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TREATMENT OF MUNICIPAL WASTEWATER WITH CALCIUM PHOSPHATE: A NEW PHYSICOCHEMICAL PURIFICATION STEP

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Abstract

An apatitic calcium phosphate gel (HaG) was elaborated and used to treat municipal wastewater in a physicochemical cycle prior to the standard biological degradation process. Preliminary laboratory batch experiments outlined the kinetics of heavy metal sorption by monitoring the concentrations found in filtered fractions as a function of treatment time. On site experiments were performed in a municipal wastewater treatment plant by derivation of real wastewater into an experimental tank. In this case, the sorption of organic and metal pollution was studied on the whole effluent. The solid and liquid phases were both characterized using elemental analysis, total and organic carbon, and thermal analysis of the solids collected. Results showed significant reductions in heavy metal contents of about 50 to 60% for main metals such as lead, aluminum and iron in the liquid phase. The concentrations went respectively from initial values of 0.07, 0.15 and 1.80 ppm to 0.04, 0.11 and 0.03 ppm in the treated waters for these elements. Organic matter also reacted with the HaG by adsorbing to the solid particles, with the contents of organic carbon increasing from zero to 80g/Kg on the solids and decreasing from 130 ppm to 24 ppm in the liquid phase. This allows foreseeing improvements in the biological treatment process following this physicochemical purification step. The elemental analysis showed that up to 50 and 90 percent of the heavy metals could be removed from the effluent. The presence of the organic matter adsorbed on calcium phosphate was confirmed by thermal methods.

*Keyword*s: calcium phosphate, heavy metals, organics, wastewater treatment

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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 (Nayek et al., 2010). To control this pollution and to remove the heavy metals, many technologies have been developed and tested (Azabou et al., 2007; Guillaume et al., 2008; Hubic et al., 1999; Mohsen-Nia et al., 2007). 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. Sorbents such as activated carbon (ElShafey et al., 2002), silica (Kim et al. 2000), zeolites (Erdem et al., 2004), clays (Celis et al., 2000), calcite (Thakur et al., 2006), activated sludge (Wang et al., 2006), or activated phosphate rock (Elouear et al., 2008) have been reported. Inorganic phosphates such as hydroxyapatite (Ca-HA) have a long history of laboratory use in experiments to remove metals from aqueous solutions (Nzihou & Sharrock, 2010). Ca-HA solids are well known and their general formula is $M_{10}(XO_4)_6Y_2$ with M a divalent cation, $(XO_4)^{3-}$ a trivalent anion and Y^- a monovalent anion (Elliott et al., 1994). The synthesis of hydroxyapatite by wet methods (Verwilghen et al., 2007; Verwilghen et al., 2009) 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 (Gomez del Rio et al., 2004). The metal- retention capacity of calcite has been described (Zachara et al., 1991). Some studies have focused on the ability of Ca-HA to retain one heavy metal in aqueous solutions. As examples, the sorption of Pb^{2+} (Baillez et al. 2007; Hashimoto et al. 2007; Xu et al., 2008), the sorption of Co^{2+} (Smiciklas et al., 2006), Ni^{2+} (Mobasherpour et al., 2011), Zn^{2+} (Meski et al., 2011; Sheha 2007), Cd^{2+} (Lusvardi et al., 2002; McGrellis et al., 2001), VO^{2+} (Vega et al., 2003) have all been reported. Some investigators have looked at the simultaneous sorption of several heavy metals in aqueous solutions (Corami et al., 2007; Oliva et al., 2010; Takeuchi et., 1988). These studies revealed the
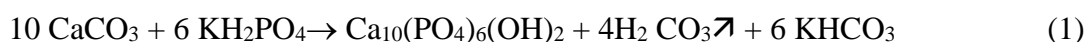
existence of a competitive sorption among the different heavy metals present (Chen et al., 1997; Cao et al., 2004; Gomez del Rio et al., 2006). In wastewaters, heavy metals are present together with many various organic molecules. The interactions of Ca-HA with different molecules, such as nitrobenzene (Wei et al., 2010), phenol (Bahdod et al., 2009; Lin et al., 2009) or textile dyes (Lemlikchi et al, 2012) have been investigated. It was found that the presence of ethylenediamine tetra acetic acid (EDTA) prevents Cu(II) ion adsorption on Ca-HA, due to the formation of complexes with chelating ligands (Fernane et al., 2010). The study of aqueous solutions containing heavy metals and low-molecular-weight organic acids (Wang et al., 2009) or EDTA (Tonsuaadu et al., 2008) confirmed that the presence of organic ligands interferes with the adsorption of heavy metals. The formation of metal-ligand complexes lowers the concentrations of free metal ions that can be exchanged for calcium in Ca-HA.

