

Kinetic and mechanism studies of the adsorption of lead onto waste cow bone powder (WCBP) surfaces

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Introduction

Contamination of groundwater and surface water by heavy metals from previously abandoned disposal sites and some currently operating sites has been a concern for some time. It has been determined that heavy metals are toxic to mammals. The presence of even low levels of heavy metals in waters is a concern primarily because the metals tend to bioaccumulate in the food chain. Therefore, considerable effort has been spent in treating metal-containing wastes at their source. Considerable progress has been made in methods such as coagulative precipitation, adsorption onto chelating resins, ion exchange, and reverse osmosis (Takeuchi et al. 1988; Takeuchi and Arai 1990). Of particular concern in Idaho, as well as in many other areas of the United States and the world, is lead contamination. Although various methods of treatment, such as those mentioned earlier, have been used to remove heavy metals from soils and waste water, solubility data suggest that an effective way to remove lead, and other heavy metals, would be by precipitation in an apatite mineral solid (Nriagu 1972). Much research has been focused on the reactions of lead with hydroxyapatite.

Nriagu (1972) looked at the precipitation of lead phosphates at a controlled pH in the presence of

either phosphoric acid or potassium hydroxide. He found that $\text{Pb}_4\text{O}(\text{PO}_4)_2$, $\text{Pb}_3(\text{PO}_4)_2$ and hydroxyapatite $[\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2]$ were the stable precipitates formed between pH 4.2 and 9.5. He then investigated the stability of chloropyromorphite $[\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2]$ (Nriagu 1973). Here, he found that chloropyromorphite was the stable solid over a pH range of 2.7–7.1. Based on the solubility data obtained in these equilibrium studies, Nriagu (1974) then calculated that, in oxidizing environments, pyromorphites $[\text{Pb}_{10}(\text{PO}_4)_6\text{X}_2]$, where (X is Cl-, F-, or OH-) and plumbgummite $[\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5 \text{H}_2\text{O}]$ were the dominant precipitates.

Investigators have attempted to determine the mechanism of reaction between Pb^{2+} and hydroxyapatite. Suzuki et al. (1982) postulated that the reaction was cation exchange based on structure, ionic radius, and stoichiometric ion replacement. Ma et al. [8], using similar observational evidence with the additional formation of pyromorphite crystals on ion exchange media saturated with Pb^{2+} and placed in a vessel containing water and hydroxyapatite, concluded that the reaction was a dissolution of hydroxyapatite followed by precipitation of pyromorphite.

Use of phosphate to remove soluble lead from the aqueous phase was suggested as early as 1974 by Nriagu, in a comprehensive study on the formation and properties of lead orthophosphates. Since then, extensive research on in situ treatment of lead-contaminated soils using phosphate as an effective additive has been performed for lead-contaminated soils. More recently, another kind of phosphate material, waste cow bone powder, has attracted researchers due to its possible use as a cost-effective additive for remediation of lead-polluted media.

Bone charcoal is being developed as a treatment for

decontaminating polluted water. An inexpensive yet efficient adsorbent of heavy metals is desired in effluent cleanup. Specifically designed adsorbents or high surface area activated charcoals tend to be expensive, whereas bone charcoal, although not as cheap as some natural adsorbents (e.g. tree bark), is relatively inexpensive. The ability of bone charcoal to remove color has been realized since the early 19th century, and in 1815 John Martineau patented the use of bone charcoal for the refining and clarification of sugar. It is still widely used in the sugar industry. More recently, interest has been shown in the possibility of using bone charcoal as a water cleanup treatment (Lewis 1995).

It is also well known that organic phosphates have high affinities for adsorption to mineral surfaces; therefore, fish bones generated as waste from fish processing could be used as a phosphate source to remediate soils or waste water contaminated by heavy metals (Misra 1984). Laperche et al. (1996) found that PbO and PbCO₃ in a contaminated soil were converted to lead pyromorphite when exposed to hydroxyapatite. Laperche et al. (1997) looked at the bioavailability of apatite-amended Pb by measuring plant Pb uptake. It was found that both synthetic and mineral apatite amendments could lower the bioavailability of soil Pb.

The main objectives of this study were to compare quantitatively the efficiency of aqueous lead removal waste cow bone powder (WCBP) adsorption isotherms, kinetics and lead removal mechanisms.

Materials and Methods

Materials

Natural WCBP was used for this study. Chemical

analysis shows that WCBP is made up of calcium (24.9 wt. %) and phosphate (33.9 wt. %), and its surface area is 8.38 m² g⁻¹ (See Table 1) and point of zero charge pHPZC is 4.5. Significant levels of sodium, potassium, chloride, magnesium and silicon are also observed in WCBP. These results are in accordance with published results (Chaala and Roy 2003; Deydier et al. 2005).

Lead solutions (1,000 mg L⁻¹, Sigma–Aldrich) were used as a stock solution, which was further diluted with deionized water to obtain the desired lead concentrations. The pH adjustment was performed using nitric acid and sodium hydroxide 0.1 N solutions.

The characteristics of the waste cow bone powder and reference bone char meal and phosphate rock in this research study are presented in Table 1. The dry temperature of waste cow bone powder is 105 °C; the dry temperatures of bone char meal and phosphate rock are 800 °C and 105 °C, respectively.

Batch adsorption studies

Adsorption study was also conducted in batch tests: a lead stock solution of 1,000 mg L⁻¹ was prepared from its standard solution. Lead concentrations ranging from 10 to 90 mg L⁻¹ were equilibrated with 1 g of WCBP into 250 mL polycarbonate bottles and equilibrated with 100 mL lead solution (liquid : solid ratio L/S:100). Bottles containing these slurries had been shaken (150 rpm) for 24 h, in the oven at temperature 25 ± 2 °C. After separation, the final concentrations of Pb²⁺ in the residual solutions were measured.

Lead sorption data were analyzed using the Freundlich and Langmuir models to evaluate the parameters

directly associated with the sorption process.

The two model equation is represented below

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<http://www.ncbi.nlm.nih.gov/pubmed/21046431>

<http://link.springer.com/article/10.1007/s10653-010-9357-z>