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Removal of Cadmium from Dilute Solutions by Hydroxyapatite. I. Sorption Studies

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ABSTRACT

The removal of toxic metals (such as cadmium) was investigated by using hydroxyapatite, an effective inorganic sorbent, at the ultrafine particle size range. In bench-scale experiments performed batchwise, the influence of the main sorption parameters were examined (i.e., solution pH, sorbent and cadmium concentrations, and temperature) and comparison was attempted between demineralized and tap water. Typical adsorption isotherms of the Langmuir type were calculated; ζ-potential measurements of the hydroxyapatite particles and the release of calcium (during the process) were also examined and related to possible mechanisms occurring during the cadmium removal process.

INTRODUCTION

The presence of priority pollutants, such as cadmium, in the effluent streams from several chemical and metal plating industries has been a major environmental problem for both industries and neighboring municipalities. Serious concerns about possible contamination of ground and surface waters by toxic metals leached from abandoned disposal sites but also, in certain cases, from currently operating ones have generated various efforts aimed at remediating contaminated soils. However, severely polluted aqueous waste streams are usually produced in this way, and also they need effective treatment (1).

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Mineral particles, such as pyrites (2), and industrial by-products (fly ash or red mud) have recently been proposed as alternative sorbents for the removal of toxic metal ions (3–5). Several materials have been suggested in the literature as suitable cadmium sorbents, such as activated carbon (6), zeolites (7), goethite (8), fungi biomass (9), streptomycetes (10), hydrous aluminum oxides (11), and supported liquid membranes (12). The list shown in Table 1 is by no means exhaustive. This great variety shows the significance of an innovative and effective metal removal process, which is particularly important for priority pollutants.

Calcium hydroxyapatite (denoted hereafter as HAP) is the prototype of an inorganic crystalline constituent in human calcified tissues, i.e., bones and teeth. Therefore, the interaction between this material and several ions in body fluids has been rather extensively studied (13). Another reason why hydroxyapatite was widely examined lies in the fact that this type of mineral exists in natural ores (fluorapatites) and is used in large amounts by the fertilizer industry. It has also been used as a raw material

TABLE 1
Application of Various Sorbent Materials for Cadmium Removal (and other metals): Examples from the Literature

Ref.	Sorbent	Notes
6	Granular activated carbon	Use of columns for Pb and Cd removal
7	Natural zeolites (chabazite and clinoptilolite)	Effects of conditioning and treatment prior to Pb and Cd removal
8	Goethite (α-FeOOH)	Effects of solution concentration, pH, and temperature
9	Fungi (fermentation by-products)	*Penicillium chrysogenum* and *Rhizopus arrhizus*, dispersed-air flotation following biosorption
10	Actinomycetes	*Streptomyces griseus* (laboratory grown) and *S. clavuligerus* (pharmaceutical waste), DAF
11	Hydrous aluminum oxides	Influence of coexisting chemical constitutents on Cu, Cd, Zn, and Pb ions by interaction with the hydrous oxides of aluminum
12	Supported liquid membranes	Stability and influence of diluents in supported liquid membranes
15	Calcium hydroxyapatite (HAP)	Effects of cadmium and other metal ions on Zn and Pb immobilization
16	HAP and carbonate apatites	As inorganic cation-exchangers for toxic ions, biological apatites

in detergents, animal feeds, and for the production of many chemicals (14).

It is worth noting that most sorbents exist in particulate form, as illustrated below by particle size measurements. The contact process between the sorbent particles and the effluent solution is usually carried out in CSTR-type equipment. Solid/liquid separation downstream, often performed by settling or filtration, can be problematic or time-consuming. This is why the coagulation and flocculation of ultrafine hydroxyapatite particles in the presence of cadmium was subsequently investigated (Part 2 of this series).

Studies of the sorption of cadmium and other metals (such as lead and zinc) were performed using hydroxyapatites (15–17) with the aim of studying the sorption parameters of HAP for the removal of cadmium by using technological conditions, rather than through a theoretical approach.