In this report, we describe for the first time laboratory experiments with Ca-HA for the treatment of real municipal wastewater comprising organic and inorganic pollution. We further describe the use of Ca-HA in pilot experiments in a small town municipal wastewater treatment plant to confirm the results obtained in the laboratory. To our knowledge this is the first time Ca-HA is described for the treatment of real municipal wastewater.

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 containing 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 (Eq. 1):

$$10\ CaCO_3 + 6\ KH_2PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 4H_2CO_3 \nearrow + 6\ KHCO_3 \qquad (1)$$

The HaG gel forms rapidly (Ca-HA small particles suspended in gel form) with release of gas due to the release of dissolved carbonic acid. The suspension was used without further filtration, washing or drying steps. Characterization of similar HaG products were previously reported in more detail (Pham Minh et al., 2012).

2.2. Batch experiments

For the first batch experiments, the wastewater was taken at the exit of the buffer tank of the wastewater treatment plant of a small town located in south-west France (Graulhet). The dissolved part of the effluent was recovered by filtration at 0.45 µm. A mass of HaG was introduced in the

liquid phase of the effluent (1 L) with a concentration of 10g HaG/L of wastewater. The contact time under stirring was 24 hours and the soluble heavy-metal concentrations were measured at the beginning (before contact) and at the end. In a second series of experiments a concentration of 25g/L was used. The stirring rate was 350 rpm, and the reaction time was 24 hours at ambient temperature. Different concentrations monitored over time included heavy metals (Cr, Cu, Fe, Pb) ,calcium and phosphate, inorganic anions (as F^-, NO_3^-, Cl^-, SO_4^{2-}) and dissolved organic carbon.

2.3. On-site pilot experiments in continuous mode.

To confirm the batch experiments, continuous experiments were carried out directly in a wastewater treatment plant (in the town of Graulhet) where the pilot reactor (180L) 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 dissociation of the solid sorbent that could release heavy metals. The effluent then entered a 180L clarifier reactor which contained a dose of HaG. The wastewater flow was 7.5 $L.h^{-1}$. The contact between the effluent and the HaG was confined to the reactor and 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. Thus, over 50 samples were taken at short time intervals at first (less than an hour between samplings), then longer time intervals (daily for 30 days). The HaG used for the treatment was also sampled, so that it could be characterized as a function of use-time. The single initial HaG dose introduced was not renewed during the 30 days trial.

2.4. Characterization methods

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 by thermogravimetric analysis (TGA) combined with differential scanning calorimetry (DSC) 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 flow rate. Samples were analysed in alumina crucibles and the reference was an empty alumina pan.

Ionic chromatography Dionex ICS 3000 was used to determine the concentration of anions such as Cl^-, SO_4^{2-}, F^-, NO_3^- and PO_4^{3-}. The Dionex ionic chromatography apparatus was equipped with a Dionex P/N 061830 conductivity detector and a Dionex IonPac AS 19 (4 x 250 mm) column. The mobile phase was constituted by ultra-pure water eluted at a rate of 1 mL/min, and the pH was regulated and kept constant at 13 by a Dionex ICS-3000 EG eluant generator. The anions listed above were identified by comparison of their retention times with those of authentic standards.

