THE BALL MILLING EFFECT ON TRIBASIC CALCIUM PHOSPHATE AND ITS CHROMIUM (VI) ION SORPTION PROPERTIES

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ABSTRACT

The ball milling effect on the sorption properties of tribasic calcium phosphate (TCP) is presented. The materials obtained were characterized by X-ray diffraction, SEM, particle size and specific surface area. The specific surface area of the prepared TCP prepared sample was 60.55 m²/g and unexpectedly decreased to 12.57 m²/g for samples where milling time was 15 hrs. In TCP samples with a milling time of 5 and 10 h, the specific surface values also diminished to 16.81 and 15.11 m²/g, respectively. Fe atoms were found in the milled TCP samples as XRD and EDS techniques revealed. An increase of Cr(VI) ion sorption with milling time was observed with a maximum chromium sorption of 14.0 x 10⁻⁴ meq/g. This increasing Cr(VI) sorption may be due to the presence of the Fe atoms found in the milled TCP samples.

Keywords: Ball milling; Tribasic calcium phosphate; Chromium (VI) ion; Sorption; XRD; SEM

INTRODUCTION

Numerous amorphous and crystalline metallic phosphates have already been synthesized and studied as selective sorbents for the removal of lanthanide, actinide and heavy metal cations from aqueous solutions.¹⁻⁴ However, this literature indicates that the actual exchange capacities of amorphous phosphates do not exceed half of the theoretical value calculated for the corresponding crystalline ion exchangers.^{5,6} The exchange capacity is most likely connected to structural and morphological changes of the powder surface, *i.e.* to the fresh surface formation. It is well known that fresh surfaces and cracks are created by the ball milling of metals and intermetallic compounds.⁷ Producing these materials in a nanocrystalline form can improve their properties because the high density of defects and interfaces can enhance adsorption. Ball milling is now a well known method in the nanocrystalline and amorphous powder mass production and was applied to the powders tribasic calcium phosphate in order to boost their sorption properties.

Tribasic calcium phosphate (TCP) is a sparingly soluble mineral with a strong affinity for radionuclides and heavy metals sorption and has therefore been proposed as an adsorbent for radioactive and non-radioactive waste.^{8,9} Tribasic calcium phosphate (TCP), adopting the hydroxyapatite structure Ca₃(PO₄)₂(OH), is structurally arranged in a hexagonal system with space group *P6₃/m* and characterized by a 6-fold *c*-axis perpendicular to three equivalent *a*-axis at 120° to each other. This structure exhibits high stability under reducing and oxidizing conditions and very low water solubility (*K_{sp}* < 10⁻⁴⁰) under alkaline conditions. Though tribasic calcium phosphate (TCP) can be synthesized through precipitation from aqueous solutions containing calcium and phosphate ions,¹⁰ other methods (hydroxyapatite) have been reported: high temperature solid-state reactions¹¹ or the calcination of animal bones,¹² where calcium is supplied as aqueous solutions of CaCl₂, Ca(NO₃)₂, CaCO₃ or Ca(CH₃COO)₂, and the phosphates are supplied as aqueous solutions of (NH₄)HPO₄, NH₄H₂PO₄, KHPO₄, N₂HPO₄, or NaH₂PO₄.¹³⁻¹⁵ In this paper, the continuous precipitation method was used to synthesize calcium phosphate with highly purified monobasic ammonium phosphate and calcium nitrate.

High-energy ball milling was employed to pulverize tribasic calcium phosphate (TCP) powders to create a fresh surface. TCP samples were modified in their morphology and particle size by varying the milling time and then compared to the corresponding parameters of the sample prepared by the continuous precipitation method. To determine the effect of these surface structure variations on sorption properties, the chromium (VI) ion sorption on synthesized and modified TCP samples was studied as a function of shaking time.

EXPERIMENTAL

Materials

The following analytic grade materials were used without further purification: Calcium nitrate Ca(NO₃)₂·4H₂O A.C.S. reagent (Merck, 99 wt%),

monobasic ammonium phosphate NH₄H₂PO₄ A.C.S. reagent (J. T. Baker, 98 wt%), potassium dichromate K₂Cr₂O₇ A.C.S. reagent (Merck, 100 wt%), ammonium hydroxide NH₄OH reagent (Baker, 99.9 wt%) and potassium bromide KBr (Madison Co. spectroscopy grade).

Synthesis of TCP by continuous precipitation method

Tribasic calcium phosphate (TCP) was prepared at room temperature by the continuous precipitation method, as reported by Rodríguez *et al.*¹⁶ To obtain 10 g of tribasic calcium phosphate, 23.51 g calcium nitrate and 6.87 g monobasic ammonium phosphate were used. The reagents were introduced at a Ca/P molar ratio of 1.67.