EXPERIMENTAL (PROCEDURES AND ANALYTICAL METHODS)

Calcium hydroxyapatite, with the general formula $Ca_{10}(PO_4)_6(OH)_2$, was studied in batch laboratory experiments. It was commercially synthesized (by Merck, catalog no. 2196), and has a molecular weight of 502.32 g/mol according to the manufacturer. Hydroxyapatites crystallize in a hexagonal structure and are often nonstoichiometric, containing some alkali metals (18).

Microphotographs of HAP were taken by using a scanning electrode microscope (SEM). The sorbent was mixed for 900 seconds with an aqueous solution in order to maintain similar conditions for sorption experiments in the absence and the presence of cadmium. Microprobe analysis, performed for specific particles and presented in Table 2, verifies the HAP composition. It is interesting to note the high cadmium concentration (0.5%) measured at certain HAP sites, which means that cadmium is spe-

TABLE 2
Results of Microprobe Analysis for HAP Particles by Electron Microscopy (theoretical and measured values)

		Ca (%)		P (%)		Cd (%)
	Sample	Theoretical	Measured	Theoretical	Measured	Measured
1	HAP	62.5	63.5	37.5	35.9	—
2	HAP + Cd	62.5	63.9	35.3	35.9	0.5

cifically sorbed mainly at these sites and not uniformly throughout the total HAP solid.

Electrophoretic measurements of HAP were also carried out in actual sorption conditions, and the results obtained were expressed as the ζ-potential; the experimental details of these measurements are described elsewhere (19). Because of the measured high solubility at pH values lower than 5 of the examined material, the point of zero charge was not apparent. An isoelectric point (i.e.p.) of 5.6 for natural apatite was elsewhere reported (13); i.e.p. was also found to vary between 6.5 for a seeded-growth synthetic HAP (20) and 7.0 for another synthesized HAP (13).

The sorption experiments were conducted in conical flasks placed in a reciprocal shaker under the following conditions (unless otherwise stated): 100 mL volume of solution, ambient temperature (297.4 K), natural pH (around 6–7), initial cadmium concentration 10 mg/L (added as a nitrate salt), and HAP concentration 0.5 g/L. Demineralized water of less than 1 μmho conductivity was used for the preparation of the metal solutions, but tap water (of 550–650 μmho) was also tested for comparison. The solution pH was measured and, if required, was modified by NaOH or HNO_3 solutions. During preliminary experiments it was observed that the initial pH values of aqueous HAP dispersions (around 7, depending on the contact time and on the HAP concentration) dropped toward more acidic pH values when cadmium was present (around 6–6.5, depending on the concentration of cadmium) (see Fig. 1).

Centrifugation was applied in these experiments as a convenient laboratory solid/liquid separation method. Chemical analysis of metals in the clear solutions was conducted by atomic absorption spectrophotometry to determine the residual (not removed) cadmium concentration in the usual way. The results were expressed as percentage removal (Re%).

The contact time necessary to obtain equilibrium conditions was also studied in preliminary experiments. Cadmium abstraction by HAP is a relatively fast process, reaching almost 100% removal after 300 seconds of contact. In the following experiments a contact time of 900 seconds was used, although elsewhere a 781.2-ks contact time was recorded for the same system (17).

Adsorption isotherms were obtained for three different temperatures by following a model equation. "Blank" experiments, i.e., without any HAP present, were also performed as controls of the sorption process.