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.

3. Results and discussion

3.1. Batch experiment

During the first few minutes following the introduction of HaG in the wastewater, a strong release of Ca and P was observed. The pH of the solution corresponding to this step dropped below neutral and reached a value of 6.6. After the first five minutes, the pH then increased and reached 7.8 after 4 hours of contact time and remained stable up to the end of our experimentation. The release of the elements Ca and P can be explained by a partial dissolution of the calcium phosphate particles (of composition Ca-HA) in the acid pH zone. When the pH became constant, calcium and phosphorus concentrations remained stable in the solution at 175 mg/L for Ca and 3.3 mg/L for P. The observed pH drop was attributed to metal ion exchange with surface protons due to the presence of HPO_4^{2-} groups on the surface of the Ca-HA immersed in water: the metal ions react with the hydrogeno-phosphate groups on the surface and release protons into solution when forming metal orthophosphates.

3.1.1. Removal of Cr, Cu, Fe, Mn, Pb

The concentrations of heavy metals (among which Cr, Cu, Fe, Mn, Pb) were monitored during the first 24h. The element concentrations analyzed were all below 1 ppm except for calcium (78 ppm),

sodium (92 ppm), phosphorous (2.99 ppm), zinc (6 ppm) and iron (1.8 ppm) (Fig. 1). The chromium and iron metals were rapidly adsorbed by the CaP gel (in less than 1 hour) and their final concentrations in the solution were close to 0. The adsorption of copper seemed limited under our experimental conditions. In the literature, competition between heavy metals (Gomez del Rio et al., 2006) has been described, i.e. some metals bind preferentially Ca-HA to the detriment of others (for example Cd>Zn>Co). For manganese, the concentration in solution decreased by 50% in 10 minutes and decreased gradually to reach 75% reduction. The analysis for lead showed low adsorption, only about 10%. Studies of lead ions adsorption on apatites showed strong adsorption (Baillez et al., 2007; Xu et al., 2008). In our case, the low values can be explained by the presence of many other competing metals and by the presence of organic matter strongly bound to the lead ions and preventing ion exchange with calcium ions.

3.1.2. Removal of Cl^-, PO_4^{3-}, SO_4^{2-}, NO_3^-

The Cl^-, PO_4^{3-}, SO_4^{2-} and NO_3^- concentrations as a function of contact time are presented in Fig. 2. During the experiments, the concentration of Cl^- reached a stable plateau value and the NO_3^- concentration remained stable. At the beginning, the PO_4^{3-} concentration decreased and then stabilized around 10 mg/L. The SO_4^{2-} concentration increased and reached 2700 mg/L. This value could be due to oxidation of sulfides into sulfates. The addition of HaG did not modify the concentrations of sodium or other anions. The Ca and P concentrations tended to decrease slightly during the reaction times used.

