

# Hydroxyapatite precipitation with Blue Hydron dye.

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## ABSTRACT

Calcium phosphate, in the form of hydroxyapatite  $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ , precipitates out of neutral distilled water solutions containing calcium and phosphate ions in the form of small agglomerates of 18 micrometer average size. The insoluble particles gradually agglomerate further to 50 micrometer sizes in the presence of Blue Hydron dye. The removal capacity of hydroxyapatite for the dye is increased when the calcium phosphate nucleates and forms in the presence of dye, leading to co-precipitates of 20 micrometer average size containing up to 60% organic matter. It is concluded that nascent calcium phosphate particles have strong potential for water pollution treatment.

Key words: hydroxyapatite, agglomeration, co-precipitation, particle-size-distributions, adsorption, flocculation.

## 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 or above neutral pH values [1]. Because the solubility product [2] is very small ( $K_{sp}$  of  $10^{-110}$  for HA), nano particles form rapidly and the initial precipitate is amorphous to X-ray diffraction [3]. Amorphous calcium phosphate has been widely investigated to understand biological mineralization through nucleation and maturation stages [4, 5]. Such amorphous HA suspensions in gel form have also been investigated recently for use in pollution control [6, 7]. 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 [8]. Indeed, near neutral pH values, HA surfaces equilibrate to hydrogenophosphate ions. The introduction of HA gel in the flow of a municipal waste water treatment plant resulted in decreases of all the metallic trace elements present. Furthermore, soluble organic matter concentrations also decreased when HA gel was mixed in with the real waste water [9]. 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  $K_{sp}$  of HA [10]. Industrial textile dye pigments could be removed from textile waste waters by adsorption on HA at neutral pH values and 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 neutralization of the acid [7].

In this work, we compare the decolorization reactions of Blue Hydron vat dye solutions at neutral or basic pH values depending on whether the dye is either 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 co-precipitation reaction occurs. In both cases the dye can be removed, but at different rates. The particle size distributions are different in both cases.

## MATERIALS AND METHODS

The blue Hydron dye was procured via the Algerian 'Cotitex' Manufacturing Industry Co. and used without further purification. 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 analyser from TA Instruments. A Malvern Mastersizer was used to measure particle size distributions in a 500mL beaker without ultrasounds. Calcium nitrate monohydrate, anhydrous tri-sodium phosphate and disodium monohydrogen phosphate dodecahydrate from VWR (Germany) were used to make salt solutions in distilled water. Stoichiometric amounts were pipeted into 400 mL water to form precipitates with Ca/P ratios of 1.5. The blue dye was added in solution form to the analyzed sample mixed at 1500 rpm, either before or after the introduction of the calcium phosphates. The pH values were not adjusted and corresponded to the pH resulting from the reaction (near neutral for the hydrogenphosphate, and basic for the tri-sodium phosphate)

## RESULTS AND DISCUSSION

When dilute solutions of calcium and phosphate ions are mixed together in distilled water, loss of transparency occurs immediately and a milky white precipitate forms. The colloidal suspension remains opaque for a long time before any sedimentation occurs. Laser diffraction gives a mean particle size of 10 to 15 micrometers for the calcium phosphate (CaP) formed at pH = 7.3, and from 15 to 20 micrometer size at pH = 10.6. When CaP is formed in the presence of Blue Hydron

(BH) dissolved in water, the particle sizes formed range from 15 to 20 micrometers at pH 7.3 and from 20 to 30 at pH 10.6. At rest, the particles slowly form flocs and precipitate and the clarified solution is colorless or slightly colored depending on the concentrations involved. CaP particles of smaller sizes were reported by sol-gel formation in ethanol [11].

The UV-visible spectra are illustrated in Fig.1 and show a wavelength of maximum absorption at 600 nm for the blue pigment. For low dye concentrations (up to 25 mg/L) the blue color disappears following 15 min of decantation. For higher dye concentrations (50 to 100 mg/L) the solution is also decolorized but takes longer time (1h for 100mg/L) to clear. On the other hand, when the dye solution is introduced into the pre-formed CaP gel, decolorization is not as complete and only partial removal of dye is observed for the same amount of CaP.

