(31) PERFORMANCE OF A Ca-BASED SORBENT CONTAINING LARGE PORES FOR PHOSPHORUS REMOVAL AND RECOVERY

大きな細孔構造を有する多孔質カルシウム系担体のリン除去および回収特性

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Abstract; In this investigation, the feasibility of phosphorus removal and recovery using a laboratory prepared Ca-based sorbent containing relatively large pores was experimentally demonstrated. Obtained results from the column experiment showed that the removal was accompanied by a leaching of Ca and relatively high pH values at the beginning of the experiment due to the hydration of CaO. After that, the elution of Ca ceased and the pH values decreased gradually to finally stabilize between 8 and 7.5. It was suggested that phosphorous uptake by the sorbent was governed by both sorption and precipitation/crystallization phenomena. The sorption capacity slightly increased with an increase in the flow rate and was associated with the increasing amount of the dissolved calcium. Maximum removal capacity was equal to 30.5 mg-P/g-sorbent, corresponding to a quantity of treated water equivalent to 4000 bed volumes. Pore sizes of the sorbent were entirely shifted to lower values due to the formation of hydroxyapatite on the surface. Furthermore, more than 75% of the sorbed phosphate was recovered using a mechanical sieving of the sorbent. X-ray measurement and P_2O_5 determination revealed that the recovered product was quantitatively and qualitatively similar to a phosphate mineral ore. The sorbent was efficiently reused for a second time. However, its removal capacity was severely degraded upon the third utilization, probably because most of its calcium content was consumed. From these results, it was concluded that the fabricated sorbent could be effective for phosphorus removal and recovery.

Keywords; Calcium-based sorbent, porous sorbent, phosphorus removal, phosphorus recovery, recycle.

1. INTRODUCTION

The continuous release of phosphate compounds to the environment and the depletion of the high quality phosphate reserves are of increasing concern. Input of phosphate to water bodies is associated with eutrophication phenomenon notably observed in closed systems. Preventing phosphate from reaching the receptor media can not only minimize the environmental burden, but might also minimize the excessive exploitation of natural resources once that phosphorus is recovered for recycling.

The effort to reduce phosphate discharge to the receiving water bodies has been already implemented by several wastewater treatment methods. Among them, chemical precipitation and biological treatment are the most widely used techniques (Morse *et al.*, 1998). Yet these processes only have the possibility to convert the phosphate pollution from a liquid phase to a solid waste, which in turn causes handling and disposal problems.

Adsorption method is one of the treatment techniques which is becoming comparatively more useful and economical for phosphate removal (Dongye and Arup, 1998; Hano *et al.* 1997; Ugurlu and Salman, 1998; Urano and Takachiwa, 1991). The main advantages of this method over conventional treatment processes are: less sludge production, operational simplicity and the possibility to recover a high quality-phosphate compound in usable forms once the adsorbent is properly selected. With this in mind, Ca-based sorbents made from either industrial solid wastes or natural products are some of the extensively tested materials. Yamada *et al.* (1986)

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and Tsitouridou and Georigiou (1987) used Slag and fly ashes, respectively, to remove phosphate from wastewater. Roques *et al.* (1991) investigated phosphorus uptake using half-burned dolomite and reported a removal capacity of 4.7 mg-P/g-solid and surface sorption mechanism governing phosphorus uptake. Nur *et al.* (1996) demonstrated that phosphorus removal increased with an increase in the surface area by using porous natural pumice. However, a poor removal capacity, nearly 0.31 mg-P/g-sorbent, was obtained. Nishimura *et al.* (1998) employed a Ca-based sorbent made from oyster shell and clay mineral and reported a phosphorus sorption capacity of 20.4 mg-P/g-sorbent. From these former studies, it also appears that the removal capacity of Ca-based sorbents seems to depend mainly on calcium content and porosity.

