**Synthesis and Properties of Alumina-Hydroxyapatite
Composites from **Natural Phosphate** for Phenol Removal from Water**

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Abstract

Phenol is very abundant in the aquatic environment and therefore requires an effective treatment using porous and low-cost adsorbents. Alumina-hydroxyapatite composites were prepared from natural phosphate ore in the presence of Al^{3+} ions via a wet-chemical method. Porous composites were characterized and the Al-surface modification was produced by facile and inexpensive route to uptake adjacent toxic species. Supplementary active sites on their surface may improve their phenol remediation. Nanocomposites exhibit higher phenol sorption rates than pure hydroxyapatite. It is concluded that the specific surface area, surface charge and Al content are suitable for phenol removal from aqueous solution using Alumina-hydroxyapatite composites. The results show that the retention power of these composites depends on a complex interaction between intermolecular and molecule-solid interactions. These findings are relevant to better understand the contribution of alumina content in Alumina-hydroxyapatite composites to the fate and uptake of phenol from aquatic environments.

Keywords. Alumina; Hydroxyapatite; Composites; Phenol; Adsorption

1. Introduction

Various harmful organic substances are released by human activities [1-3]. Among them, phenol is abundantly detected in the aquatic environment owing to its use as an intermediate in the plastic, cosmetic and pharmaceutical industries [4]. Despite abundant studies on phenol decontamination [5], the development of separation techniques using new porous systems able to remove this toxic specie from water is an active research topic. Research has focused on the use of the abundant natural materials namely clays and natural apatites [6,7]. Synthetic apatite has been used to immobilize heavy metal ions in aqueous solutions or in soils due to its adsorption and ion exchange capabilities [8-10], but few studies were conducted on the elimination of phenolic compounds using natural adsorbents such as natural phosphate [11-13]. The conversion of natural phosphate into

porous hydroxyapatite was described in our earlier work [14], based on dissolution/precipitation methods. The possibility of adding surface modifiers such as Al^{3+} ions to the converted hydroxyapatite can improve the adsorption efficiency for organic species. Technically, the ability of alumina to adsorb organic and inorganic compounds depends on several factors like the pH of the solution and its surface modification. Various alumina chemical treatment studies have been reported elsewhere [15,16] and the results show an improvement in the performance of these adsorbents versus organic pollutants in wastewater. It can also be concluded that the adsorptive efficiency of Al_2O_3 is very limited to removing phenol and its derivatives from aqueous solutions. However, fluoride immobilization by adsorption on pure alumina and activated alumina is very efficient and very well known, which is not affected by the presence of competitive ions [17]. It appeared that this process was much less expensive than anion exchange resins. Adding together, the presence of aluminum in several materials may more efficiently adsorb or catalyze the oxidation of numerous organic pollutants [15, 18-20]. Its association with apatite to form porous nanocomposites may be cost effective and widely used in biomedical applications, especially to improve the mechanical properties of implants [21, 22]. This approach relies on the preparation of nanocomposites associating hydroxyapatite with alumina, leading to homogeneous mesoporous materials. In this context, the pathways of soft chemistry may be preferred to stabilize apatite in the presence of aluminum oxide. For this purpose, we prepared Al_2O_3 -hydroxyapatite composites using natural phosphate as calcium and phosphorus precursors in order to yield low-cost porous adsorbents. This study also reveals the interactions and affinities of these composites with phenol for water remediation.

2. Materials and techniques

2.1. Preparation and characterization of the Al_2O_3 -HAp composites

The pure hydroxyapatite powder (HAp) was prepared as previously described by a dissolution/precipitation method from a natural phosphate ore extracted from the Bengurir region in Morocco [14]. Dissolution of the natural phosphate was carried out by introducing 30 g of this

