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ScienceDirect

Journal of Hazardous Materials 152 (2008) 876–884

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Factors influencing the removal of divalent cations by hydroxyapatite

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Received 11 October 2006; received in revised form 17 July 2007; accepted 17 July 2007
Available online 25 July 2007

Abstract

The effect of pH, contact time, initial metal concentration and presence of common competing cations, on hydroxyapatite (HAP) sorption properties towards Pb^{2+}, Cd^{2+}, Zn^{2+}, and Sr^{2+} ions was studied and compared using a batch technique. The results strongly indicated the difference between the sorption mechanism of Pb^{2+} and other investigated cations: the removal of Pb^{2+} was pH-independent and almost complete in the entire pH range (3–12), while the sorption of Cd^{2+}, Zn^{2+} and Sr^{2+} generally increased with an increase of pH; the contact time required for attaining equilibrium was 30 min for Pb^{2+} versus 24 h needed for other cations; maximum sorption capacity of HAP sample was found to be an order of magnitude higher for Pb^{2+} (3.263 mmol/g), than for Cd^{2+} (0.601 mmol/g), Zn^{2+} (0.574 mmol/g) and Sr^{2+} (0.257 mmol/g); the selectivity of HAP was found to decrease in the order $Pb^{2+} > Cd^{2+} > Zn^{2+} > Sr^{2+}$ while a decrease of pH_{PZC}, in respect to the value obtained in inert electrolyte, followed the order $Cd^{2+} > Zn^{2+} > Pb^{2+} > Sr^{2+}$; neither of investigated competing cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) influenced Pb^{2+} immobilization whereas the sorption of other cations was reduced in the presence of Ca^{2+}, in the order $Sr^{2+} > Cd^{2+} \geq Zn^{2+}$. The pseudo-second order kinetic model and Langmuir isotherm have been proposed for modeling kinetic and equilibrium data, respectively. The sorption of all examined metals was followed by Ca^{2+} release from the HAP crystal lattice and pH decrease. The ion exchange and specific cation sorption mechanisms were anticipated for Cd^{2+}, Zn^{2+} and Sr^{2+}, while dissolution of HAP followed by precipitation of hydroxypyromorphite ($Pb_{10}(PO_4)_6(OH)_2$) was found to be the main operating mechanism for Pb^{2+} immobilization by HAP, with the contribution of specific cation sorption.

Keywords: Hydroxyapatite; Cation sorption; Equilibrium; Kinetics; Sorption mechanisms; pH_{PZC}

1. Introduction

The toxicity of solid substances containing heavy metals is closely related to their solubility. For this reason, phosphate stabilization resulting in formation of highly insoluble phosphates which are stable over almost the entire pH range found in the natural environment represents an efficient strategy for reducing heavy metals toxicity by decrease of their mobility and bioavailability [1]. A large number of apatite based materials (mineral phosphates [2–5], synthetic apatite [6–10], bone meal [11,12] and bone char [13]) have been considered as matrixes for remediation of metal contaminated water and soil. Generally, calcium-hydroxyapatite (HAP) $Ca_{10}(PO_4)_6(OH)_2$, has demonstrated the best removal efficiency due to its moderate solubility—between highly insoluble and highly soluble phosphate bearing materials such as phosphate rock and phosphate fertilizers, respectively [14].

Reported data indicate that divalent metal sorption capacities on HAP, as well as the sorption mechanisms strongly depend on: (a) type of divalent metal, (b) HAP physico-chemical properties and (c) other factors, such as metal concentration, solution pH, contact time, presence of other ionic species etc. [15,16]. In our previous work the influence of HAP properties on divalent cation retention was investigated [17,18]. HAP powders were synthesized by neutralization method. Preparation conditions, HAP physico-chemical properties and sorption behavior towards heavy metal cations were correlated using the experimental design approach [17]. It was found that among investigated parameters (temperature, reagent concentration, reagent addition rate, mixing speed, inert atmosphere, and aging time) synthesis temperature has the strongest influence on HAP structural and sorption properties. Powders obtained at room temperature, without aging, having small crystallite size, low crystallinity, and high specific surface area exhibit the best

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0304-3894/$ – see front matter
doi:10.1016/j.jhazmat.2007.07.056

Nomenclature

C_0	initial metal ion concentration (mmol/dm^3)
C_e	residual metal ion concentration at equilibrium (mmol/dm^3)
C_s	HAP concentration (g/dm^3)
h	initial sorption rate (mmol/g min)
k_1	pseudo first order sorption rate constant (min^{-1})
k_2	pseudo second order sorption rate constant (g/mmol min)
pH_{PZC}	the point of zero charge
K	Langmuir sorption constant (kg/mmol)
q	amount of metal ion sorbed (mmol/g)
q_e	amount of metal ion sorbed at equilibrium (mmol/g)
q_t	amount of metal ion sorbed at time t (mmol/g)
R^2	regression coefficient
t	time of equilibration (min)
T	solution temperature (°C)
X_m	Langmuir sorption constant (mmol/g)

sorption properties towards Pb^{2+}, Cd^{2+}, Zn^{2+} and Sr^{2+} [18]. On a larger scale, variations in HAP stoichiometry (Ca/P ratio) and pH_{PZC} had little effect on the metal sorption.