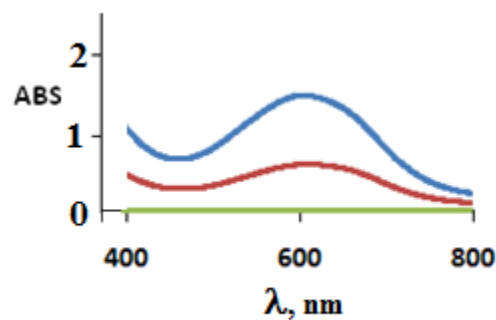


Fig.1. UV-VID spectrum of BH dye solution at  $100\text{mgL}^{-1}$  (top spectrum), and following decantation after sorption on CaP solids (middle spectrum) or after coprecipitation with CaP (bottom line)

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). A typical thermogram is presented in Fig.2 and reveals an endothermic loss of water between 20 and  $200^{\circ}\text{C}$  followed by an exothermic combustion of organic matter from 200 to  $600^{\circ}\text{C}$ .

A similar result for thermal stability of a red dye was reported on mica [12], and for methylene blue adsorbed on bio-waste consisting of seeds [13]. The degradation of the organic matter comprises two steps. The major weight loss occurs centered near  $400^{\circ}\text{C}$  and corresponds to graphitization, whereas the second weight loss centered near  $700^{\circ}\text{C}$  is related to combustion of graphitic carbon. Thus visible spectroscopy and TGA could be used to quantify dye removal from solution. 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. Four types of experiments were carried out to explore the decolorization reaction: 1) adsorption of dye on CaP gel made at pH 7.3 (1a) or at pH 10.6 (1b); 2) co-precipitation of dye with a CaP gel made in situ at pH 7.3 (2a) or at pH 10.6 (2b).

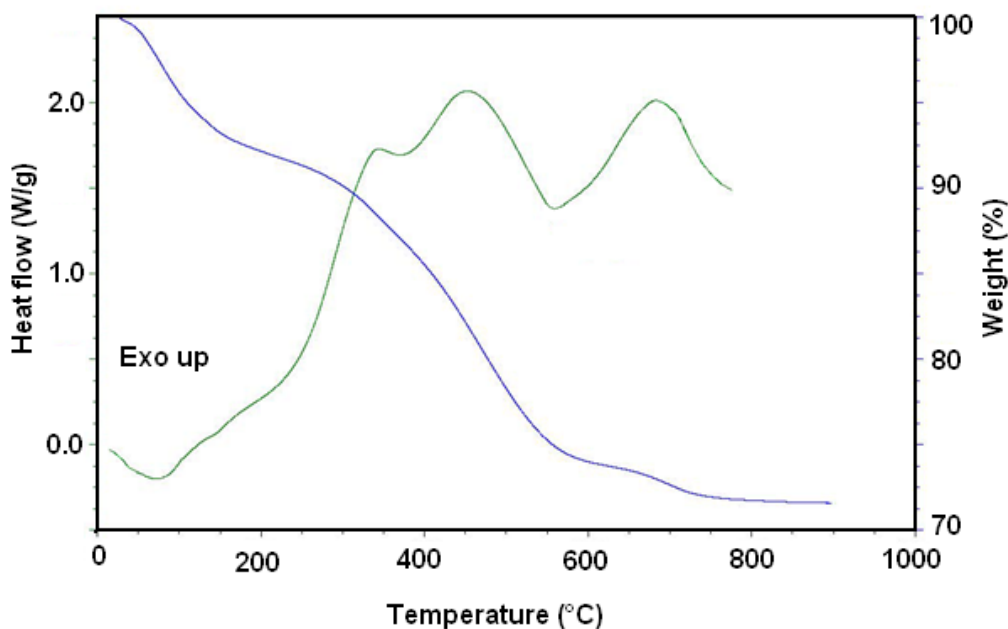


Figure 2 : TG-DSC analysis of BH dye sorbed on calcium phosphate solids

In reactions 1a and 1b, the CaP gel was made in distilled water, equilibrated one hour at room temperature (295K) then introduced into the dye solutions at various concentrations. In reactions 2a and 2b, the CaP gel was formed directly in the dye containing solutions.

Table 1 summarizes the results obtained by TGA using dye concentrations varying from dilute (50 mg/L) to concentrated (1g/L), a small amount of CaP (68.8 mg) and long equilibration time (one hour of decantation following 10 min of mixing). Because only 100 mL of solution were used, the contents in dye ranged from about 6 to 60 % of the total mass of solids introduced initially in the solutions.

Table 1: Evaluation of dye removal by thermogravimetric analysis

Mi (mg)	Mr ads.(mg)	Mr copr. (mg)	%E ads.	%Ecopr.
100	21.3	99.50	21.30	99.54
50	13.8	49.9	27.60	99.80
20	7.48	19.96	37.42	99.82
10	8.41	9.98	83.94	99.68
5	4.41	4.99	88.24	99.85

$M_i$  is initial mass of dye introduced,  $M_r$  is mass of dye removed and found in solid phase after co-precipitation (copr.) or adsorption (ads.) %E is the percentage of dye elimination found. The conditions used were: total volume 100 mL, pH = 7.6, temperature 25°C, time 75 mn.