Yet this relatively low removal capacity is considered one of the reasons limiting the practical use of these sorbents for phosphorus removal. Improvement of sorbent, via chemical or physical treatment methods is necessary for achieving a high phosphorus removal level that may convey to a beneficial recovery. In this respect, increasing specific surface area via creating micro-pores is generally regarded as an effective procedure to enhance the removal capacity of adsorbents (Ames and Dean, 1970). However, in the case of the calcium-phosphate system, micro-pores are likely to be easily clogged with the phosphorus removal product, so all the created surface area may not be efficiently exploited. Consequently, phosphorus removal capacity remains low. In such cases, sorbent with larger pores might be an alternative. It is expected that pore clogging could be delayed and diffusional transport of phosphate could be maintained to a certain extent.

Regeneration of Ca-based materials was also investigated through the washing of sorbents by alkaline solution (Nur *et al.*, 1996) and more frequently by acid washing (Nishimura *et al.*, 1998). Wash, using an acidic solution, may be very efficient to liberate the sorbed phosphate, however too much material might be lost through dissolution as reported by Roques *et al.* (1991). Finding non-destructive and simple methods for phosphorus recovery and regeneration of Ca-based sorbents would be more attractive from an engineering point of view.

The primary purposes of this study were to investigate the feasibility of an enhanced phosphorus removal and recovery, using a granular laboratory prepared macro-porous Ca-based sorbent. To enhance the phosphate uptake, the pore sizes of the sorbent were enlarged by adding Yalloun coal as a solid pore-forming agent. Continuous column experiments were carried out to assess the phosphorus removal capacity of the fabricated sorbent. Effect of the influent flow rate on the sorption capacity, as well as the characterization of the recovered product, were investigated. The possibilities of the re-utilization of the sorbent and recovery of the product were examined. Based on the experimental results, the possible mechanism governing phosphorus removal was also discussed.

2. MATERIALS AND METHODS

2.1 Preparation of the sorbent
The sorbent was prepared from a mixture of bentonite, Yalloun coal and calcium hydroxide. Based on preliminary results regarding the sorbent strength and the removal capacity (Khadhraoui *et al.*, *submitted*), a powdery mixture of calcium hydroxide, coal and bentonite, 35wt%, 25wt% and 40wt% on mass basis, respectively, was kneaded with distilled water and shaped into spherical aggregates of about 0.8 cm in diameter. The prepared aggregates were dried at 100 °C and then calcined at 700 °C for 6 hours. Throughout the calcination, the coal contained in the aggregates burned out, leaving relatively large pores, and calcium hydroxide was converted to calcium oxide. The calcined aggregates were then stored for further use. Their physical structures were determined before and after phosphorus removal experiments. All solid materials used were analytical grade with the exception of Yalloun coal, which was mined in Australia and classified as a brown coal. The coal was first dried and then sieved in 400-mesh sieve before use.

2.2 Column experiments
Column experiments were performed using a Plexiglas column having 3 cm of inner diameter and 39.5 cm of height. The column was packed with 100 g of sorbent giving an effective bed volume of 280 cm^3 (1 Bed Volume (BV)) and operated in a vertical up-flow mode. The feeding solution contained 10 mg-P/l of phosphate and was prepared by dissolving 21.9 mg/l of KH_2PO_4 and 22.9 mg/l Na_2HPO_4 in distilled water. The continuous experiments were carried out under different superficial velocity (S.V), where the superficial velocity is defined as the volumetric flow rate divided by the cross sectional area of the empty column. At the

end of the run, the phosphorus removal product was recovered and the sorbent was subjected to further utilisation.

2.3 Phosphorus recovery

Two non-destructive methods were employed to recover the sorbed phosphorus in a usable form: (1) mechanical sieving of the sorbent, and (2) washing with distilled water. For the mechanical sieving, an exhausted column was drained off and the sorbent was completely dried in an oven set at 105°C, the sorbent was then shaken in a sieve until no dust came out. The white-looking powder that passed through the sieve was collected, quantified and characterized. The method using a rinse with distilled water was conducted as follows: the exhausted sorbents of a similar column, operated under the same conditions, were transferred into a beaker, 200 ml of distilled water was then added, and the beaker was gently shaken manually. These steps were repeated three times. After separation, the water was evaporated to finally obtain a white-looking, dry solid.