ore in a 2 L reactor containing 500 mL of bidistilled water acidified to pH 2 by the addition of 20 mL of concentrated nitric acid (HNO_3 , 65%), with continued stirring for 3 h at room temperature. After vacuum filtration, the recovered filtrate containing Ca^{2+} ions and phosphoric acid H_3PO_4 was brought to pH 10 by the addition of concentrated ammonia (NH_4OH 25%). The resulting precipitate was aged for 24 h, filtered and washed three times with deionized water with intermediate ultrasound irradiation steps to optimize grain dispersion. Finally, the powder was dried at 100 °C for 24 hours and calcined at 800 °C for 3 hours. Among the available methods for aluminum oxide synthesis [23] and considering the conditions of HAp synthesis reported previously, alumina was prepared by addition of concentrated ammonia (NH_4OH , 25% Merk KGaA) at pH 10 to aluminum nitrate solution ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99% Sigma-Aldrich). The precipitate was filtered, redispersed in deionized water under sonication and filtered again. The final precipitate was dried overnight at 100°C. For the alumina-hydroxyapatite preparation, the aluminum precursor was firstly added to 200 mL of the calcium and phosphate solution from the dissolution of natural phosphate and then neutralized by ammonia NH_4OH (25%) until pH 10 under continuous stirring at room temperature. The amount of Al-precursor added was varied to obtain a theoretical final Al_2O_3 :HAp weight ratio $w=5, 10, 20\%$ and the resulting materials were named wAlHAp ($w = 5, 10, \text{ and } 20 \%$). The precipitates obtained were aged for 24 h under continuous stirring at room temperature. After dispersion under ultrasound in water, the precipitates were filtered under vacuum and washed with distilled water. Another ultrasonic step was needed to optimize the grain dispersion. Finally, the powders were dried at 100°C overnight and calcined at 800°C for 3 hours to study their thermal stability.

2.2. Sorption experiments and modeling

Phenol solutions with concentrations ranging from 5 to 100 g L^{-1} were prepared. 0.2 g of the different wAlHAp samples were added to 100 mL of phenol solutions and stirred at 25°C to reach sorption equilibrium. Based on the preliminary studies carried out, kinetics of the phenol sorption process were first studied at 20 mg L^{-1} concentration with an adsorbent dose of 2 g L^{-1} without

adjustment of pH 5.6. Aliquots of the supernatant solution were taken with a propylene syringe equipped with a 0.45 mm filter. After filtration, the phenol content of the supernatant was determined by UV-visible spectroscopy at $\lambda_{\max}=273$ nm. The adsorbed amount q_t (mg g⁻¹) at time t was calculated as follows: $q_t=(C_0-C_t).V/m$, where C_0 and C_t are the initial phenol concentration (in mg L⁻¹) in the liquid phase initially and at any time t respectively, “ m ” is the mass (g) of the adsorbent in the solution, and V is the solution volume (L). The kinetic parameters and the rate constants for adsorption were estimated using pseudo-first-order and pseudo-second- order kinetic equations of linear form and the Ho equation [24]. In order to study the isotherms of the phenol uptake by the wAlHAp surface, Langmuir and Freundlich adsorption equilibrium models were considered in order to fit experimental data [25, 26].

3. Results and discussion

3.1. Characterization of wAlHAp composites

In a first step, the wAlHAp composites were analyzed by X-ray diffraction (XRD) to determine the influence of the apatite formation on the presence of Al³⁺ ions. As shown in Figure 1a, the as-received apatite powder dried at 100°C exhibits a broad diffraction peak centered at $2\theta=31.5^\circ$, together with two overlapping large peaks at ca. 50° and 60° (JCPDS file 09-0432) and no reflections of the independent aluminum species were observed. It can be suggested that this corresponds to an amorphous alumina phase attached to apatite structure. When the Al₂O₃:HAp ratio increases, the diffraction peaks corresponding to the HAp structure merge with the broad peaks of the Al₂O₃ phase with absence of any calcium phosphate or aluminum phosphate phases other than HAp crystals. The crystallite size was estimated using the Scherrer formula based on the main (002) and (301) planes of apatite. Their average values are 22 nm, 18 nm and 12 nm for 5AlHAp, 10AlHAp and 20AlHAp, respectively. They are lower than that of a pure HAp (30 nm). XRD results indicate that increasing the alumina content affects the crystallinity of HAp by inhibiting crystal growth of its nanoparticles. As result, the significant reduction in crystallite size with increasing the Al content shows a preferential interaction of the Al³⁺ ions with HAp. On the