The specific surface area of HAP, as measured by the single-point BET method (using liquid N_2), was found to be 52 m^2/g. Finally, size distribution analysis of the particles was obtained by laser diffraction analysis, shown in Fig. 2 as both cumulative and differential curves. The existence of an ultrafines fraction is apparent: the average diameter of HAP particles

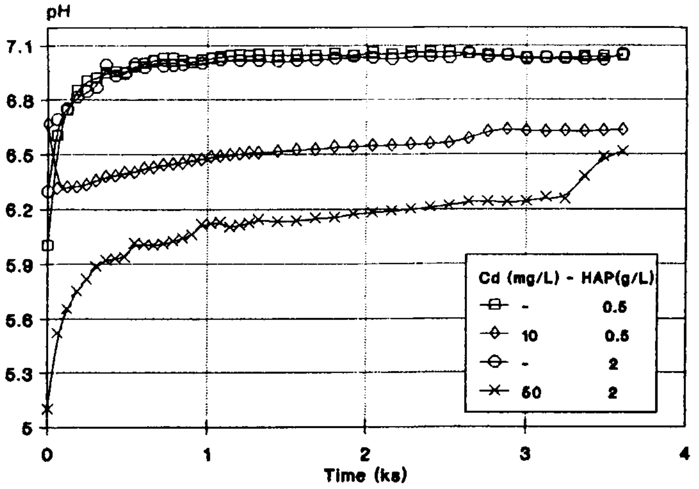

FIG. 1 Influence of time on pH changes of HAP dispersions (0.5 and 2 g/L concentrations) with and without the presence of cadmium, examined at 10 and 50 mg/L concentrations, respectively.

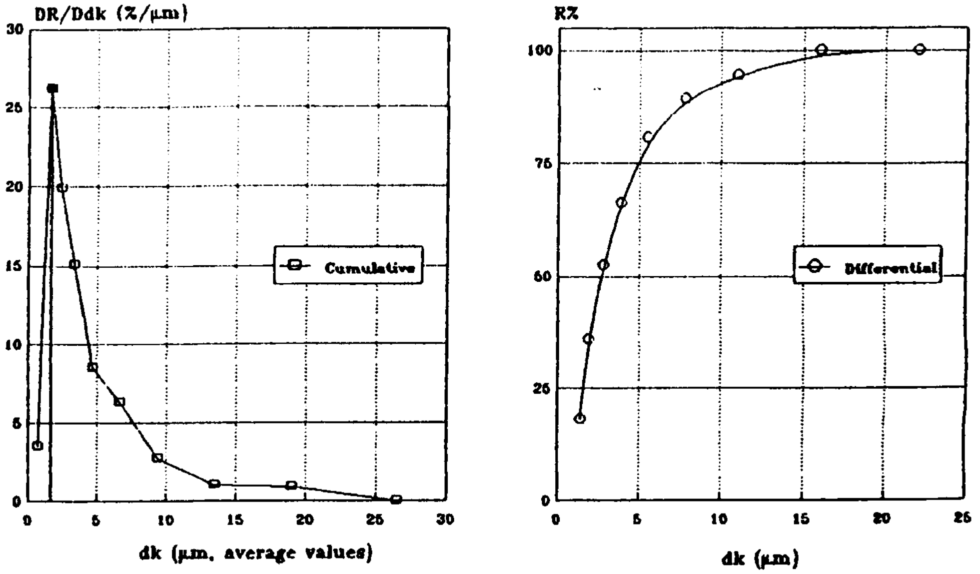

FIG. 2 Particle size analysis of HAP; particles under similar conditions as used for the sorption experiments.

was around 2.5 μm, and 50% of them had diameters below 3.5 μm. This may mean there is a need for a coagulation stage of the metal-loaded particles before any further separation step can take place.

RESULTS AND DISCUSSION

Cadmium removals obtained by two different initial HAP additions (0.5 and 1 g/L) are presented in Fig. 3a vs the solution pH, which is probably the most significant parameter controlling the removal process. Various possible reactions that apatite can undergo in water and the mechanisms by which pH determines the surface potential have been suggested (13). Precipitation is the conventional treatment process, especially for more concentrated metal solutions. Special care is necessary when evaluating the results of these experiments because of metal speciation in aqueous solutions. Precipitate flotation of cadmium from dilute aqueous solutions has been also studied and recently reported (21).