2.4 Analytical methods

Prior to each analysis of the dissolved components, samples were filtered through a 0.2 μm-membrane filter. Phosphate concentrations were measured using an ion chromatograph (IC-7000-Series II, Yokogawa Analytical Co.). The pH was determined by a pH/ORP-meter. Calcium concentrations were analyzed by a flame atomic absorption spectrophotometer (A-2000, Hitachi) according to standard methods (APHA *et al.*, 1998). Specific surface area of the sorbent was measured by means of the nitrogen adsorption method (Autosorb-1-MP, Quantachome Co.) and calculated by BET adsorption isotherm. The pore volume and pore size distributions were analyzed using the mercury intrusion method (Autoscan 33, Quantachome Co.).

Phosphorus and calcium content of the recovered product was measured as follows: a known mass of the dried solid was dissolved in 0.5 ml of hydrochloric acid and then adjusted with distilled water to a known final accurate volume. Phosphate and calcium concentrations in the solution were thus determined. A powdery x-ray diffraction analysis using a Rigaku x-ray diffractometer was also conducted for the recovered products, for a phosphate mineral ore, and for a reagent analytical grade hydroxyapatite.

3. RESULTS AND DISCUSSION

3.1 Breakthrough curve

A typical breakthrough curve obtained from the continuous experiment is shown in Fig.1. The curve could be divided in two parts. In the first part, before the breakthrough appeared, there was a large uptake of phosphate, but this lasted only for a short time. The concentration of calcium ions in the effluent was relatively high and showed a sharp decrease. The pH values were also elevated due to a leaching of calcium from the sorbent followed by its hydration. In the second part of the curve, phosphorus uptake continued and lasted for a long period. The elution of calcium practically ceased and the amount dissolved from the sorbent remained nearly equal to zero throughout the rest of the experiment. The pH continued to decrease, but this time gradually and finally stabilized between 8 and 7.5.
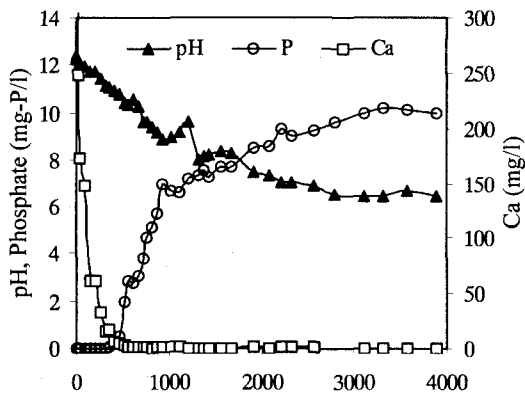

Fig. 1. Typical example of phosphorus breakthrough curve. (Superficial Velocity = 0.85

The total amount of the removed phosphorus estimated from the breakthrough curve was about 3.05 g, equivalent to a removal capacity of 30.5 mg-P/g-sorbent, which was higher than those reported by Roques *et al.* (1991), Nur *et al.* (1996) and Nishimura *et al.* (1998). This high removal capacity is probably due to the contribution of the wide pores created, which are believed to maintain the diffusional transport of phosphate ions from the bulk phase to the internal surface of the sorbent.

Table 1 shows the mass balance of calcium corresponding to the results shown in Fig.1. The effectiveness of calcium utilization was estimated to be nearly 22.5%. The amount of unused calcium is relatively high and this suggests that if the removal product could be recovered, the reutilization of the sorbent is possible.

Table 1. Efficiency of Ca-utilization at the end of the experiment (Superficial velocity: 0.85 m/hr).

