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Calcium phosphate sorbent for environmental application

Nathalie Lyczko[a]*, Ange Nzihou[a], Patrick Sharrok[a,b]

[a]*Université de Toulouse, Mines Albi, CNRS, Centre RAPSODEE, Campus Jarlard, F-81013 Albi Cedex 09, France*
[b]*Université de Toulouse, SIMAD, IUT de Castres, av. Pompidou, Castres 81104, France*

Abstract

Heavy metal pollution in soils, wastewater or fly ashes is a persistent environmental problem. This pollution in water or wastewater is an ongoing environmental problem and the rules to control and decrease this pollution are increasingly strict. The extreme toxicity of heavy metals even at low concentration and their bio-accumulation cause a lot of environmental problems. Minerals such as the calcium phosphate of general formula $M_{10}(XO_4)_6 Y_2$ with M a divalent cation, $(XO_4)^{3-}$ a trivalent anion and Y^- a monovalent anion are well know for trapping metal ions. The retention of heavy metals by calcium phosphate has been already widely studied in aqueous solutions.
In this study, a low cost calcium phosphate gel (Ca-HA) synthesized from a calcium carbonate industrial waste was used as a sorbent for wastewater treatment. We have characterized this sorbent before and after use. The physical characterization showed a decrease of the specific surface area and density. The granulometry measurements showed an increase of the particles diameter explained by the sorption of pollutants (organic molecules). The presence of these molecules was confirmed by total and organic carbon measurement and thermal analysis. The elemental measurements confirmed also the heavy metal sorption by the Ca-HA. A calcination of the contaminated Ca-HA was carried out at different temperatures. After calcination the solid contained less organic molecules and heavy metals were concentrated in the matrix.

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Keywords: calcium phosphate, wastewater treatment, heavy metals, organic molecules.

1. Introduction

Before returning to the natural environment, contaminated wastewaters are treated mostly by a biological digestion of the organic matter. In France the cost of such biodegradation accounts for half the cost of drinking water and produces sludge which must be disposed of particularly when contaminated by heavy metal ions. Heavy metal pollution in water or wastewater is an ongoing environmental problem and the rules to control and decrease this pollution are increasingly strict. Pollution problems arise from the bio-accumulation of toxic metals which are directly or indirectly discharged into the environment. The accumulation of heavy metals in biochemical processes has been reviewed [1]. To control this pollution and to remove the heavy metals, many technologies have been developed and tested [2, 3, 4, 5]. These technologies have drawbacks because the elimination of heavy metals is not complete and the cost is high. Therefore, continued efforts are being deployed to develop inexpensive separation methods for non-biodegradable pollutants, particularly toxic heavy metals, from aqueous solutions. For use in sorption, innovative products should be low cost and have minimal environmental impact. Materials such as activated carbon [6], silica [7], zeolites [8], clays [9], calcite [10], activated sludge [11], or activated phosphate rock [12] have been reported for use as sorbent for heavy metals. The cost of activated carbon is increasing due to more environmental applications

* Corresponding author. Tel.: +33-563493122; fax: +33-563493243.
E-mail address: nathalie.lyczko@mines-albi.fr

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and reaches now 3 000 dollars per ton, which is more than twice the cost of calcium phosphate sorbent cost made with waste calcium carbonate (negative price). The manufacture of the calcium phosphate does not require any sophisticated installation other than a simple mixing reactor, and storage tanks.