Cadmium forms hydroxides over a pH range of approximately 9 (21). Therefore, cadmium removal in the absence of a sorbent is due to the precipitation mechanism. In our investigation, the advantage of applying HAP as a sorbent is apparent. The sorption tests were repeated on a larger scale (3 L), using tap water instead of demineralized water, and found to be successful (see Fig. 3b).

The influence of HAP concentrations in the dispersion has been subsequently examined for three different initial cadmium concentrations (see Fig. 4). Dilute metal solutions, equal or less than approximately 5 mg/L concentration, usually require specific consideration because the quantitative removal of cadmium is much more difficult when dealing with dilute than with concentrated solutions. The influence of cadmium content in the feed has been also investigated (Fig. 5) by using three fixed sorbent concentrations. Cadmium removals of nearly 100% were found under the optimum conditions.

Typical adsorption isotherms have been determined: the results are presented in Fig. 6 and the relevant calculations are given in Table 3 for ambient temperature (297.4 K) and also for 303 and 313 K. In the respective equation, m (mg/g) is the maximum adsorption capacity and b (L/mg) is the adsorption constant, which shows the binding strength of HAP for cadmium. The value for the maximum adsorption capacity, 0.432 mmol Cd/g HAP (which is equal to 8.31 μmol/m^2 or 217 mmol Cd/mol HAP), is lower than those encountered for modified HAPs, 603 mmol Cd/mol synthetic carbonate apatites (16) and 490 mmol Cd/mol pyromorphite apatites (containing lead ions instead of calcium) (15), but quite similar to the value reported elsewhere (297.4 mmol Cd/mol HAP or 7.9 μmol/m^2) (17).

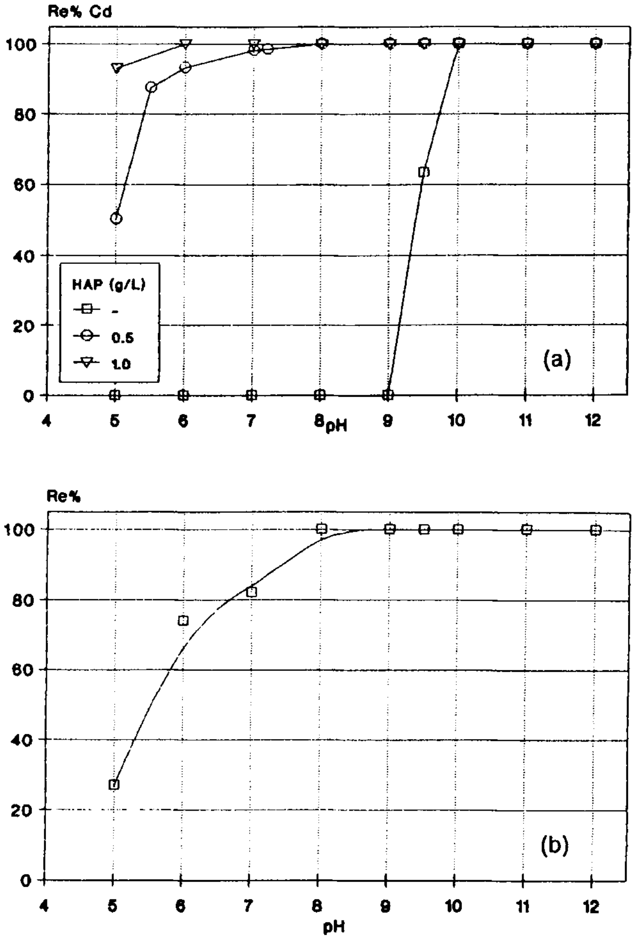

FIG. 3 Effect of solution pH on cadmium removal: (a) in the presence (at two different concentrations) and absence of HAP; (b) using tap water for an initial Cd concentration 20 mg/L, 3 L batch.

