



Research article

Hydroxyapatite precipitation with Hydron Blue dye



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ABSTRACT

Calcium phosphate, in the form of amorphous hydroxyapatite, precipitates out of neutral water solutions containing calcium and phosphate ions in the form of small agglomerates of 18 μm average size. When Hydron Blue dye (HB) is added, the insoluble particles gradually agglomerate further to 50 μm sizes. However, the removal capacity of hydroxyapatite for the dye is increased when the calcium phosphate nucleates and forms in the presence of dye. When coprecipitates form, the particles average 20 μm size and contain up to 60% organic matter. Nascent calcium phosphate particles have strong capacity for Hydron Blue dye removal. Thus smaller calcium phosphate particles increase the amount of dye molecules in water pollution control.

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1. Introduction

Hydroxyapatite, $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ (HA), is the least water soluble calcium phosphate and forms whenever calcium and phosphate ions are present in aqueous solution at above neutral pH values (Carlson et al., 1997). Because the solubility product (Larsen, 1966) is very small (K_{sp} of 10^{-110} for HA), nanoparticles form rapidly and the initial precipitate is amorphous to X-ray diffraction (Tsuji et al., 2008). Amorphous calcium phosphate has been widely investigated to understand biological mineralization through nucleation and maturation stages (Kazanci et al., 2006; Brundavanan et al., 2015). Such amorphous HA suspensions in gel form have also been investigated recently for use in pollution control (Lemlikchi et al., 2008; 2013). The reaction of HA gel with aqueous lead ions was found to proceed faster than with HA particle suspensions. The presence of smaller particles with larger surface areas explains the increased reactivity of HA gel because lead ions first exchange with surface bound protons, before reacting

with calcium ions in an ion exchange mechanism (Pham Minh et al., 2012). Indeed, near neutral pH values, HA surfaces equilibrate to hydrogenophosphate ions. The introduction of HA gel in the flow of a municipal wastewater treatment plant resulted in decreases of all the trace metals present. Furthermore, soluble organic matter concentrations also decreased when HA gel was mixed in with the real wastewater (Lyczko et al., 2014). The exact mechanism of this reactivity is not well understood but thought to proceed via a surface adsorption or surface complexation by organic chelating functional groups. It was found that surfactants like dodecylsulfate ions decreased the solubility product of HA (Shimabayash et al., 1989). Industrial textile dye pigments could be removed from textile wastewater by adsorption on HA at neutral pH values. The adsorbent could be regenerated, following thermal treatment to burn out the organic fraction, by dissolution in acid solution of the solids followed by re-precipitation of a new gel by acid neutralization (Lemlikchi et al., 2008).

In this work, we compare the decolorization of Hydron Blue dye solutions at neutral and basic pH values depending on whether the dye is added to the HA gel, or the gel is formed in the presence of the dye. In the first case, an adsorption reaction is described, whereas in the second case a coprecipitation reaction occurs. In both cases the dye can be removed, but at different rates. The particle size distributions are different in both cases.

Abbreviations: CaP, calcium phosphates; HA, hydroxyapatite; HB, Hydron Blue; PZC, point zero charge.

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2. Materials and methods

2.1. Chemicals

Hydron Blue dye was obtained via the Algerian 'Cotitex' Manufacturing Industry Co. and used without further purification. Calcium nitrate monohydrate, anhydrous trisodium phosphate and disodium monohydrogen phosphate dodecahydrate (from VWR, Germany) were used to make salt solutions in distilled water. Stoichiometric amounts (at 1.5 Ca/P molar ratio) were added in order to form CaP precipitates in 100 mL of distilled water at the required pH values (295 K): $[Ca^{2+}] = 6.6$, $[H_2PO_4^-] = 2.6$, and $[PO_4^{3-}] = 1.8$ mmol/L at pH 7.3; $[Ca^{2+}] = 6.6$ and $[PO_4^{3-}] = 4.4$ mmol/L at pH 10.6. The pH values were not adjusted and corresponded to the pH resulting from the reagent used. HB dye was dissolved in water and added to the CaP preparation in order to obtain the required concentration. The analyzed samples were mixed at 1500 rpm, either before or after the introduction of the calcium phosphates.

2.2. Physico-chemical techniques

UV-VIS spectra were recorded on a UV-1601PC SHIMADZU spectrophotometer using quartz cells. TGA and DSC analysis was carried out with a Q600 thermal analyzer (TA Instruments). A Malvern Mastersizer was used to measure particle size distributions in a 500 mL beaker without ultrasounds.