3.1.3. Removal of total and organic carbon

The total and organic carbons also varied in the soluble phase of the effluent. The carbon decreased during sorption. During the first hours (0 to 4 hours) the total carbon decreased from 180 to 116 mg/L and the organic carbon from 87 to 57 mg/L. After 4 hours of reaction, these values decreased slowly to reach 66 mg/L for the total carbon and 49 mg/L for the total organic carbon. So, the removal of the total carbon is 64% and for the total organic carbon is 54% after 24H of reaction. This fact shows that the HaG simultaneously adsorbs part of the soluble organic matter present in the effluent together with some of the heavy metals.
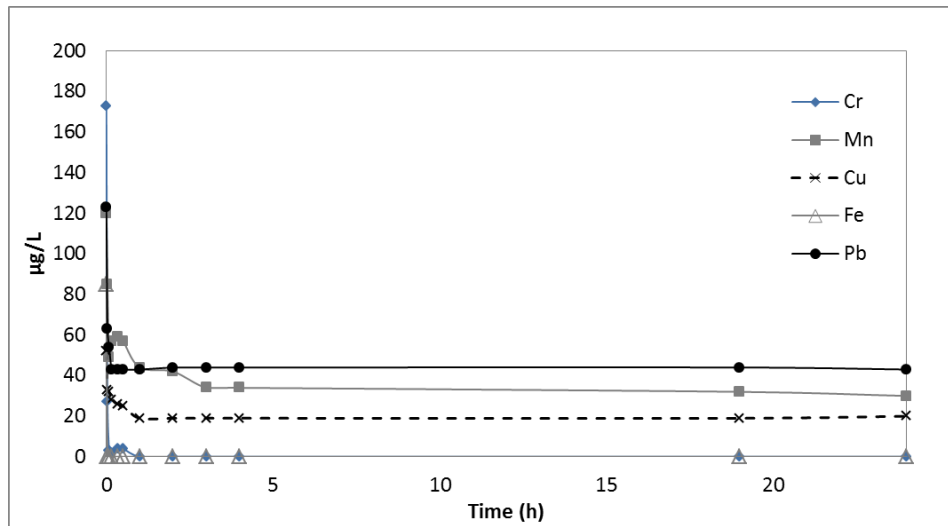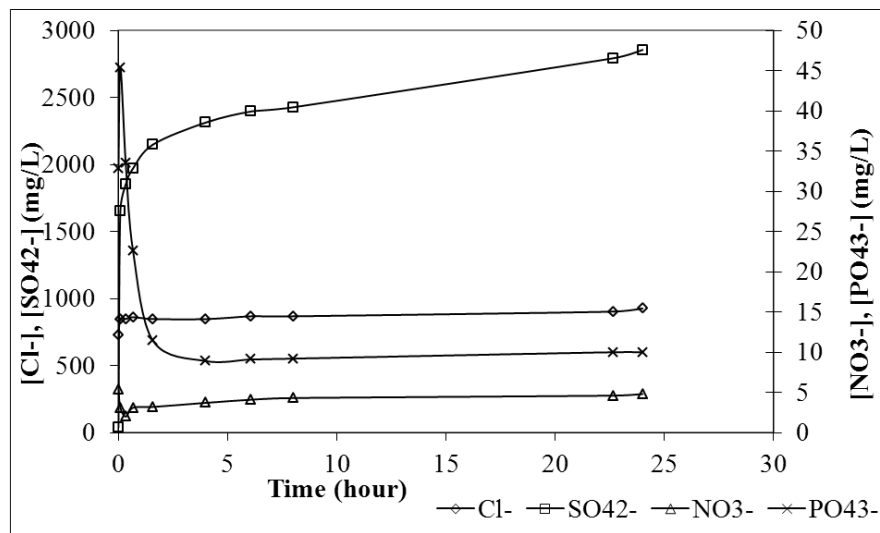
Fig. 1. Heavy metals concentrations

Fig. 2. Soluble anion concentrations present in the aqueous phase during treatment with calcium phosphate gel

3.2. Pilot experiments

To confirm the first results obtained in the laboratory with the batch experiments, trials were run on pilot scale with continuous introduction of wastewater on one initial dose of CaP introduced in the reactor connected to the wastewater treatment plant. The total effluent was analysed (insoluble solid fraction in the reactor and liquid soluble fraction leaving the reactor).

3.2.1. Elemental analysis of wastewater

In Fig. 3, the contents of different heavy metals present in the wastewater are presented. The reductions were calculated with respect to the inital concentrations and are listed for different time

lengths of 7, 15 and 30 days. The initial wastewater contained 72mg/L of heavy metals. Major metals are aluminum, chromium, iron, lead concentrations are respectively 73, 10 5, 51 and 1 mg/L