Inorganic phosphates such as hydroxyapatite (Ca-HA) have a long history of laboratory use in experiments to remove metals from aqueous solutions [13], but have never been tried in the industrial scale treatment of real waste water.The apatites are well known and their general formula is $M_{10}(XO_4)_6 Y_2$ with M a divalent cation, $(XO_4)^{3-}$ a trivalent anion and Y^- a monovalent anion [14]. The synthesis of hydroxyapatite by wet methods [15, 16] has been reported as yielding a high specific-surface-area solid, which can be used directly following precipitation when the starting products do not contain counter-ions such as nitrate and ammonium. Ca-HA can be of natural or synthetic origin and both have been investigated as sorbents for heavy metals [17]. The metal- retention capacity of calcite has been described [18]. It was found that divalent metal ion sorption depended on aqueous calcium concentration and that desorption was correlated with hydration energies of the metal sorbates. Some metals (Cd, Mn) behave as surface precipitates that dehydrate rapidly while others (Zn, Co, Ni) form surface complexes that get incorporated into the structure by recristallization. Some studies have focused on the ability of Ca-HA to retain one heavy metal in aqueous solutions. As examples, the sorption of lead [19, 20, 21], Ni^{2+} [22], Zn [23, 24], Cd [25, 26] have all been reported. Some investigators have looked at the simultaneous sorption of several heavy metals in aqueous solutions [27, 28, 29]. These studies revealed the existence of a competitive sorption among the different heavy metals present [30, 31, 32]. In wastewaters, heavy metals are present together with many various organic molecules. The interactions of Ca-HA with different molecules, such as nitrobenzene [33], phenol [34] or textile dyes [35] have been investigated. It was found that the presence of EDTA prevents Cu(II) ion adsorption on Ca-Ha, due to the formation of complexes with chelating ligands [36]. The study of aqueous solutions containing heavy metals and low-molecular-weight organic acids [37] or EDTA [38] confirmed that the presence of organic ligands decreases the adsorption of heavy metal. The formation of metal-ligand complexes lowers the concentrations of free metal ions that can be exchanged for calcium in Ca-HA. Thus, the role of Ca-HA in waste water purification is as yet unknown and undescribed.

2. Materials and methods

2.1. Calcium phosphate

The hydroxyapatite (Ca-HA) used was synthesized in the laboratory according to an industrial process developed for valorization of calcium carbonate wastes which contain some heavy metals. The calcium-carbonate waste was suspended in water and potassium phosphate added and mixed at ambient temperature. The reaction equation is the following:

$$10\ CaCO_3 + 6\ KH_2PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 4H_2\ CO_3\nearrow + 6\ KHCO_3$$

A Ca-HA gel forms rapidly with release of gas due to the decomposition of dissolved carbonic acid. The suspension was used without further filtration, washing or drying steps.

2.2. Continuous experiments

Continuous experiments were carried out directly in a wastewater treatment plant where the pilot reactor was located after the buffer tank in order to obtain a homogeneous effluent and to avoid flow variations due to rainfall and entering effluents. Dilute NaOH was added to stabilize the pH of the effluent to a value above 8. This value is important to prevent partial dissolution of the solid sorbent that could release heavy metals. The effluent then entered a clarifier reactor which contained the Ca-HA gel. The contact between the effluent and the Ca-HA was confined to the reactor. Further processing took place in the decanter with a residence time of 24 hours before the purified effluent left by overflow. The samples to be analyzed were taken from the reactor at regular time intervals. The Ca-HA used for the treatment was also sampled, so that it could be characterized as a function of use-time. The single initial Ca-HA dose introduced was not renewed for 30 days.

2.3. Characterizations

For elemental analysis, samples were mineralised with hydrofluoric acid and then quantified by ICP-AES (Inductively coupled plasma - atomic emission spectroscopy). The apparatus used was an Ultima 2 from HORIBA Jobin Yvon.

The carbon measurements were made with a Shimadzu analyzer (Model TOC VCPH 5050A). The three quantifications were: 1- the total carbon content (TC), which corresponds to all carbon in the sample. 2- the inorganic carbon (IC) content, which corresponds to inorganic carbonates and hydrogenocarbonates. 3- the total organic carbon (TOC) content, which corresponds to the organic molecules in the sample. The TC and IC were directly measured and the TOC was deduced from the two first terms according to the equation: TOC (%) = TC(%) – IC(%).

Thermal analyses were carried out with a TGA/DSC apparatus, SDT Q600 by TA Instruments. Samples near 15mg of the solid were heated over the temperature range from ambient to 1000°C at a heating rate of 5°C/min. in air atmosphere with a 100 $mL.min^{-1}$ flow rate. Samples were analysed in alumina crucibles and the reference was an empty alumina pan.

The particle-size distribution measurement was carried out by laser diffraction, with a Masterzizer 2000 HYDRO from Malvern Instrument. The dispersing agent used was ethanol, to prevent dissolution of particles during the measurements. The range of the particle- size measurement was from 0.02 to 2000 µm.

Scanning electron microscopy (SEM) measurement was performed on a Philips XL30 ESEM apparatus. The voltage used for the analysis was 20 kV and the sample was not sputter-coated.