All other parameters remaining constant, it can be observed that introduction into the gel removed from 4.41 to 21.30 mg of dye whereas co-precipitation removed from 4.99 to 99.50 mg of dye. The percentage of dye elimination from solution worked well by adsorption on CaP gel when dilute (88.2 % removal) but failed for concentrated solutions (21.3 % removal). On the other hand, co-precipitation removed the dye efficiently at all concentrations, from 99.85 % to 99.54 %. Reactive dyes were also removed almost completely by combined coagulation with Al(III) and soption on carbon [14].

These differences are clearly seen in graphical form (see Fig. 3) where the removal of dye is plotted as a function of the content of dye present in solution. Co-precipitation yields a linear relation whereas adsorption levels near 12 to 13.6 %. The graph illustrates the fact that the experimentally TGA determined mass loss corresponds linearly to the expected one calculated from the concentrations of products involved, except for the adsorption case, where decolorization occurs only partly.

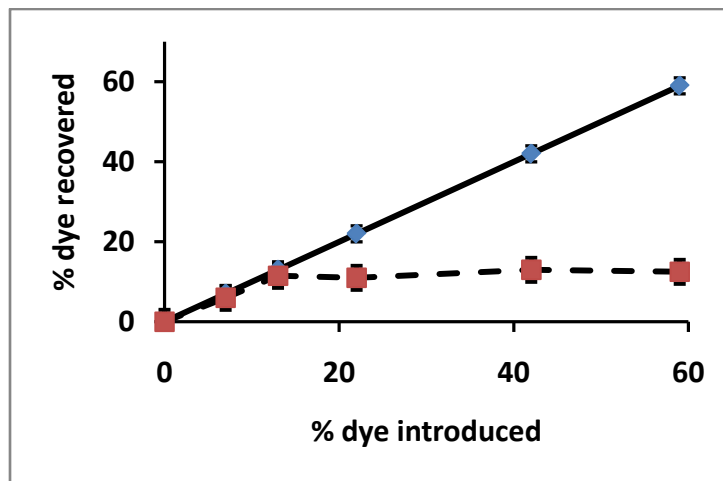
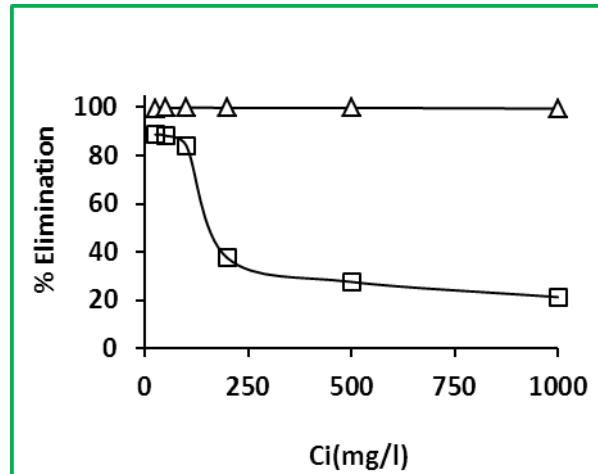
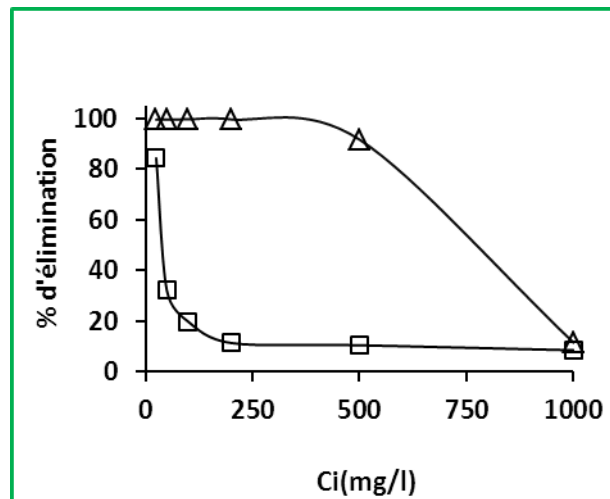


Figure 3: BH mass loss on CaP by sorption (dashed for adsorption mode and full line for coprecipitation mode, with increasing concentrations of BH dye (50; 100; 200; 1000 mg.L-1) after 75 minutes of equilibration time and at pH7.3.