In Fig. 3, the changes in heavy metal concentrations show that the reduction was generally more than 50% (except for Cadmium and Cobalt). This reduction reached 90% for elements such as chromium and copper. The main heavy metals in the wastewater were aluminium, chromium and iron. The treatment with HaG allowed reducing these elements by more than 60%. The treatment allowed a reduction 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 reduction decreased indicating saturation of the HaG capacity. The reduction 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 HaG particles. These organic molecules interacted with metal ions and their precipitation on the solid phase.
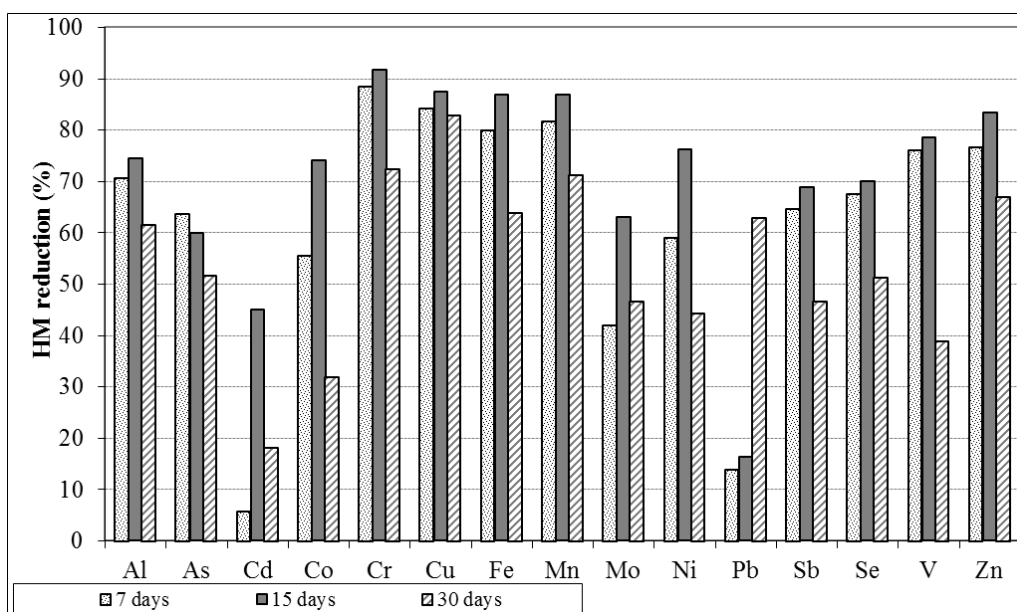

Fig. 3. Heavy metals presence during treatment of wastewater during one, 2 or 4 weeks

3.2.2. Elemental analysis of the HaG during reaction

During the treatment, the HaG solid (recovered and dried) 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 (sorption) of heavy metals by the CaP solids. The initial product contained 8.6 g HM/kg Ca-HA (dry matter). After fifteendays, the solids contained 23.8 g HM/kg Ca-HA, which corresponds to a sorption

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of 15.2 g HM/kg Ca-HA. This sorption occurred dynamically throughout the treatment to achieve 27.9 g HM/kg Ca-HA after 30 days. The main elements adsorbed were aluminium, chromium, iron and zinc, which correlates with the results of the laboratory tests and the elemental analysis of the liquid effluent (Fig. 3). Indeed, these elements are increasingly found sorbed on the solid phase residues listed in table 1.The quantity of lead present in the solid increased slowly (70 to 100 g HM/kg Ca-HA in 30 days). The results point to the gradual formation of complex metal phosphate precipitates, possibly comprised of metals and organic ligands bound together in mixed ligand-type complexes.