3. Results

The experiments were run on pilot scale with continuous introduction of wastewater on one initial dose of Ca-HA introduced in the reactor connected to the wastewater treatment plant. The whole resulting effluent was analysed (insoluble solid fraction in the reactor together with the liquid soluble fraction leaving the reactor), ie without filtration before analysis.

3.1. Elemental analysis of wastewater

In Fig.1, the contents of different heavy metals present in the wastewater are presented. The abatement was calculated from the following equation:

$$\text{Abatement}(\%) = \frac{[\text{HMi}]_o - [\text{HMi}]_t}{[\text{HMi}]_o} \times 100$$

with $(HMi)_o$ the concentration of the heavy metal "i" present in the waste water before treatment, $(HMi)_t$ the concentration of the heavy metal "i" in the wastewater after the contact with Ca-HA at the time t (t = number of treatment days).
In Fig.1, the changes in heavy metal concentrations show that the abatement was generally more than 50 percent (except for Cadmium and Cobalt). This abatement reached 90% for elements such as chromium and copper. The main heavy metals in the wastewater were aluminium, chromium and iron. The treatment with Ca-HA allowed reducing these elements by more than 60%. The treatment allowed an abatement of more than 50% for lead. Thus, treatment over a period of fifteen days gave good results for the continuous removal of heavy metals in real wastewater. At 30 days, the abatement decreased indicating saturation of the Ca-HA capacity. The abatement variations can be explained in part by the incoming concentrations of heavy metals, which varied by a factor of ten on a day-to-day basis. A second parameter played an important role in the adsorption of heavy metals. The organic matter present in the effluent was also picked up by the Ca-HA particles. These organic molecules interfered with metal ions and their precipitation on the solid phase.

3.2. Elemental analysis of the solid Ca-HA

During the treatment, the Ca-HA solid was monitored to measure the quantity of heavy metals incorporated. The pH of the wastewater was maintained around 8 to avoid partial dissolution of Ca-HA particles. The results are presented in Table 1 and confirm the uptake of heavy metals by the Ca-HA solids. The initial product contained 8.6g HM/kg Ca-HA (dry matter). After fifteen days, the solids contained 23.8g HM/kg Ca-HA, which corresponds to a sorption of 15.6g HM/kg Ca-HA. This sorption occurred dynamically throughout the treatment to achieve 27.9g HM/kg Ca-HA after 30 days. The quantity of lead present in the solid increased slowly (70 to 100g HM/kg Ca-HA in 30 days). The results point to the gradual formation of complex metal phosphate precipitates.

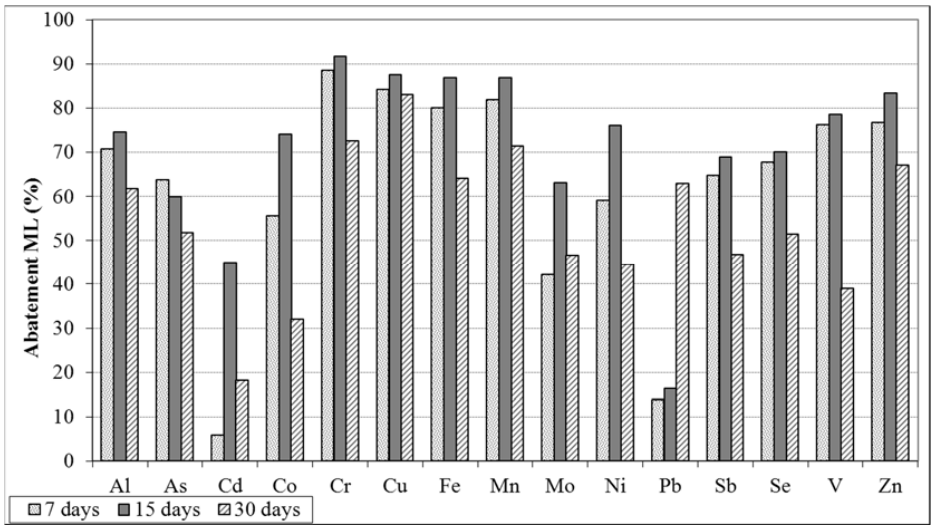

Fig. 1 Heavy metals presence during treatment of wastewater

Table 1 Element analysis

(mg/kgMS)	Initial Ca-P	Ca-P used 7 days	Ca-P used 15 days	Ca-P used 30 days
Al	1304	2214	3432	4505
As	< 0.001	16	26	36
Cd	9	1	1	1
Co	< 0.001	6	6	9
Cr	0.2	224	492	590
Cu	< 0.001	52	84	97
Fe	3417	7654	10697	11872
Mo	< 0.001	71	101	129
Mn	68	72	5	10
Na	3650	5456	8744	10342
Ni	< 0.001	13	11	56
Pb	70	66	72	100
Sb	7	6	11	26
Se	48	4	9	14
V	8	15	10	13
Zn	25	72	160	197
TOTAL	8606	15944	23861	27957