To prepare the calcium nitrate aqueous solution a polyethylene-coated magnetic stirrer and a glass beaker were used to prevent metallic contamination. 23.51 g Ca(NO₃)₂·4H₂O were dissolved in 545 mL distilled water with an initial pH of 5. 62.0 mL of concentrated NH₄OH was then added to the Ca(NO₃)₂·4H₂O solution. The final pH of this solution was 12. Finally, distilled water was poured into the beaker until a total volume of 890 mL was obtained. The aqueous solution of monobasic ammonium phosphate was prepared under the same purity criteria as following: 6.9 g of NH₄H₂PO₄ was dissolved in 833 mL of distilled water with a pH of 5 while 37 mL of concentrated NH₄OH was added to reach a pH of 12. Finally, the solution obtained was diluted with distilled water up to a volume of 1500 mL. To obtain the TCP, the ammonium phosphate solution was slowly poured into the calcium nitrate solution under vigorous stirring during 24 hrs, the suspension then being settled for another 24 h to discard the supernatant. The precipitate was washed four times with distilled water under stirring for 18 h, and finally the solid and liquid phases were separated by centrifuging. The obtained calcium phosphate was dried at 120 °C for 2.5 h and calcined at 1050 °C for another 2.5 h. This thermal treatment made calcium nitrate tribasic more crystalline while destroying and volatilizing the nitrate and ammonium traces trapped in the solid.

Ball milling

The mechanical milling was carried out with a high energy ball mill (Spex 8000). TCP samples were milled for different periods: 0, 5, 10 and 15 h to obtain TCP, TCP-5, TCP-10 and TCP-15 samples, respectively. The tribasic calcium phosphate powder was placed into a stainless steel container together with 9 stainless steel balls (1/4 inch diameter) and 18 stainless steel balls (3/16 inch diameter) without controlled atmosphere. The ball-to-powder ratio in weight was 6:1 and methanol was used as a lubricant agent (0.25 mL). Small amounts of the powder were taken from the mill at 5, 10 and 15 hrs. Once finished with ball milling, the samples were characterized and the chromium sorption from aqueous solutions by TCP was studied using a batch technique.

Characterization

The structure of non-milled (original TCP sample) and ball milled samples were characterized by X-ray powder diffraction with Cu K_α radiation. A Siemens D-5000 diffractometer coupled to a copper anode tube was used to obtain the X-ray diffraction patterns and to identify the crystalline compounds. The K_α wavelength was selected with a diffracted beam monochromator. The crystallite sizes were estimated with Sherrer's approximation.

To test its purity, the synthesized material was mixed with KBr and infrared spectra were then obtained using a 550 Nicolet spectrophotometer.

Morphology was determined by using a XL-30 Philips scanning electron microscope (SEM). The chemical compositions of the samples were analyzed by energy dispersive X-ray (EDS) spectroscopy. Specific surface areas and pore total volume of TCP samples were obtained by nitrogen adsorption with the aid of the BET method with a surface area analyzer Micromeritics Gemini 2360.

Chromium (VI) sorption

Batch experiments were carried out at room temperature by mixing 0.1 g of each TCP sample (ball milled and original powders) and 10 mL of 1×10^{-4} M Cr(VI) ion solution at pH of 5.5 in closed vials. Previous kinetics studies of chromium (VI) sorption on TCP showed that the equilibrium sorption is attained after 24 h of shaking time. Thus, samples were stirred for 10 seconds and shaken for 24 h. The liquid phases were separated from the solid phases by centrifuging (5 minutes at 3000 rpm). The Cr(VI) ion concentration in each aliquot of 5 mL was determined with a Shimadzu ultraviolet-visible 265 spectrophotometer analyzer at $\lambda = 540$ nm by using the 1,5 diphenylcarbazide method.¹⁷

RESULTS

Compound identification

In Fig. 1 the X-ray diffraction patterns of pulverized TCP samples obtained at different milling times were compared with the pattern of the non-milled TCP sample as prepared by the continuous precipitation method. The sharp and well defined peaks observed in all samples correspond to the TCP (hydroxyapatite structure, JCPDS file 9-0432). As can be seen in Fig. 1, the peaks in the XRD patterns become broader and their intensity slightly decreased as the milling time increased from 0 to 15 h. The broader peaks in the milled powders indicated a decrease in the crystallite size of the TCP from 57 nm (non-milled sample) to 13 nm (15 h milling time), as found when the particle size was calculated by using the Sherrer equation. On the other hand, in relation to the infrared spectroscopy results, the IR spectra showed no band attributable to inorganic residues.