Table 1. Removal of elements from wastewater using HaG (in ppm found in the recovered solids)

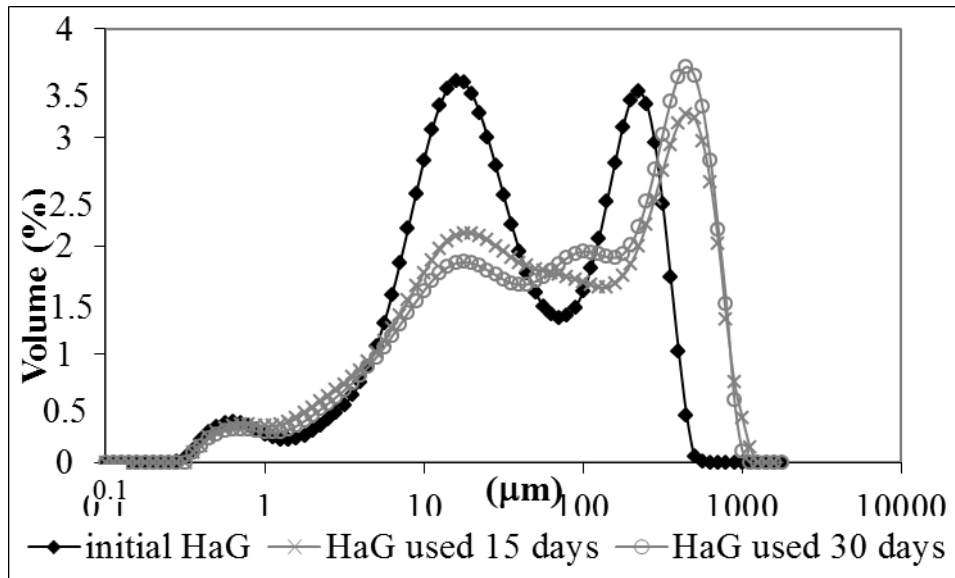| Elements (mg/kgMS)	HaG unused	HaG used 7 days	HaG used 15 days	HaG used 30 days
Al	1304	2214	3432	4505
As	< 0.001	16	26	36
Cd	9	1	1	1
Co	< 0.001	6	6	9
Cr	0.2	224	492	590
Cu	< 0.001	52	84	97
Fe	3417	7654	10697	11872
Mo	< 0.001	71	101	129
Mn	68	72	5	10
Na	3650	5456	8744	10342
Ni	< 0.001	13	11	56
Pb	70	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**

Fig. 4. Particle size distribution of Ca-HA prior to and after use

3.2.3. HaG particle-size distribution

The particle-size distribution (PSD) of HaG Fig.4 presents the PSD changes occurring during wastewater treatment. was measured before and after use. The initial calcium phosphate gel had a polymodal distribution with peaks centred respectively at 16 and 200 µm and a median diameter of 30 µm. For the PSD of HaG after use, a wider spread was observed with a main peak around 450 µm. 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 (they were not lost in the overflow). It can be concluded that the medium sized particles (16 µm) were consumed to form larger agglomerates (450 µm). It should be noted that primary decantation of the incomming effluent generates large amounts of sludges and sand deposits which are sent to landfill as waste, and the precipitates could include the decanted solids made by the adsorption of pollution on the HaG.

3.2.4. 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.5. 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 nearly its weight in organic molecules. This was confirmed by the thermal analysis of the solids recovered by filtration.
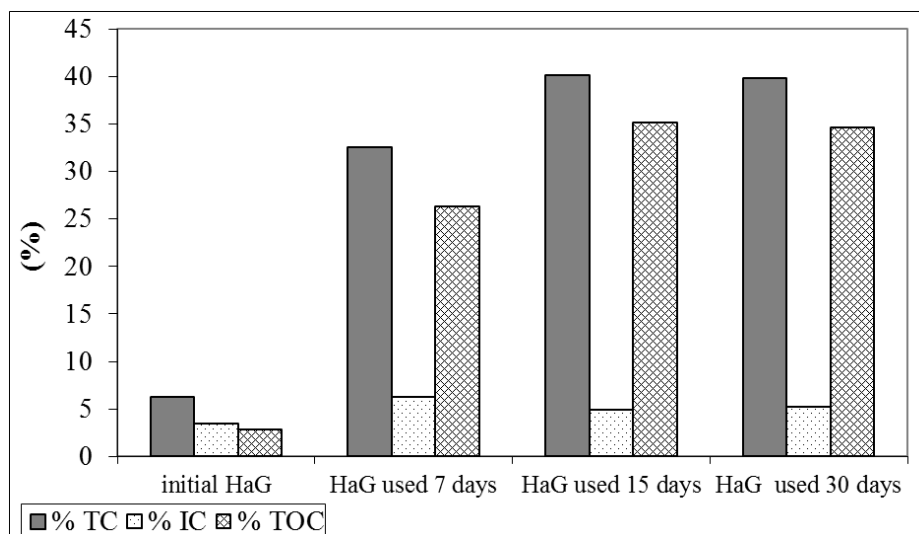