Total calcium content par g-sorbent	283 mg/g-sorbent
Amount of Ca consumed based on reaction No. 1 (Table 3)	64 mg/g-sorbent
Amount of Ca washed out from the column	104 mg/g-sorbent
Amount of Ca lost during the recovery by mechanical sieving	11 mg/g-sorbent
Amount of Ca remained in the sorbent	104 mg/g-sorbent
Efficiency of Ca utilization	22.5%

3.2 Effect of superficial velocity on phosphorus removal

The relationships between the superficial velocity, the quantity of the treated water and the phosphorus removal capacity are shown in Fig. 2. The removal capacity of the sorbent tended to increase with an increase in the superficial velocity and was associated with the increase of the dissolved calcium. Further investigation showed that the amount of the eluted calcium from the column increased with increasing the influent flow rate (Fig. 3), probably because of an erosion phenomenon occurring on the surface of the sorbent. A part of this leached calcium reacted with phosphate, either via precipitation or crystallization phenomenon in the bulk pahse, inside the column and led to the increase of the removal capacity of the sorbent. The quantity of the treated water also increased with an increase in the influent flow rate as shown in Fig. 2.
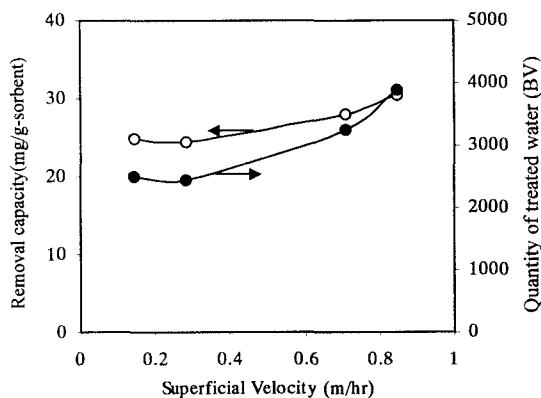

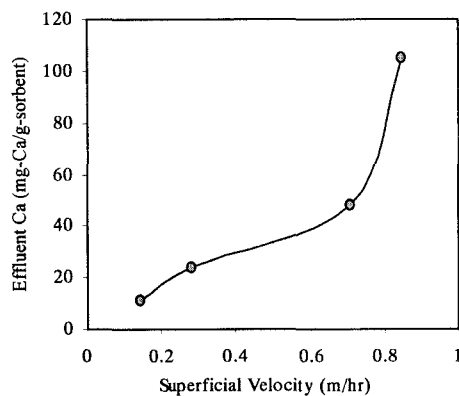**Fig. 2.** Effect of flow rate on phosphate removal capacity and quantity of treated water.

Fig. 3. Amount of Ca released from the column vs superficial velocity.

3.3 Change in the physical structure of the sorbent after phosphorus removal

Table 2 shows the change in the physical properties of the sorbent after the first usage. The physical characteristics of a virgin sorbent are also presented. Compared to the virgin sorbent, the pore volume and the mean pore radius of the sorbent showed a decrease after phosphorus removal, whereas the specific surface area increased. Surface sorption and growth of hydroxyapatite (Hap) are thought to be the main causes of the decreases in pore volume and pore radius of the sorbent. Lemos and Fereira (2000) showed that crystalline Ca-phosphate precipitates preferentially in the pores and pore boundaries, or in other strained sites at the surface area, of a bioactive macro-porous calcium carbonate. Guillemin et al. (1989) found that larger pores in the

Table 2. Change of physical properties of the sorbent after phosphorus removal.

Sample	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Mean Pore Radius (μm)
Virgin sorbent	20.6	1.0	0.470
Spent sorbent	118	0.50	0.175

range of a few μm enable a faster re-sorption and development of new bone through Hap formation on porous natural corals. The increase in the surface area was mainly due to the leaching of calcium and formation of the hydroxyapatite -which is known as a porous compound (Furuta et al., 1998)- on the outer surface of the sorbent. Joko et al. (1992), in an investigation on phosphate removal using Coral Reef limestone, had noticed a similar phenomenon. Figure 4 shows a typical example of the pore size distribution of the sorbent before and after phosphate removal. It can be seen that the pore radii of the sorbent after phosphorus removal were entirely shifted to lower values, mainly due to Hap accumulation inside those sites.