other hand, when the powder is heat-treated at 800°C (Fig. 1b), other phases are appeared and attributed to Al_2O_3 and $\beta\text{-Ca}_3(\text{PO}_4)_2$, those presence can demonstrate the affinity of Al^{3+} ions with apatite structure as established in several studies developed for biomedical applications [27, 28]. Moreover, it has been shown that the heat treatment of $\text{Al}_2\text{O}_3/\text{HAp}$ nanocomposites above 1000°C promotes the formation of calcium aluminates by the diffusion of Ca^{2+} from HAp in alumina [29], but at 800 °C only the $\beta\text{-TCP}$ phase was clearly observed especially in the case of 20AlHAp. In order to maintain the porosity of prepared wAlHAp sorbents, the high-temperature heat treatment becomes useless.

Fig. 1

Infrared spectra of the various wAlHAp products display the [stretching](#) vibration modes of PO_4 groups at 1100, 1050, 960 [and bending](#) at 605 and 564 cm^{-1} characteristic of the apatite structure ([Fig. SI.1](#)). The bands at 1410 and 1430 cm^{-1} are attributed to carbonates starting natural phosphate, which disappear after calcination [at 800°C](#). [In heating](#) the sample at 800°C, the converted HAp from natural phosphate exhibits an individual band at 3560 cm^{-1} linked to the OH groups of apatite structure, which disappeared in wAlHAp cases, revealing the chemical affinity between Al^{3+} ions and the HAp structure.

[Crystal shapes of the wAlHAp which are quite different from those of the pure HAp depend largely on the \$\text{Al}^{3+}\$ content](#) ([Fig SI.2](#)). Most of them had flake-like morphology, but usually agglomerates that were sometimes identifiable particularly in the 20AlHAp case. There was also the appearance

of a new elongated particle in wAlHAp composites suggesting the association of alumina with apatite and homogeneously distributed in the 20AlHAp sample. However, crystallite size was much smaller in 5AlHAp than in other composites and its fine particles should have a larger specific surface area. The EDX analysis showed that there was more aluminum in 20AlHAp with a lower Ca/P ratio, confirmed by ICP-AES analyses. Chemical analyses of wAlHAp composites are summarized in Table 1. As a result, the synthesis conditions greatly influenced the composition of the wAlHAp powders especially the associated aluminum content with apatite network. With unvarying calcium and phosphorus contents in phosphate rock, the added of Al^{3+} ions affect the Ca/P molar ratio of the wAlHAp precipitates such as demonstrated elsewhere [29]. Two apatite suggestions can be made: (i) small Al content can be inserted into the apatite network and (ii) the mass of Al in the final wAlHAp products affects the different percentages. For larger Al content, the Ca/P values are close to 1.5, characteristic of $\beta\text{-Ca}_3(\text{PO}_4)_2$ visibly detected by XRD for 20AlHAp thermally treated at 800°C.

The porous features of the wAlHAp composites were studied by N_2 -sorption measurements using BET method (Fig.2a). The isotherms exhibit a hysteresis loop which indicates that the composites act as mesoporous materials. The S_{BET} analysis showed an increase in specific surface area of composites compared to pure HAp (Table 1). Only moderate increase in specific surface area was observed for high Al-association levels with apatite. For a low Al_2O_3 content, the mesoporosity becomes more obvious, as indicated by the enlargement of the hysteresis. The distribution of mesopore volumes in samples is presented in Fig. 2b. The application of the BET model indicates that wAlHAp composites have large specific surface areas ranging from 145 to 206 $\text{m}^2 \text{g}^{-1}$ compared to pure HAp (ca. 100 $\text{m}^2 \text{g}^{-1}$) (Table 1). The introduction of small Al_2O_3 content (5%) in the apatite phase mostly improves the specific surface area.

Fig. 2

BJH pore size distribution indicates that the mesopores are present in wAlHAp composites; their size depends on the alumina content. Except for 20AlHAp, the narrow pore size distribution resulting from apatite and alumina particles suggests that Al_2O_3 is dispersed into the apatite matrix having two pore distributions related to both phases.

Table 1.