Fig. 5. Carbon measurements in the sorbent as a function of reaction time

3.2.5. Thermal analysis

Fig. 6 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, corresponding to loss of adsorbed water, and the second step, from 600°C to 1000°C, to a weight loss of 13%, corresponding to loss of carbonates present in the HaG as described previously (Phan-Minh 2012). 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 during 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 Ca-HA. 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 small amounts of brushite impurities ($CaHPO_4.2H_2O \rightarrow CaHPO_4 + 2\ H_2O$). 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. Indeed, the exothermic peak at 300°C disappeared under nitrogen. These results confirmed that HaG 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 and inhibit metal ions uptake (sorption) by Ca-HA (Fernane et al, 2010) in laboratory conditions, sorption of both metal ions and organic molecules was confirmed in the case of real wastewaters.
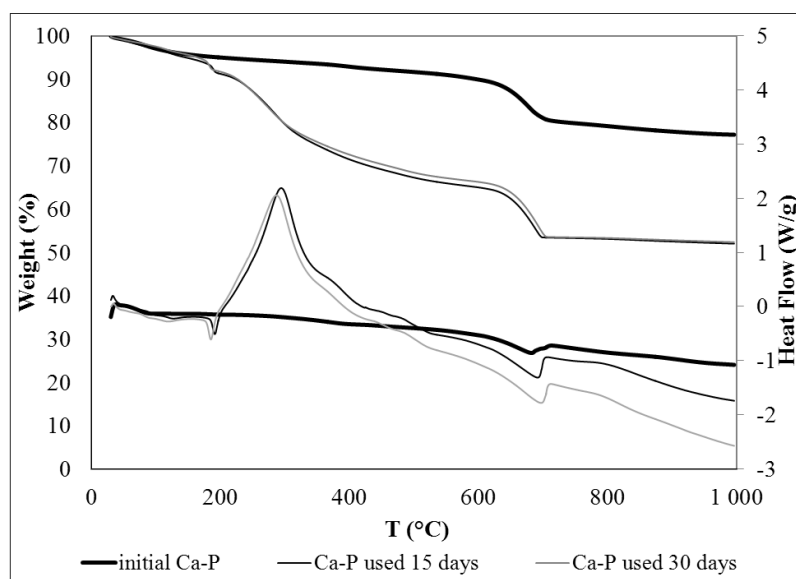

Fig. 6. TGA and DSC curves of the sorbent under air atmosphere. The DSC curves illustrate the endo (down) or exothermal (up) reactions corresponding to weight losses.

3.2.6. SEM analysis

The SEM observations show the initial Ca-HA to be composed of agglomerated particles with a cauliflower appearance before use (Fig. 7). At higher magnification, the surfaces are seen to be porous with entangled nano-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 the starting Ca-HA into a different more heterogeneous solid phase. Such transformations have been observed for hydroxyapatite-metal ion interactions and termed chemical weathering (Monteil-Rivera 2004). On the other hand, no such interactions have been reported yet for simultaneous interactions between

organic matter and metal ions with calcium phosphates. Our results show that HaG effectively removes from solution heavy metals and dissolved organic matter. This is expected to enhance the subsequent biological treatment.

