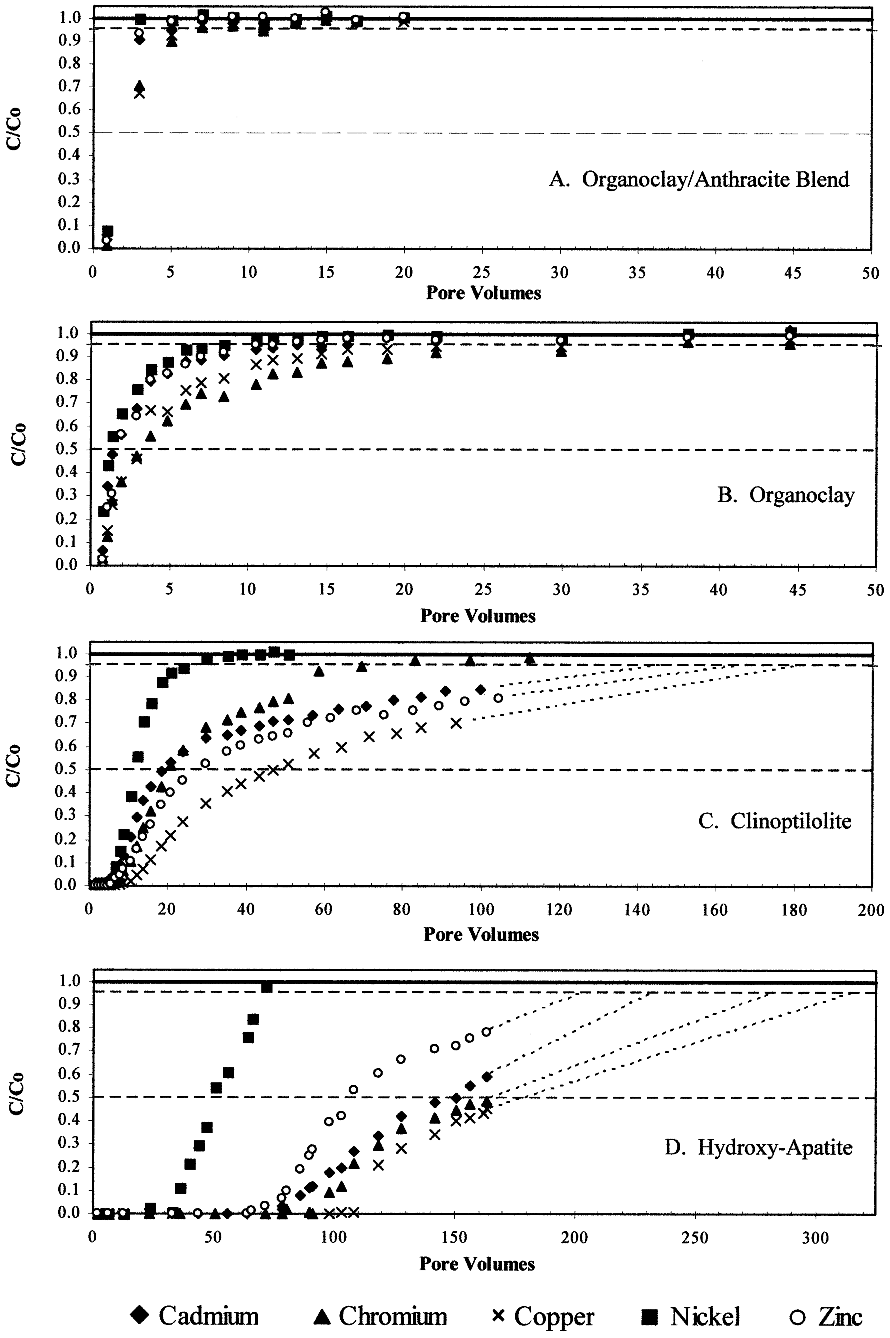

**Figure 1.** Breakthrough curves for column experiments.

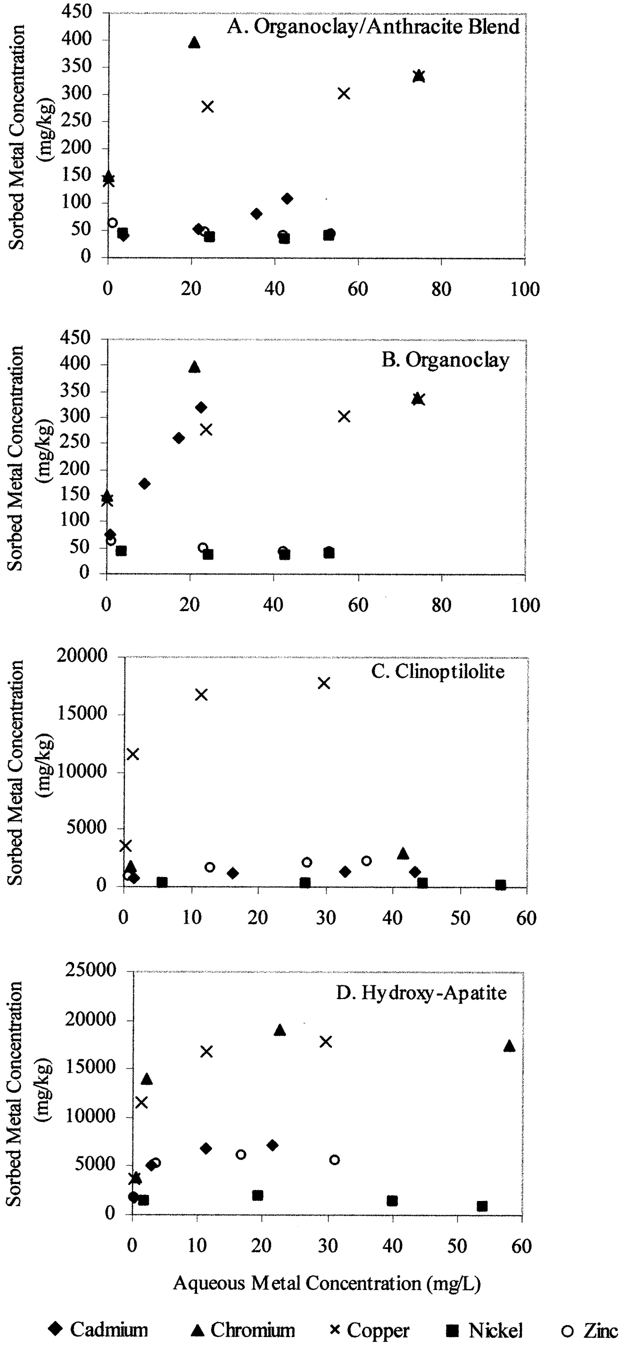

**Figure 2.** Competitive sorption isotherms for each sorbent.

Table 4 presents information on the mass of metals sorbed at equilibrium in the column experiments. These data were calculated from the breakthrough curves shown in Figure 1. We define breakthrough as the point where the relative concentration equals 0.95. For the transport of some metals through the clinoptilolite and hydroxy-apatite columns, relative concentrations of 0.95 were not reached during the experimental monitoring period, so the breakthrough curves were extrapolated to calculate the values in Table 4. The extrapolated curves are shown in Figure 1 as dashed lines. These data are compared to the Langmuir isotherm parameter, $N_{max}$ which represents the sorption capacity of the solid (Langmuir 1997).

For nearly all sorbent-metal combinations, the sorption capacity estimated from the column experiments is less than the value of $N_{max}$ calculated from the batch isotherm data. It is possible that the column experiments have not achieved complete breakthrough and the sorbents are not at capacity with regard to metal sorption. If sorption is rate limited, sorption may continue at a slow rate even after the effluent concentration is close to being equal to the influent concentration. Sorption rate limitations can be caused by intraparticle diffusion limitations or rate-limited mass transfer between mobile and immobile water regions in the porous media. A longer residence time than that used in the column experiments may be necessary to achieve maximum sorption efficiency when considering the use of these sorbents in treatment systems.

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