As the temperature increases, the maximum sorption capacity decreases, an indication that weak sorption forces (such as those encountered in physical sorption or in ion exchange) are predominant in the cadmium/HAP system. This behavior is in good agreement with the literature (17). The consistency obtained for the Langmuir isotherm is perhaps *the first indication* of a possible ion-exchange mechanism between cad-

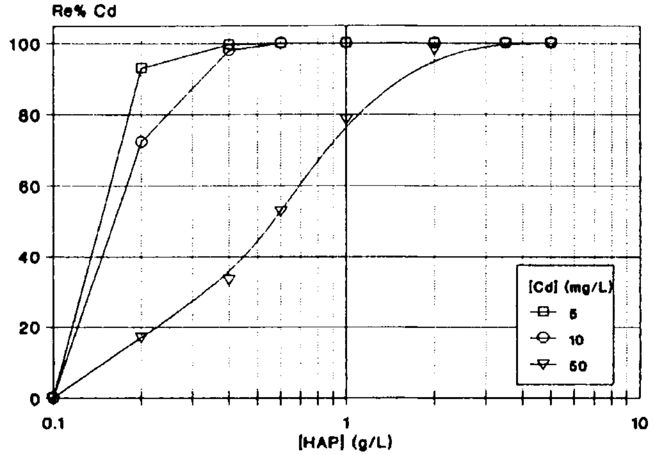

FIG. 4 Influence of sorbent feed additions at three different cadmium initial concentrations (fixed value).

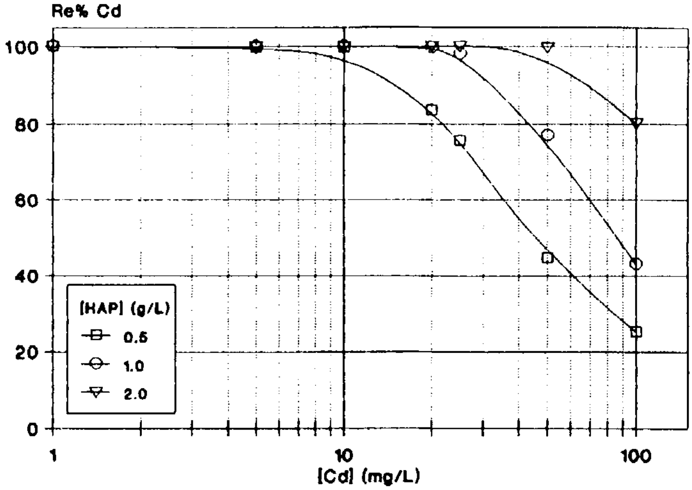

FIG. 5 Influence of cadmium initial concentrations at three different HAP initial additions (fixed values).