The difference between adsorption and co-precipitation is also seen clearly in Fig. 4, where the % elimination of dye is plotted as a function of the dye concentration. To check for kinetic effects, the same series of trials were conducted but with shorter decantation times.



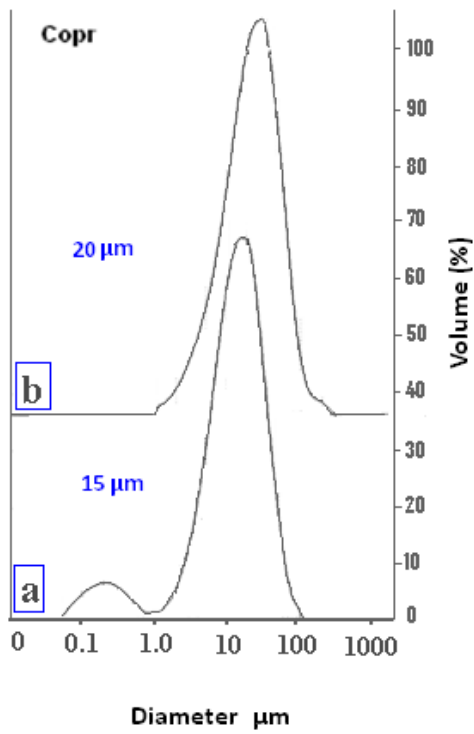
**Figure 4 :**Variation of BH dye removal (%) with the initial dye concentration at pH 7.3 and after 75 minutes of equilibration time. Triangles represent co-precipitation and squares adsorption



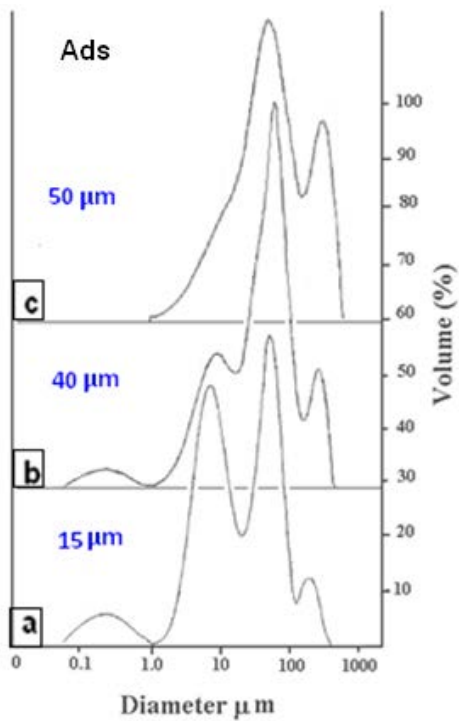
**Figure 5 :**Variation of BH dye removal (%) with the initial dye concentration at pH 7.3 and after 15 minutes of equilibration time. Triangles represent co-precipitation and squares adsorption.

Fig. 5 represents the % removal of dye by both methods following 15 min of clarification. Again, the co-precipitation removed more dye, even though complete decolorization was not obtained at the higher dye concentration of 1g/L.

Particle size distributions were followed during the first 15 min of reaction. In the case of co-precipitation sizes ranged from 15 to 20 micrometers and remained stable (see Fig 6). These values were very close to the 10 to 15 micrometer sizes observed for CaP without dye. The particles tend to stay in suspension by forming hydrogen bonds with solvent and hydration water molecules, as demonstrated by the formation of a gel phase. On the other hand, in the dye adsorption method, average particle sizes started at 15 micrometers and continuously rose to 50 micrometers, as illustrated in Fig. 7.



**Figure 6.** Particle size distribution of CaP precipitates formed at pH 7.4, following mixing with BH, at a) 5 min, and b) 15 min.



**Figure 7.** Particle size distributions of CaP agglomerates in the presence of BH as a function of time: a) after initial mixing, 5min. b) after 10 min. c) after 15 min.

It can be observed that smaller particles gradually agglomerated into larger ones during the first 15 minutes of decantation. The formation of CaP agglomerates can be observed by microscopy as illustrated in figure 8. It may be assumed that the composite material formed containing mineral and organic phases has a lower density and could remain longer in suspension in water before precipitating. A possible explanation for the more limited capacity of CaP to remove dye by adsorption may be related to the fact that once the particles agglomerate they tend to precipitate out of solution (with some dye on the surface) thus preventing further reaction with the dye molecules still in solution. We hypothesize that the dye adsorbs on the outer particles of the agglomerates, and cannot diffuse inside, thus limiting the amount of accumulated organics. In the co-precipitation case, the dye contents immediately react with the nucleating particles before they have time to agglomerate, and fall out of solution when the agglomerates form containing both CaP and dye, and reach 20 micrometer sizes.