Fig. 4. Typical example of the change in the sorbent structure after phosphate removal.

3.4 Possible phosphorus removal mechanism by the sorbent

According to the change in the physical characteristics of the sorbent and based on the breakthrough experiment, the possible phosphate uptake mechanism might include sorption and precipitation/crystallization of hydroxyapatite intermediates listed in Table 3 (Kibalczyc et al. 1990). The fact that pH values and calcium concentrations were sufficiently high before reaching the breakthrough point may favor precipitation/crystallization (Baker et al., 1998). However, once the effluent calcium concentration decreased and practically ceased, especially after the breakthrough occurrence, sorption phenomenon seemed to be predominant. Indeed, we calculated the apparent ionic products of Hap precursors at 860 bed volumes (see Fig.1), where pH was nearly 9, calcium concentration equaled to 0.3 mg/l and PO_4^{3-}-P was taken equal to the influent concentration. The result was tabulated in Table 4. This approximate calculation showed that the solubility products of tri-calcium phosphate (TCP), octa-calcium phosphate (OCP) and di-calcium phosphate (DCP) were not exceeded at 860 bed volumes. Thus, after breakthrough point, the bulk phase seemed to be under-saturated with respect to those minerals. This suggests that, in this region of the curve, phosphorus may have been removed via a sorption phenomenon of these precursors. These intermediates later converted to Hap, the most thermodynamically stable form of calcium phosphate minerals, in accordance with Ostwalds' rule (Buffle and Devitre, 1994). However, before breakthrough point, a similar calculation showed that the bulk phase was supersaturated with respect to these precursors, implying the possibility of their formation through a precipitation/crystallization mechanism. It is also worthwhile to note that phosphorus removal in mediums with high calcium content was reported to be due either to a precipitation (Holtan et al., 1988) or sorption of a calcium phosphate mineral (Nur et al., 1996), obviously depending on pH and phosphate concentrations. This is in agreement with the deductions made in this study.
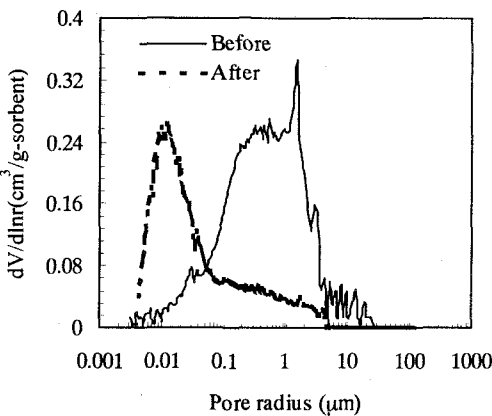
Table 3. Possible calcium phosphate minerals that might be formed and their Ca/P molar ratio (Moutin et al., (1992)).

Calcium-phosphate reactions	Ca/P Molar ratio	Ks
1. HAP: $5Ca^{2+} + 3PO_4^{3-} + OH^- \rightarrow Ca_5(PO_4)_3OH$ (crystalline phase)	1.67	10^{-57}
2. TCP: $3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2$ (precursor of Hap)	1.50	$10^{-25.2}$
3. OCP: $4Ca^{2+} + 3PO_4^{2-} + H^+ + H_2O \rightarrow Ca_4H(PO_4)_3 \cdot 3H_2O$ (Precursor of Hap)	1.33	$10^{-46.9}$
4. DCP: $Ca^{2+} + HPO_4^{2-} + 2H_2O \rightarrow CaHPO_4 \cdot 2H_2O$ (Precursor of Hap)	1	$10^{-6.6}$

Hap: hydroxyapatite, TCP: tri-calcium phosphate, OCP: octa-calcium phosphate, and DCP: di-calcium phosphate.

Table 4. Apparent Ionic Product (AIP) of hydroxyapatite precursors at 860 bed volumes.