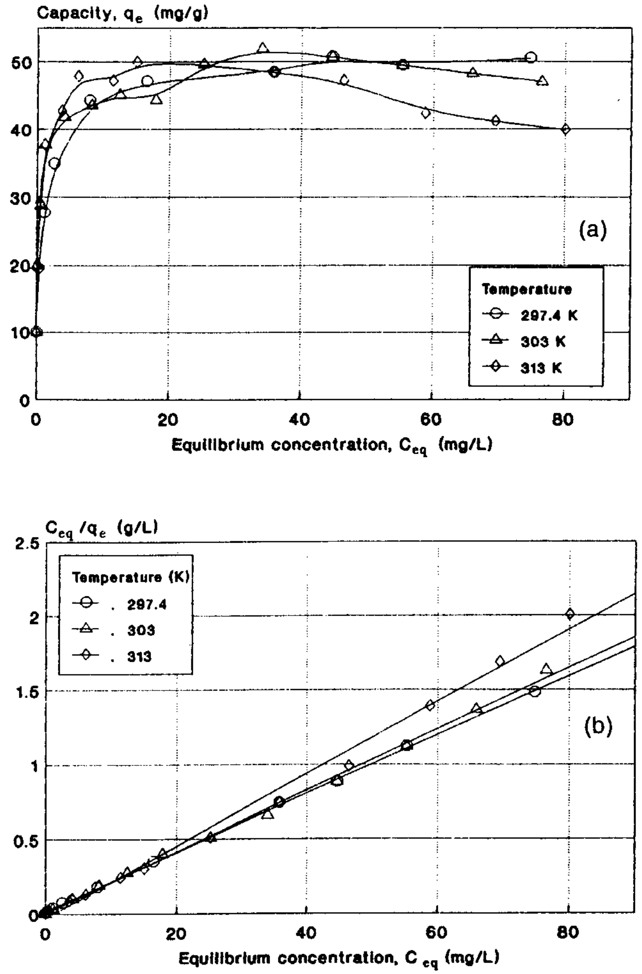

FIG. 6 (a) Adsorption isotherms at three temperatures (cadmium concentrations: 0–100 mg/L) at natural pH; (b) Langmuir-type plot.

mium and the HAP surface. In fact, an ion-exchange reaction can be described by this isotherm model; the reverse is not always true. However, the explanation might not be so simple. The ionic radius of cadmium is close to that of calcium, therefore, the possibility of ion exchange between these cations is enhanced.

TABLE 3
Adsorption Isotherm Calculations; Capacity of Hydroxyapatite q_e (mg/g) as a Function of Equilibrium Concentration C_{eq} (mg/L). The Langmuir Equation $q_e = mbC_{eq}/(1 + bC_{eq})$ was applied, where m and b are constants

Temperature (K)	Equation	r^2
297.4	$y = 9.7187 \times 10^{-3} + 0.0205x$	0.997
303	$y = 3.944 \times 10^{-3} + 0.0206x$	0.998
313	$y = -0.03 + 0.0242x$	0.996

Temperature (K)	m (mg/g)	m (mmol/g)	b (L/mg)	b (L/mmol)
297.4	48.78	0.431	2.11	237
303	48.54	0.432	5.22	587
313	41.32	0.368	0.807	91

It has been proposed that the abstracted cadmium ions were located in the Ca-(2) sites, which are close to the channels along the hexagonal screw-axes. It is worth adding that calcium occupies two different sites in the HAP structure: site Ca-(1) on the ternary axes at $x = 1/3$ and $y = 2/3$, and site Ca-(2) with symmetry m at $z = 1/4$ or $3/4$ (25).

The electrokinetic measurements are presented in Fig. 7. It is observed that the ζ-potential of the sorbent particles in the presence of cadmium changes toward less negative values, partly neutralizing the initial (without any cadmium present) negative surface charges, a fact attributed to the attachment of cadmium cations onto the surface. This is also in agreement with actinomycetes biomass measurements during cadmium removal (22). During examination of a similar process, i.e., crystallization and seeded-growth of HAP under equilibrium conditions in the presence of cadmium, different results were obtained in the alkaline pH range (20).

Surface complexation, as well as protonation and deprotonation on the calcium mineral/water interfaces, which are important phenomena for sorption, have already been examined (17, 23). The amphoteric properties of hydrous fluorapatite and HAP, in contrast to oxide surfaces, were stressed, and the dominating surface groups in the case of apatites and at a pH near i.e.p. were found to be mainly $Ca—OH_2^+$ and $P—O^-$. When cadmium is present, H^+ cations can be partially displaced from HAP surfaces by the adsorbed cadmium ions and can be partially generated from coprecipitation reactions.

Various values are found in the literature for the molar ratio of Ca/Cd when the exchange of cations on HAP was examined. This ratio was

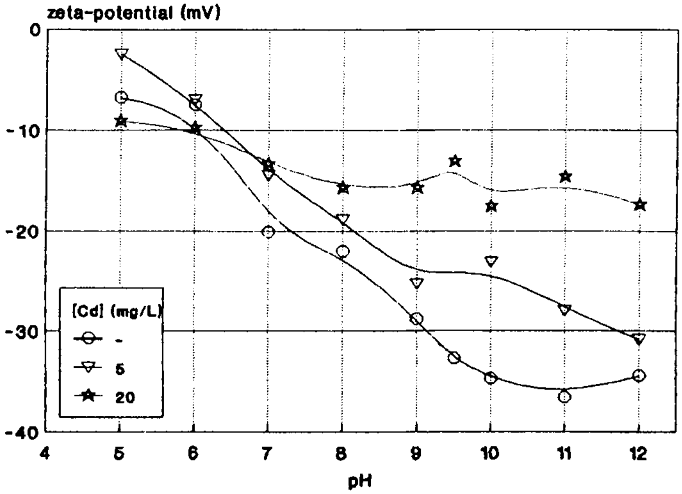

FIG. 7 ζ-potential measurements of HAP against the solution pH; effect of solution pH and of cadmium concentrations.