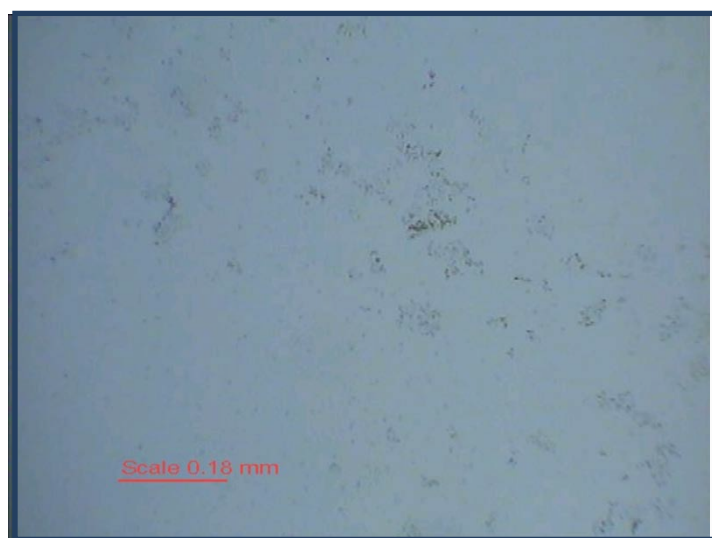


Fig. 8. View of the agglomeration of CaP particles in water.

Under basic pH conditions ( $\text{pH} = 10.6$ ), it was noted that CaP particles formed ranged from 20 to 30 micrometer size, values slightly larger than those determined at neutral pH values (15 to 20 micrometers). When co-precipitation of CaP with BH took place at  $\text{pH} 10.6$ , 99.7% elimination occurred within 15 min for a 50mg/L dye concentration and only 10 % elimination for a dye concentration of 1g/L. This could be related to adsorption of hydroxyl ions occupying the adsorption sites at this pH. 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 colored blue. With both methods, the average particle sizes were between 20 to 30 micrometers in size, identical to the values found without the dye.



## CONCLUSION

When interacting with BH dye in neutral pH solutions, near the PZC of HA, CaP particles in gel form slowly agglomerate to form large flocks of 50 micrometer size. Co-precipitation of CaP in the presence of BH dye reacts faster and forms smaller flocks of 20 micrometer size and removing larger amounts of dye. The solids recovered after filtration may contain up to 60 % of organic matter. We hypothesize that smaller nascent particles react quickly with dye molecules to form co-precipitates whereas on pre-formed CaP particles, adsorption of dye proceeds gradually to form large flocks with more limited removal capacity. Further research would be needed to better understand how CaP particles contribute to water purification under more complex situations. A dissolution-re-precipitation mechanism could contribute to progressively remove larger amounts of pollutants from contaminated solutions, at least near neutral pH conditions.

## ACKNOWLEDGMENTS

W.L. thanks the Algerian government for a stipend for post-doctoral research abroad.

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## Legends to the figures

Fig.1. UV-VID spectrum of BH dye solution at 100mgL<sup>-1</sup> (top spectrum), and following decantation after sorption on CaP solids (middle spectrum) or after coprecipitation with CaP (bottom line)

Figure 2: TG-DSC analysis of BH dye sorbed on calcium phosphate solids

Figure 3 : BH mass loss on CaP by sorption (dashed within gel mode (G) an coprecipitation mode (P) for increasing concentrations of BH dye (50; 100; 200; 1000 mg.L<sup>-1</sup>) after 75 minutes of equilibration time and at pH7.3.

Figure 4: Variation of the BH dye removal rate (%) with the initial concentration at pH 7.3 and after 75 minutes of equilibration time.

Figure 6. Particle size distribution of CaP precipitates formed at pH 7.4, following mixing with BH, at a) 5 min, and b) 15 min.

Figure 7. Particle size distributions of CaP agglomerates in the presence of BH as a function of time: a) after initial mixing, 5min. b) after 10 min. c) after 15 min.

Figure 8. View of CaP agglomerates formed in water using optical microscopy.

Table I: Removal of Blue Hydron dye by hydroxyapatite adsorption (ads) or co-precipitation (copr) at pH = 7.3 ; T = 25°C and time t =75 min.