Mineral	Ks	Ionic Product (AIP)
TCP (IP $= [Ca^{2+}]^3[PO_4^{3-}]^2$)	$10^{-25.2}$	10^{-29}
OCP (IP $= [Ca^{2+}]^4[PO_4^{3-}]^3[H_3O^+]$)	$10^{-46.9}$	$10^{-49.9}$
DCP (IP $= [Ca^{2+}][HPO_4^{2-}]$)	$10^{-6.6}$	$10^{-8.6}$

The square brackets denote the concentrations of the species in question (mol/l). $[PO_4^{3-}]$ and $[HPO_4^{2-}]$ were determined based on the equilibrium constants of phosphoric acid and with the respect to the pH of the medium.

3.5 Phosphate recovery and characterization of the recovered product

To recover phosphorus in a form that could be directly used by the phosphate industry, mechanical sieving and repeated rinses of the sorbent with distilled water were examined. Qualitative and quantitative measurements of the recovered product were then carried out. The recovery efficiency using the sieving method and the repeated wash was about 76.5% and 35% of the total amount of the sorbed phosphorus, respectively. Since sieving of the sorbent seemed to be more effective, only the former procedure was used in the subsequent experiments. The phosphorus content of the recovered product by mechanical sieving was 141 mg-P/g-product, which is equivalent to 32.3% (P_2O_5) on mass basis. Note that the phosphorus content in currently mined rocks ranges from below 5% (P_2O_5) to over 40% (P_2O_5).

Moreover, we measured the phosphorus content of a phosphate mineral ore purchased from a Japanese fertilizer company. The results revealed that the concerned ore contained 31% (P_2O_5) on mass basis, almost the same amount found in the recovered product. In addition, a comparison of the x-ray powder diffraction patterns of a phosphate mineral ore, the recovered product and an Hap analytical grade was conducted. The obtained results are presented in Fig. 5. The principal peaks of Hap at $2\theta = 25^{\circ}$, 32° and 50° can be easily located in all diffraction patterns. Also, as it can be seen, the spectrum of the recovered solid shows matching peaks with those of the mineral ore and Hap reference, implying that the product has the same quality of the mined phosphate ores.

3.6 Recyclability of the sorbent

As mentioned earlier and as shown in Table 1, after phosphate removal, a relatively large amount of non-reacted calcium remained in the sorbent. This means that its re-use for phosphate capturing may be conceivable. Therefore, for an effective calcium utilization, re-using the sorbent was experimentally investigated.
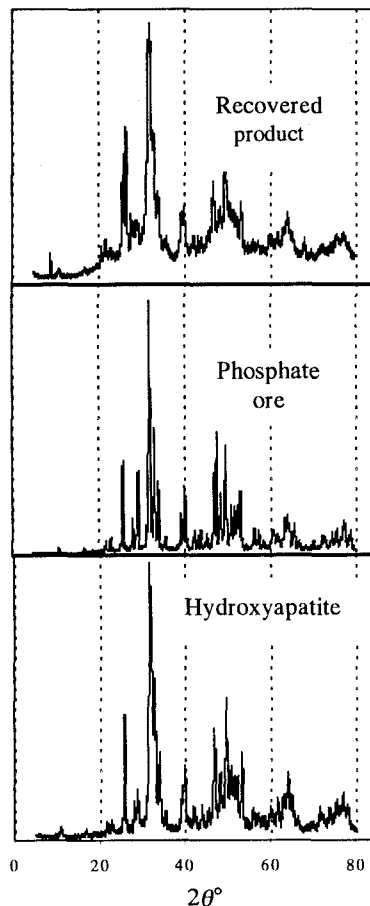
Fig. 5. X-ray diffraction pattern