Fig. 1: X-ray pattern of tribasic calcium phosphate: a) without ball mill (TCP), b) ball milling 5 h (TCP-5), c) ball milling 10 h (TCP-10) and d) ball milling 15 h (TCP-15).

Scanning electron microscopy (SEM)

The size and shape of the grains of the non-milled TCP sample and ball milled TCP samples as determined by SEM are very different (Fig. 2). The grains of the original TCP sample are large, close to $10 \mu\text{m}$, and no texture is observed. The surface is smooth and typical of a crystallized material. The treated TCP-5 sample presents homogeneous particles in agglomerated form whose size is less than $10 \mu\text{m}$. The TCP materials obtained with 10 and 15 h of milling time present a clear agglomerated structure and large agglomerates can be observed.

Fig. 2: Top-view SEM images of the calcium phosphate tribasic samples: a) CPT, b) TCP-5, c) TCP-10, d) TCP-15.

BET specific surface area and pore total volume

The specific surface area of the original TCP was found to be $60.5 \text{ m}^2/\text{g}$, while all other TCP samples had areas between 19 and $12 \text{ m}^2/\text{g}$, as seen in Table 1. The lowest value was $12.5 \text{ m}^2/\text{g}$ obtained for the TCP-15 sample treated with 15 h of ball milling. A variation of 5 h of milling time (from 5 to 10 h) diminishes the surface area more than 10 %. Thus, as observed, specific surface area decreased as a function of milling time (Fig. 3), and a milling time control is therefore essential to obtain the desired specific surface area. On the other hand, the pore total volume of TCP samples diminished from 0.2053 to $0.0256 \text{ cm}^3/\text{g}$ with the milling time from 0 to 15 h.

Fig. 3: BET specific surface areas of the tribasic calcium phosphate samples as a function of ball milling time.

Chromium (VI) sorption

Equilibrium retention values of chromium (VI) ions on TCP samples as a function of milling time are shown in Fig. 4. The chromium retention value for TCP samples obtained by 0 h ball milling time (TCP sample) was $8.1 \times$

10^{-4} meq/g, and for TCP solids, which were obtained by 5 h ball milling time (sample TCP-5) it was 11.4×10^{-4} meq/g. The retention increased to 12.0×10^{-4} meq/g for sample TCP-10 and to 14.0×10^{-4} meq/g for sample TCP-15, *i.e.*, there was a chromium retention increase on TCP samples with an increase of milling time.

Fig. 4: Cr(VI) ions sorption on tribasic calcium phosphate samples as a function of ball milling time. Experimental conditions: concentration of Cr(VI) ions = 1.0×10^{-4} M, pH 5.5, room temperature.

DISCUSSION

The specific surface area of original TCP was found to be $60.5 \text{ m}^2/\text{g}$, a value in accordance with data previously reported for tribasic calcium phosphate type hydroxyapatite;¹⁸ however, the specific surface area values for milled TCP samples followed a decreasing trend as the ball milling time was increased, as shown in Table 1. The surface area of the TCP without ball milling treatment is thus larger than that of ball milled TCP-5, TCP-10 and TCP-15 samples.

Table 1. Comparison of the obtained results of each tribasic calcium phosphate sample.

Sample	Milling time (h)	Specific surface area (m^2/g)	Pore total volume (cm^3/g)	Particle size (nm)
TCP	0	60.55	0.2053	57
TCP-5	5	16.81	0.0404	19
TCP-10	10	15.11	0.0320	16
TCP-15	15	12.57	0.0256	13

On the other hand, for the surveyed powders, the TCP-15 sample presented the smallest crystallite size (13 nm) and the original TCP sample showed the biggest crystallite size (57 nm), as shown in Table 1. As can be seen with 15 h of ball milling, the particle size diminished approximately 4.4 times lower than that of TCP without ball milling; this must be an effect of the particle fracture caused by the high energy impacts of the balls during milling. It was expected that the specific surface area values of the samples treated with ball milling would increase with milling time because of a decrease of particle size; nevertheless the obtained results show the contrary. An explanation is that the balls of the high energy ball mill strike on TCP grains, thus breaking and fracturing the grains until the sizes of particles previously mentioned were obtained. In addition to grain fracture, the particles generated must have undergone a compression by the strokes of the steel balls, so that the pores of these particles were reduced in volume, thus causing a reduction of the total pore volume, and consequently a reduction of the specific surface area values of TCP samples, as shown in Table 1. To prove this explanation, the total pore sample volume of TCP samples treated with the ball milling was measured and compared with the TCP sample without any ball milling treatment, and the values were found to be 0.2053, 0.0404, 0.0320 and $0.0256 \text{ cm}^3/\text{g}$ for TCP, TCP-5, TCP-10 and TCP-15 respectively, which confirms the explanation given for the unexpected low values of the specific surface areas.