reported to be almost equal to 1.0 in one case (24), while in another (17) the ratio was found to be slightly lower (0.857). Figure 8a presents some related results for the three temperatures examined in the present study. They show the relation between the amount of cadmium sorbed on the particle's surface and the (total) calcium concentration found in the solution after a contact time of 900 seconds. A nearly linear relationship occurs in a certain sorbed cadmium concentration range, which possibly leads toward an ion-exchange mechanism, a fact supported elsewhere (25). Nevertheless, it is noted that the pH was not controlled during these experiments. Therefore, it is possible that small pH changes occurred in the presence of cadmium (see also Fig. 1), which may result to a slight HAP dissolution, and hence to a nonstoichiometric release of calcium ions in the solution. This was also supported by the measured calcium release into the solution under the influence of pH but in the absence of cadmium (Fig. 8b). Repeating some selected experiments of Fig. 8a after eliminating the interference caused by the slight pH differences resulted in the higher release of calcium concentrations compared with the case without cadmium present, a fact which could be attributed to the coexistence of an ion-exchange removal mechanism. A further increase of sorbed cadmium concentration led to rather abnormal results, indicating the possible coexistence of other mechanisms (see Fig. 8a).

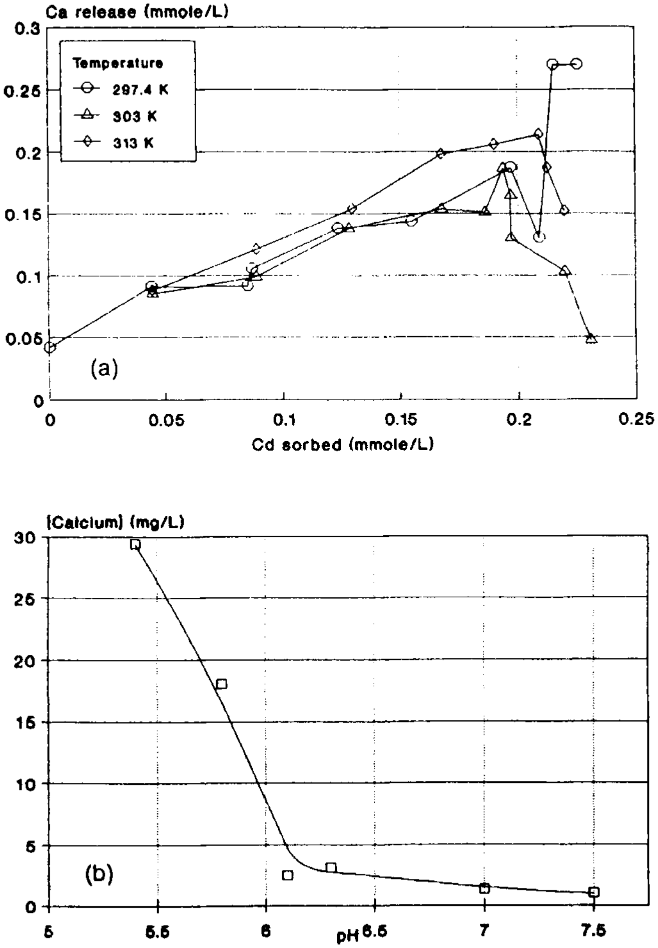

FIG. 8 Calcium release in solution: (a) effect of cadmium sorbed (during cadmium removal) using HAP, and (b) effect of pH influence (without any cadmium present).