Figure 6 (**a**) shows the breakthrough curves of a repeatedly utilized sorbent. After the second utilization, the breakthrough occurred almost at the commencement of the experiment, probably because of the absence of an excessive calcium dissolution. The re-used sorbent continued to uptake phosphate for a long period, quite similar to the one when the virgin sorbent was used. Figure 6 (**b**) shows the change in effluent pH values
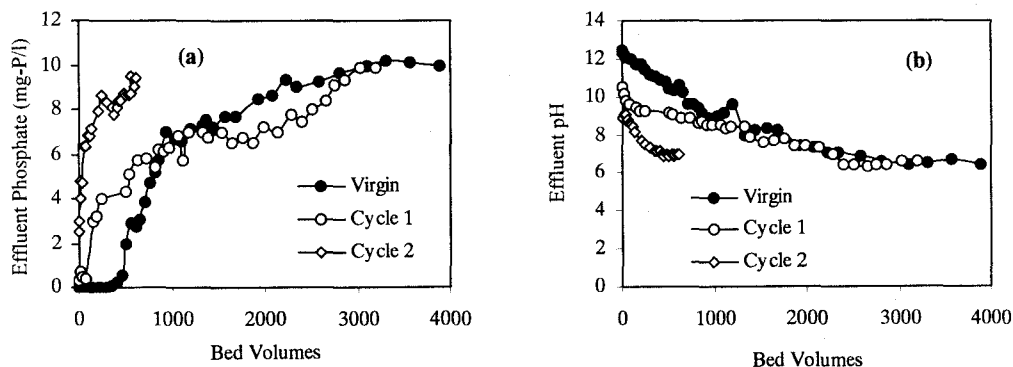
Fig. 6. Breakthrough curves (**a**) and change in effluent pH (**b**) at different cycles.
(Superficial Velocity = 0.85 m/hr).

during the three utilizations. Compared to the first usage, effluent pH values showed a significant decrease in the second and third usage. Yet, it still remained relatively high at the beginning of the second re-utilization, again due to a slight dissolution of calcium. Figure 7 shows the phosphate removal capacity as a function of the number of cycles. The removal capacity in the second usage was nearly 28 mg-P/g-sorbent, corresponding to an effectiveness of calcium utilization of 56%. Upon the third run, it appeared that the removal capacity of the sorbent was distinctly reduced, most likely because more than 72% of the total calcium contained in the sorbent was consumed. By this time, the phosphate removal decreased to 5.6 mg-P/g-sorbent. The efficient utilization of calcium and the recyclability of the sorbent would be more promising if the leaching of the calcium could be prevented.
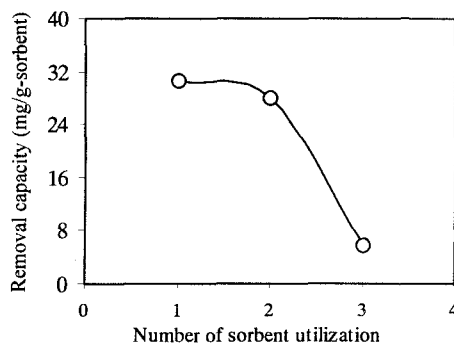

Fig. 7. Removal capacity as a function of the number of cycles.

4.CONCLUSION

Continuous experiments were carried out to evaluate phosphorus removal and recovery by using a porous Ca-based sorbent made from $Ca(OH)_2$, bentonite and Yalloun coal. The obtained results indicated that the prepared sorbent showed higher removal capacity compared to those reported previously in spite of the large diameter of the aggregates used. With the increase in the flow rate, the phosphorus removal capacity of the sorbent increased due to the increase in the dissolved calcium in the bulk solution, which then reacted with phosphate inside the column. The quantity of the treated water also increased. The maximum removal capacity estimated from the column run was equivalent to 30.5 mg-P/g-sorbent. Phosphorus uptake by the sorbent appeared to be governed by a sorption and precipitation/crystallization of a Ca-phosphate identified as hydroxyapatite. More than 76.5% of the sorbed quantity was recovered by a simple mechanical sieving from the first usage of the sorbent. The recovered product had similar quality to mined phosphate rocks, which seems to be attractive to be used by the phosphate industry. Furthermore, the efficient utilization of calcium and the recyclability of the prepared sorbent will be even more promising once the leaching of the calcium can be prevented.

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