The pilot experiments carried out on-site in the wastewater treatment plant confirmed these novel results and further demonstrated the efficiency of this HaG in the treatment of the total effluent load. 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.
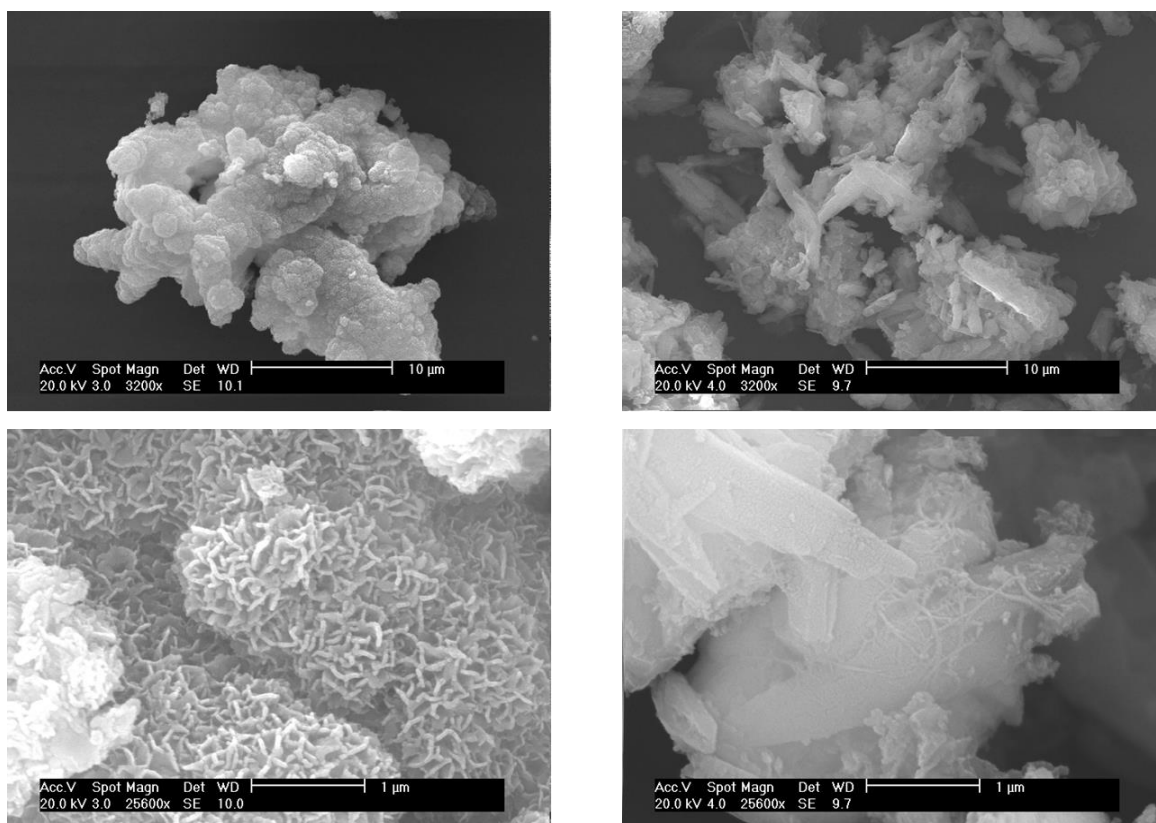

Fig. 7. SEM observations illustrating the appearance of the CaP nanoparticles before reaction (left side) and after use (right side)

4. Conclusions

A low cost reagent can be made by valorisation of industrial limestone waste to produce a calcium phosphate gel for wastewater treatment. We showed that this gel removed heavy metals from effluents if acidic pH values are avoided. Further work is needed to investigate the complex interactions between organic matter and metal ions interacting simultaneously on the solid phosphate

surfaces. Development of this new industrially prepared reagent could improve biological wastewater treatment processes by reducing appreciably the pollution load and enable the microbiological process to digest the remaining contents.

Acknowledgement

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