On the other hand, it is well known that the higher the specific surface area of an inorganic sorbent, the higher the cation or anion retention on the sorbent.¹⁹ As in this paper a decreasing surface area was found with milling time as described above, it was expected that a lower number of chromium (VI) ions were adsorbed on the TCP milled particles. However, it was found that chromium (VI) ions were increasingly retained on TCP milled samples as the corresponding surface area decreased. This contradiction can be clarified upon observing the presence of Fe in the milled TCP samples as detected by XRD and EDS measurements.

The presence of Fe in the ball milled TCP samples, as determined by X-ray diffraction patterns (see Fig. 1) and the EDS probe (Table 2), must have originated from the steel balls. It should be noted that Fe is present in the TCP-15 ball milling sample in considerable amounts. The peak centered at 45° in 2θ degrees of the X-ray pattern (Fig. 1) is intense and corresponds to Fe. In our study, such conditions can facilitate the Cr(VI) ion sorption, since the Fe present in the milled TCP samples modifies their particle surface. In sorption processes, the sorption of metal ions on mineral surfaces may occur because of metal ion interactions with sorbed functional groups, such as hydroxyl groups on the mineral surfaces.

Table 2. Chemical composition of the sample milled for various times (wt%).

Sample	Milling time (h)	O	P	Ca	Fe
TCP	0	39.89	17.84	42.26	-
TCP-5	5	42.89	14.77	42.34	-
TCP-10	10	41.31	15.99	41.64	1.06
TCP-15	15	37.58	15.67	38.47	8.28

Such behavior may be compared with results reported for other compounds such as zeolites,²⁰ in which their Fe modified surface facilitates the behavior of sorption of arsenate metal present in an aqueous solution; thus the observed slightly increasing Cr(VI) sorption on milled TCP samples may be due to the presence of Fe coming from the steel balls and adsorbed on the TCP particle surface.

Studies carried out to examine the influence of pH on chromium ion sorption²¹⁻²³ show that percentage sorption is higher at acid pH and decreases when the pH increases to alkaline media. Baral *et al.*²³ found that the maximum sorption of chromium ions on sawdust occurred at the pH range 4.5-6 and when the pH is further increased, a sharp decrease in percentage of adsorption was observed. Similarly, Bendezu *et al.*²⁴ found a very high sorption capacity (657.27 mg/g) of activated carbon for Cr(VI), at pH 3.0. On the other hand, in an aqueous solution with a pH higher than 5.5, Cr(VI) is present in the chemical form of CrO_4^{2-} ions^{25,26} and at lower pH values, Cr(VI) is present either as HCrO_4^- or as $\text{Cr}_2\text{O}_7^{2-}$, depending on the Cr concentration. In this paper, the Cr(VI) sorption on TCP samples was carried out with a $1 \times 10^{-4} \text{ M K}_2\text{Cr}_2\text{O}_7$ aqueous solution with a pH value of 5.5; thus, Cr(VI) must have been sorbed onto the tribasic calcium phosphate surface as HCr_2O_7^- ions, mainly.

Solutes interact with mineral surfaces because these materials acquire an electrical surface charge due to the reactions involving functional groups (H^+ , OH^-) on the mineral or Fe-modified solid surface and ions in solution. Results show that the electrical properties of this material surface, *i.e.*, the charge of the surface groups, are partially responsible for the ion sorption. Therefore, Cr(VI) species sorption on TCP may be partially attributed to the direct exchange of ions with a specific group on an adsorbing surface and to the presence of Fe ions on TCP surfaces.

CONCLUSIONS

The ball milling provides TCP samples with very small particle size (less than 20 nm). As milling time increased to 15 h, the particle size and the specific area of the milled TCP samples decreased because the small particles were compacted by the strokes of the highly energized steel balls of the mill. This compactness caused the pores of TCP particles to be reduced in volume, effecting a reduction of the total pore volume and, consequently, a reduction in the specific area of ball milled TCP samples. On the other hand, chromium (VI) sorption on milled TCP samples increased, also unexpectedly, as the specific

area became smaller. The presence of Fe originated from the steel balls in the milled samples explains the increasing Cr(VI) sorption. Fe is deposited on TCP nanometric particles surface causing an enhance of Cr(VI) ions sorption through interactions of these ions with the hydroxyl groups attached to Fe atoms.

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