3.3. Ca-HA particle-size distribution

The particle-size distribution (PSD) of Ca-HA was measured before and after use. Fig.2 presents the PSD changes occurring during wastewater treatment. The initial calcium phosphate had a polymodal distribution with peaks centred respectively at 16 and 200 µm and a median diameter of 30 µm. For the PSD of Ca-HA after use, a wider spread was observed with a main peak around 450 µm. In Table 2 are presented the particle diameters. The shift of the main peak to larger dimensions corresponds to the growth and/or agglomeration of the Ca-HA solid particles and also to the potential coating of particles by the organic molecules present in the effluent. The amount of particles smaller than 1µm did not change during the treatment, which confirmed the stability of these particles in the decanter.

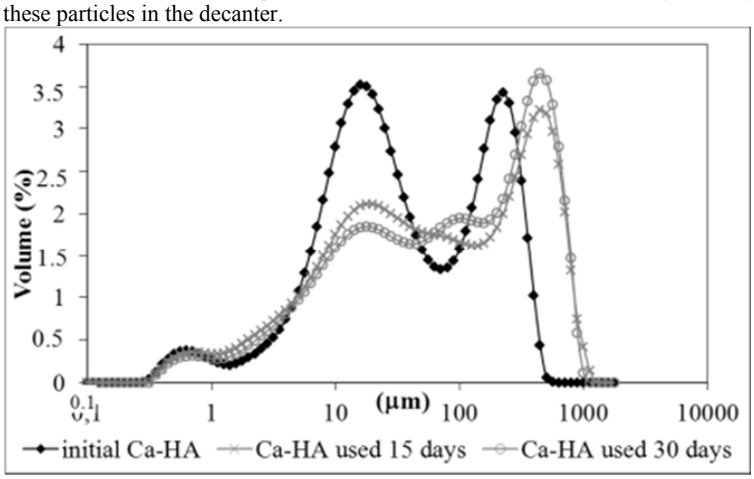

Fig. 2 Particle size distribution of Ca-HA

Table 2 Particle size distributions

(μm)	Initial Ca-HA	Ca-HA used 15 days	Ca-HA used 30 days
D10	5.9	4.8	5.5
D50	30.6	65.9	90.7
D90	268.8	573.6	570.5
D [4, 3]	91.2	191.3	202.8
D [3, 2]	9.4	9.9	11.1

3.4. Carbon measurements

To confirm the presence of organic molecules, the type of carbon (inorganic, organic, total) incorporated in the solid Ca-HA was quantified. The results are presented in Fig.3. The initial Ca-HA contained about 5% total carbon of which 44% corresponded to organic carbon. During the treatment, the total carbon increased from 5 to 40%. The amount of inorganic carbon remained unchanged while the TOC increased significantly. This observation shows that during the treatment of the effluent, the calcium phosphate adsorbed or incorporated organic molecules. This was confirmed by the thermal analysis of the solids recovered by filtration.