Although the sorption of heavy metals on HAP has been extensively studied, many questions concerning sorption mechanisms under specific experimental conditions remained unresolved, while comparison of data is difficult because of the differences in origin and physico-chemical properties of the HAP sorbents applied.

In order to investigate factors influencing sorption of Pb^{2+}, Cd^{2+}, Zn^{2+} and Sr^{2+} ions, the low-crystalline HAP sample, with high specific area was selected. Pb^{2+}, Cd^{2+} and Zn^{2+} ions were chosen as typical heavy metals, with wide presence in surface and ground waters, soils and sediments caused by anthropogenic activity. If these heavy metals occur in nature in ionic form, they easily enter the food chain, causing various toxic effects on living organisms. Sorption of Sr^{2+} was investigated as it is a representative of alkaline earth cations, but also because Sr-90 (beta emitter, with $t_{1/2} = 29.1$ years), the important radioactive isotope in the environment behaves chemically similar to calcium and tends to concentrate in the bones and teeth whose principal inorganic constituent is hydroxyapatite [19]. Besides having different toxicity, the selected sorbates also have different ionic radii and hydrolysis behavior, which makes the comparison of their sorption mechanisms interesting.

The objectives of the present study were: (i) to investigate the effects of pH, contact time, initial metal concentration and presence of competing cations on the sorption of selected divalent cations by HAP, (ii) to compare HAP sorption properties and selectivity for investigated metal cations, and (iii) to propose the theoretical models for describing equilibrium and kinetic data.

Presented results strongly indicate the difference between sorption mechanism of Pb^{2+} and other investigated cations, under all experimental conditions, as well as that buffer properties of HAP represent an important factor influencing efficacy of immobilization of toxic metals.

2. Materials and methods

2.1. Starting material

HAP sample used in this study was synthesized by neutralization of $Ca(OH)_2$ with H_3PO_4, at room temperature (20 °C) [17]. Chemical and X-ray diffraction (XRD) analyses have confirmed that the sample is a low-crystalline HAP with Ca/P ratio of 1.60. Specific surface area of 67 m^2/g was determined by the single point nitrogen adsorption method, after degassing the sample at 250 °C for 2 h, using a Micrometrics ASAP 2000 instrument. The point of zero charge (pH_{PZC}) determined by batch technique [17] with 0.1 mol/dm^3 KNO_3 as an inert electrolyte was found to be 6.2 ± 0.1.

2.2. Sorption experiments

Sorption of Pb^{2+}, Cd^{2+}, Zn^{2+} and Sr^{2+} was studied by batch method, under different experimental conditions. All metal solutions were prepared from their nitrate salts (p.a. purity) and distilled water. Generally, sorption experiments were performed by equilibrating 0.1000 g of sorbent with 20.00 ml of metal solution (solid/liquid ratio 1:200) at room temperature (20 ± 1 °C). The pH measurements were performed with a glass electrode pH meter (Inolab, WTW), using original WTW buffers (pH 4, 7 and 10) for the calibration of the instrument. The initial pH values were adjusted to 5.0 ± 0.1, unless otherwise stated, by adding minimum amounts of HNO_3 or KOH solutions, since K^+ and NO_3^- ions are inert in respect to HAP surface. This particular pH was selected because HAP solubility increases significantly at $pH < 5$, while at higher pH values hydrolysis of heavy metal cations may occur. The final pH values were those measured after interaction of HAP with the solution of known initial pH. Due to various processes that may occur at the solid surface/solution interface (preferential dissolution of certain constituents of crystal lattice, ionization of surface groups, physical adsorption of ions or formation of complex compounds between surface groups and ions from the solution) the final pH values differ from the initial ones. The suspensions were equilibrated in acid washed 50 ml PVC flasks, on a horizontal shaker.

- Sorption behavior of Pb^{2+}, Cd^{2+}, Zn^{2+} and Sr^{2+}, for the same initial concentration (2×10^{-3} mol/dm^3) and equilibration time (24 h), was studied as a function of pH. The initial pH values were adjusted from ∼3 to ∼12, using HNO_3 or KOH solutions.
- The influence of contact time on each metal sorption was analyzed from 15 min up to 2 days. Initial metal concentrations were 2×10^{-3} mol/dm^3.
- Sorption isotherms were obtained for different initial metal concentration in the range 10^{-4} to 10^{-2} mol/dm^3 for Cd^{2+}, Zn^{2+} and Sr^{2+}, and 10^{-4} to 5×10^{-2} mol/dm^3 for Pb^{2+}. The contact time in all experiments was 24 h. Initial low-