2.3. Experiments

When solutions of calcium and phosphate ions were mixed together at pH 7.3, loss of transparency occurred immediately and a milky white precipitate formed. The colloidal suspension remained opaque for a long time before any sedimentation occurred. For low dye concentrations (up to 25 mg/L) the blue color disappeared following 15 min of decantation. For higher dye concentrations (50–100 mg/L) the solution is also decolorized but took longer time (1 h for 100 mg/L) to clear. When CaP was formed in the presence of HB (experiment 1a), the particle sizes formed ranged from 15 to 20 μm at pH 7.3 as measured by Laser diffraction. Such CaP particles of small sizes were recently reported by sol-gel formation in ethanol (Bakan et al., 2013).

On the other hand, when the dye solution was introduced into the pre-formed CaP gel (experiment 2a), decolorization was not so complete and only partial removal of dye was observed for the same amount of CaP. To confirm the transfer of the dye from the liquid phase to the solid phase, the suspensions were filtered and the dried solids subjected to thermogravimetric analysis (TGA). In a typical thermogram (Supplementary Materials; Fig. 1S) an endothermic loss of water occurred between 20 and 200 °C followed by an exothermic combustion of organic matter from 200 to 600 °C. The degradation of the organic matter comprised two steps. The major weight loss occurs centered near 400 °C and corresponds to graphitization, whereas the next weight loss centered near 700 °C was related to combustion of graphitic carbon. Thus visible spectroscopy or TGA could both be used to quantify dye removal from solution.

3. Results and discussion

Four types of experiments were carried out to explore how calcium phosphates could decolorize Hydron Blue: 1) coprecipitation of dye with a CaP gel made in situ at pH 7.3 (1a) and at pH 10.6 (1b); 2) adsorption of dye on CaP gel made at pH 7.3 (2a) and at pH 10.6 (2b). In experiments 1a and 1b, the CaP gel was formed directly

in the dye containing solutions. In experiments 2a and 2b, the CaP gel was made in distilled water, equilibrated one hour at room temperature (295 K) then introduced into the dye solutions at various concentrations.

3.1. Coprecipitation and adsorption of dye at neutral pH (Experiments 1a and 2a)

The UV–visible spectra of Hydron Blue aqueous solutions show an absorption maximum at around 600 nm. The weight loss observed by TGA corresponds to the organic matter sorbed on CaP solids and removed from water leading to the visible absorption spectrum decrease. The results from the TGA analysis in experiments 1a and 2a are reported in Fig. 1. These differences in the two precipitation modes are clearly seen in graphical form where the dye removal is plotted as a function of the dye content present in solution. Coprecipitation yields a linear relation whereas adsorption levels near 12–13.6%. The graph illustrates that experimentally determined TGA losses correspond to the expected ones calculated from the concentrations of products involved. However, for the adsorption mode, decolorization occurs only partly. The difference between adsorption and coprecipitation is also clearly seen in Fig. 2, where the percentage of dye elimination is plotted as a function of the dye concentration.

3.2. Coprecipitation and adsorption of dye at basic pH (experiments 1b and 2b)

Similar experiments for coprecipitation (1b) and adsorption (2b) are performed at pH 10.6. Fig. 3 represents the percentage of dye removal by both methods following 15 min of clarification. In fact, at higher pH values the nucleation of CaP gel is faster than in neutral pH conditions. Again, the coprecipitation mode removes more dye, even though complete decolorization is not obtained at the dye concentration higher than 500 mg/L, and only 10% elimination is obtained for a dye concentration of 1 g/L. This could be related to hydroxyl ions adsorption occupying the adsorption sites at this pH value. These figures changed little with time, reaching 99.8% for dilute dye and only 11.35% for concentrated dye following 5 h of settling. The adsorption reactions gave very poor results, with insignificant removal results even though the particle surfaces were blue colored.

Under basic pH conditions (pH = 10.6), the CaP particles formed ranged from 20 to 30 μm size, values slightly larger than those determined at neutral pH values (15–20 μm).

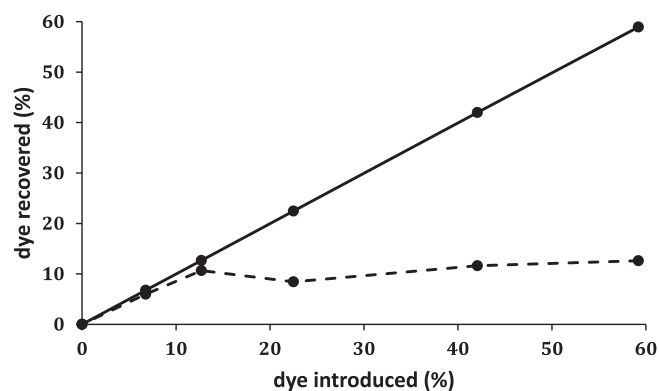


Fig. 1. BH mass loss on CaP ($[Ca^{2+}] = 6.6$ mmol/L; 1.5 Ca/P molar ratio) by adsorption mode (dashed line) and coprecipitation mode (solid line) for increasing concentrations of HB dye (0; 50; 100; 200; 500; 1000 mg/L) after 1 h of equilibration time at pH 7.3.

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