3.5. Thermal analysis

Fig.4 presents the weight losses from ambient temperature to 1000°C for the Ca-HA before and after use. For the initial Ca-HA, there were two steps in the thermal degradation. The first one, between 20°C and 600°C, corresponded to a 10 % weight loss, and the second step, from 600°C to 1000°C, to a weight loss of 13%. For the used Ca-HA, three steps appeared. The first one, between 20°C and 200°C, corresponded to weight losses of 8.1 and 9%, after a use of 15 and 30 days respectively. The second step, between 200 and 600°C, was accompanied by a weight loss of 25.4 and 26.1%. The third weight loss occurred above 600°C and corresponded to 13.9 and 12.8% loss for the two used samples examined. Thus, the total weight loss was near 20 % for the initial Ca-HA and 50% for the used one. To identify the phenomena associated with the different weight losses, the DSC curves were recorded. The DSC curves under air atmosphere showed, for the starting Ca-HA, only one small endothermic peak was present near 700°C, corresponding to the decarbonation of carbonated hydroxyapatite. For the samples analysed after use, the first weight loss corresponded to an endothermic peak at 180°C. This peak corresponds to the dehydration of the brushite ($CaHPO_4.2H_2O \rightarrow CaHPO_4 + 2\ H_2O$). In the second step, an exothermic peak appeared centered near 300°C. This peak corresponds to the oxidation of organic molecules present on the used Ca-HA. As for the initial Ca-HA, the decarbonation peak was present around 700°C. To confirm the presence of organic matter, the same analysis was made, but this time in an inert nitrogen atmosphere. The DSC curves under nitrogen confirmed the absence of exothermal combustion of organic matter (one example is presented in Figure 4). Indeed, the exothermic peak at 300°C disappeared under nitrogen. These results confirmed that Ca-HA adsorbed both heavy metals and organic molecules present in the wastewater. The weight losses corresponding to the oxidation of organic matter represented 30 percent. This amount is in agreement with results obtained in the carbon measurements. The TOC is between 60 and 35% of the total carbon. Despite previous results indicating that organic ligands interfere with metal ions uptake by Ca-HA, sorption of both metal ions and organic molecules was confirmed in the case of real wastewaters.

Many functional groups of organic matter react with metal ions, including carboxylic acids, alcohols (particularly phenols or polyphenols), amines, sulfides, etc. Some authors have described metals bound to organic matter as one class of tightly bound metals in speciation studies.

However, in the case of calcium ions introduced in waste water streams, the calcium is bound to orthophosphate in insoluble form, and shows complex chemistry, wiht calcium forming and retaining carboxylates on its surface, and other metals such as zinc or iron incorporated in the apatite particles capable of complexing sulfides and other types of organic functional groups. Finally, the pores in calcium phosphate particles may retain organic macromolecules by simple adsorption or insertion into the porous structures.