It has recently been reported that the dissolution/coprecipitation reaction is a more significant mechanism for the removal of cadmium using HAP than of zinc (17). This observation was consistent with the result that more Cd^{2+} was removed from the solution to HAP surfaces than Zn^{2+}. It was also suggested that surface complexation and possibly ion exchange play a critical role in the overall removal of these metals from aqueous solutions. The effects of dissolved mineral species on the dissolution/precipitation characteristics of calcite and apatite have been discussed previously (26). Apatites were reported to show a certain selectivity for metal cations, and the following order was proposed, based on the amount exchanged: Cd, Zn > Ni > Ba, Mg (24).

FIG. 9 SEM microphotographs of the studied hydroxyapatite: (a) HAP without any treatment or contact with water; (b) HAP dispersion (1 g/L concentration) in aqueous solution without cadmium, and (c) in the presence of 10 mg/L Cd (contact time 900 seconds). Both samples (b) and (c) were filtered through a 0.45-μm membrane and dried at room temperature.

(continued)

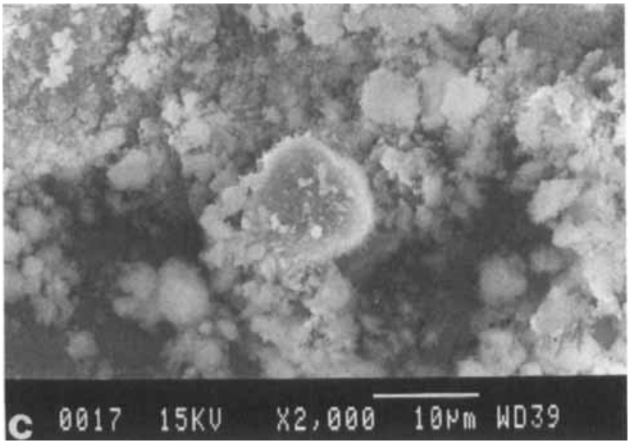

FIG. 9 Continued

The HAP particles examined without water contact did not show the existence of appreciable aggregate formation, while the presence of ultrafine particles with diameters below 1 μm is apparent (Fig. 9a). The same observations were made when the HAP particles were in contact only with water (Fig. 9b). The presence of cadmium ions caused a significant aggregation of HAP particles and the formation of "precipitates" (Fig. 9c). The appearance of these solid phases, although they were not detected by XRD, indicates that at least some retention of cadmium ions may be due to the incorporation of these ions into "precipitates."

Further work may be needed to study the possible formation of cadmium phosphates, i.e., the surface precipitation of cadmium onto HAP, or the possible existence of a new surface Ca-Cd phase, in analogy to the Ca-Mg phase known to exist in similar systems (20). It has also been reported that HAP (also containing sodium) showed no modification of the crystallites and no occurrence of a new phase after cadmium fixation (25).

Sorption is by definition a general term describing the attachment of charged species from a solution to a coexisting solid surface. Three types of processes are mainly identified for the sorption phenomena: (a) surface adsorption, which is limited to the accumulation of sorbate on the external surface of a solid, including several mechanisms such as ion exchange and surface complexation; (b) absorption or diffusion into the solid; and (c) precipitation or coprecipitation (17).

In the case of cadmium removal by HAP, the interaction between them cannot be explained by simple adsorption. It is quite possible that more than one mechanism may be simultaneously responsible to some extent for the removal process, e.g., adsorption, ion exchange, surface complexation, precipitation, or coprecipitation (among others), and it is difficult to estimate quantitatively the proportion of any specific mechanism occurring.

In conclusion, the selection of synthetic hydroxyapatite as a sorbent was found to be successful. HAP proved suitable for effectively removing dilute concentrations of cadmium and possibly of other metal cations from aqueous solutions, i.e., wastewaters. A limitation of HAP application for treating toxic metal-laden wastewaters is the relatively high solubility of this material at acidic pH values. Therefore, these wastewaters must first be neutralized.

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