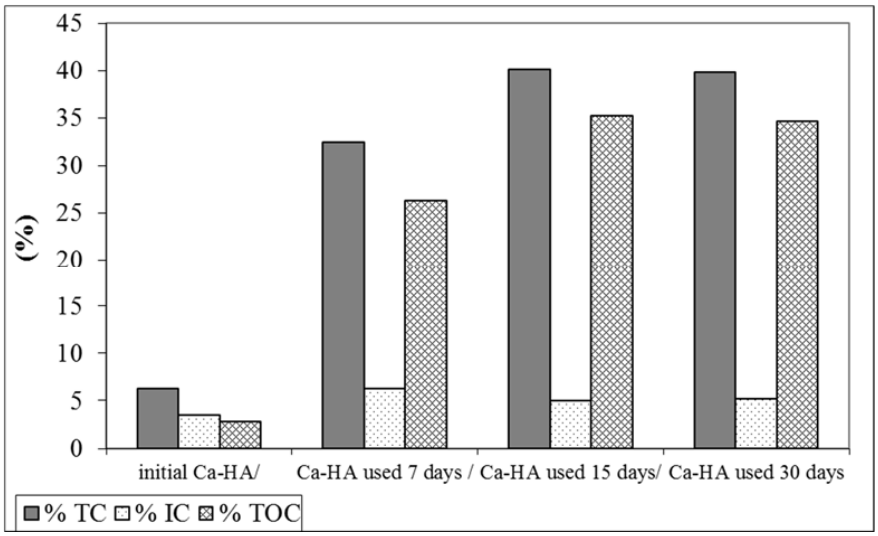

Fig. 3 Carbon measurements in the sorbent

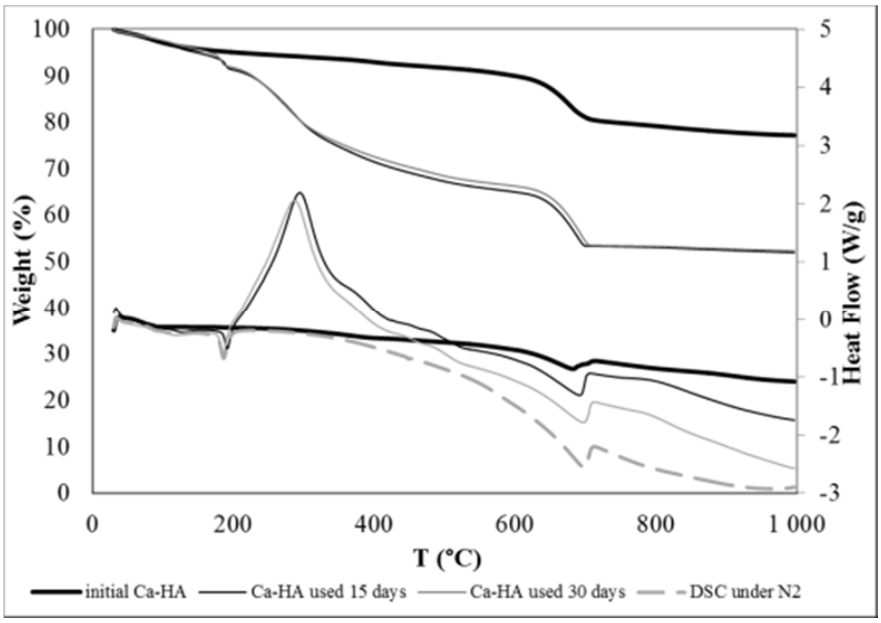

Fig. 4 TGA and DSC curves of the sorbent under air and N_2 atmosphere

3.6. SEM

The SEM observations show the initial Ca-HA to be composed of agglomerated particles with a cauliflower appearance before use (Fig.5). At higher magnification, the surfaces are seen to be porous with entangled sized flakes assembled into micron-sized, rounded particles. After use, needle like crystals are observed with more dense and compact packing and heterogeneous appearance. These results plead for a transformation involving recrystallization of a new more crystalline solid phase.

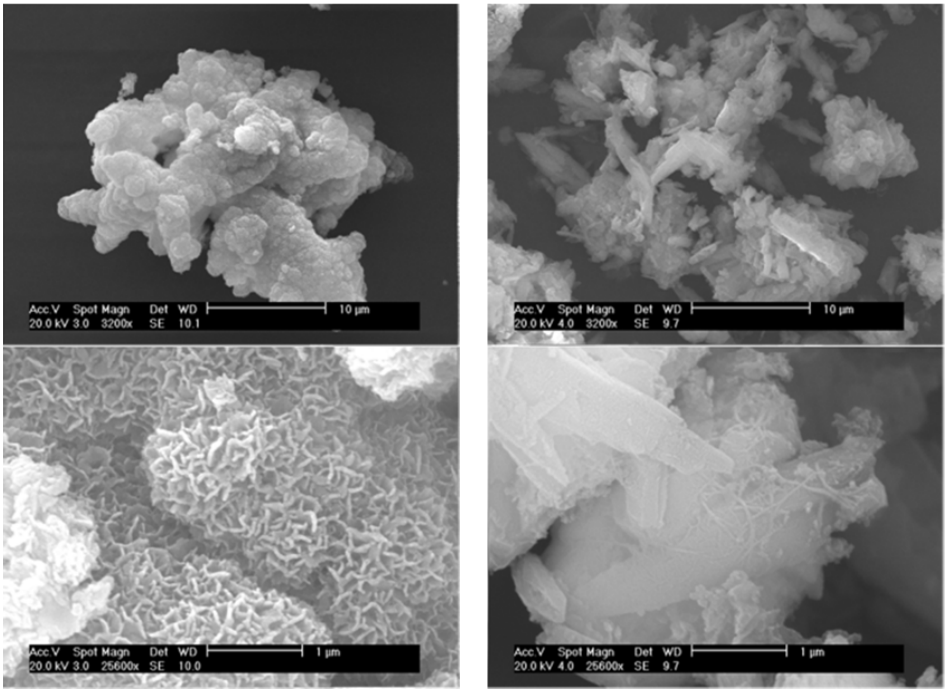

Fig. 5 SEM observations illustrating the appearance of the nanostructured Calcium phosphate particles before reaction (left side) and after use (right side).

3.7. Calcination of the contaminated Ca-HA

The contaminated Ca-HA was heated to different temperatures (400, 600 and 800°C) at a heating rate of 10°C/min. With the increase of the calcination temperature, the solid density increases and the specific surface area decreases when sintering occurs. Starting at 600°C, the specific surface area decreases accompanied by an increase of the density when the solid sintering takes place. The carbon analysis showed a decrease of the carbon contents in the solid from 40% to 3% with the increase of the calcination temperature due to the combustion of the organic matter. Thermal analysis was carried out to confirm this reduction (Fig. 6). The DSC curve obtained for the contaminated solid shows an exothermic peak between 250 and 500°C corresponding to the organic matter. This peak disappears for the calcined solid at the temperature of 800°C. The elemental analysis of the contaminated Ca-HA shows an increase of the heavy metal contents in the solid after the calcination. The concentration went from 53 g HMs/kg dry matter to 106 g HMs/kg dry matter after the calcination. So, heavy metals are concentrated in the Ca-HA matrix during the calcination when the organic matter is removed by oxidation.

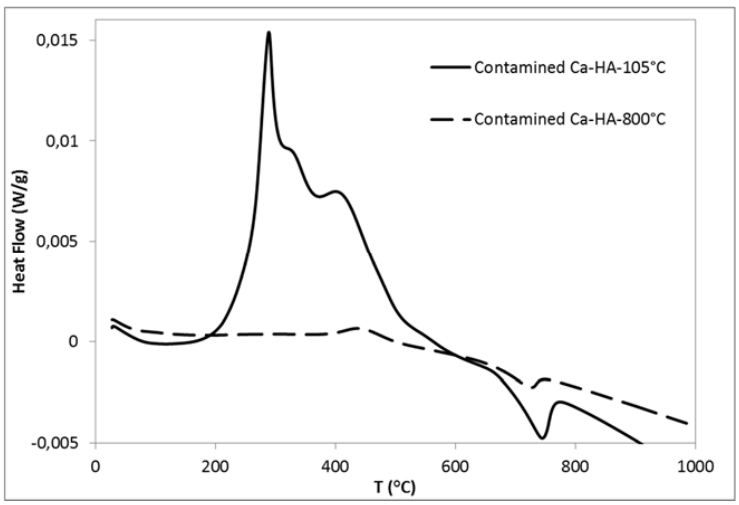

Fig. 6 DSC curves of the sorbent under air atmosphere

Table 3 Calcination results showing density (ρ) and surface area (S) changes as a function of temperature.#

	Ca-HA-105°C	Ca-HA-400°C	Ca-HA-600°C	Ca-HA-800°C
ρ ($kg.m^{-3}$)	1991.2	2498.1	2804.5	3084.0
S ($m^2.g^{-1}$)	15.6	27.4	19.4	11.1

4. Conclusions

A low cost Ca-HA gel synthesized from a calcium carbonate industrial waste could be used for the treatment of municipal wastewater. This treatment effectively removes from solution heavy metals and dissolved organic matter. This is expected to enhance the subsequent biological treatment.

The ability of the CA-HA particles to remove heavy metals was demonstrated by analysis of the decreasing amounts of soluble metals present in treated wastewater. Results further revealed a decrease in dissolved organic carbon in the wastewater after the treatment, confirming its incorporation in the calcium phosphate minerals.

The results of the pilot experiments carried out on site in the wastewater treatment plant demonstrated the efficiency of this Ca-HA in the treatment of the total effluent. The elemental analysis showed that up to 50 and 90 percent of the heavy metals could be removed from the effluent. The quantity of metals retained in the Ca-HA sorbent was multiplied by three following 30 days of use. The carbon analysis of the solid phases separated by filtration showed that the Ca-HA removed from the liquid phase not only heavy metals but also organic matter. The presence of the organics was confirmed by thermal methods. The calcination of the contaminated Ca-HA shows a sintering of the solid from 600°C. The calcination burns off the organic matter contained in this solid but heavy metals remain in the calcium phosphate matrix.

This study reveals that a low cost Ca-HA material can be made by valorisation of industrial limestone waste to produce particles that can be used as an environmental reactant in wastewater treatment. We showed that this apatitic calcium phosphate removed heavy metals present in effluents and that the pH should be regulated to prevent dissolution of the solids. Further work will be needed to explain the complex interactions between organic matter and metal ions interacting simultaneously on the Ca-HA solid surfaces during this physicochemical process. Development of this new industrially prepared reagent promises to improve the usual biological wastewater treatment processes by eliminating an appreciable part of the pollution load to enable the microbiological process to digest the remaining contents.

Acknowledgements

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