	Atomic ratio Ca/P	Al (%)	S_{BET} (m^2g^{-1})	V (cm^3g^{-1})	D_p (nm)
HAp	1.95	-	100 $\pm$ 2	22.22 $\pm$ 0.20	12.4 $\pm$ 0.2
5AlHAp	1.70	2.59 $\pm$ 0.02	206 $\pm$ 3	45.102 $\pm$ 0.40	(3.7; 8.4) $\pm$ 0.1
10AlHAp	1.72	4.44 $\pm$ 0.03	152 $\pm$ 2	32.17 $\pm$ 0.30	(3.8; 9.5) $\pm$ 0.1
20AlHAp	1.59	11.40 $\pm$ 0.05	145 $\pm$ 2	28.48 $\pm$ 0.25	17.5 $\pm$ 0.2

3.2. Surface properties- Phenol adsorption

To investigate the surface properties of wAlHAp composites, phenol was selected to understand its affinity for the prepared composites. On the other hand, phenolic compounds are also known to be toxic and abundant pollutants in industrial wastewaters. The adsorption kinetics of the phenol is an important parameter for the selection of optimum operating conditions for full-scale batch process. Fig. 3 illustrates the adsorption kinetics of phenol onto wAlHAp surfaces according to the reaction

time. From the shape of the kinetic curve, it was evident that the phenol adsorption on wAlHAp is characterized by two-step process, i.e. an initial rapid adsorption during the first 30 minutes and slow rate of adsorption until the equilibrium was reached, but depended on the nature of the phenol $\leftrightarrow$ wAlHAp interactions. Indeed, apatite is well known for its lower efficiency in phenol removing, but it is a good adsorbent for metallic species.

Fig. 3

The results of Figure 3 clearly show that the phenol adsorption on wAlHAp is proportional to the Al(III) content in the composites. In fact, the charge surface of apatite is generally anionic, which explains the weak interactions of phenol with PO_4^{3-} or Ca-OH groups. In parallel, several studies devoted to the sorption of organic species on hydrated Al_2O_3 phases have shown that the binding process mainly involves a cationic charge of Al^{3+} [3, 4, 30]. Thus, the adsorption of phenol on wAlHAp composites can be established by electrostatic attraction or by the formation of the hydrogen bonding between the OH groups of phenol or π -electrons of the aromatic nucleus and alumina surface such as evidenced by the adsorption of phenolic compounds on clay where aluminum is abundant [3, 4]. In order to elucidate this point, the experimental data were fitted following the Lagergren pseudo-first-order and pseudo-second-order equations to describe the experimental kinetics data. The best-fit model was selected based on the linear regression

correlation coefficient values (R^2) and sorption capacity $q_{e,i}$, according to the fitting plots with the pseudo-first-order equation. It was noticed that non-linear plots were observed within pseudo first order equation for all adsorbents except for 5AlHAp with poor correlation coefficients (**Table 2**). However, the pseudo-second order is the best fit model where the regression coefficients are rather high closes 0.999. From the Table 2, the calculated value of the $q_{e,2}$ parameter obtained from the pseudo-second-order kinetic equation is in good agreement with the experimental $q_{e,max}$. As alumina content increased in wAlHAp composites, the amount of adsorbed phenol also increased and was probably related to the increase in surface area and the nature of interactions of “phenol-wAlHAp”. However, 20AlHAp sorbent has lesser surface area than those of 5AlHAp and 10AlHAp materials and so far it adsorbs better. As consequence, the phenol adsorption onto wAlHAp samples is not mainly related to the surface area, but mainly to the Al_2O_3 loading. It should be noted that the aluminum and oxygen atoms have dissimilar electronegativity, therefore, Al-O bond can be considered ionic, largely different from that of Ca-O and this can promote the binding of the phenol being a polar molecule.

Table 2

	$q_{e,exp}$	Pseudo-first-order			Pseudo-second-order		
		k_1 (min^{-1})	$q_{e,1}$ ($mg\ g^{-1}$)	R^2	k_2 (min^{-1})	$q_{e,2}$ ($g\ mg^{-1}min^{-1}$)	R^2
HAp	3.01	0.020	1.342	0.8811	0.0386	3.204	0.9993
5AlHAp	4.87	0.0292	3.752	0.9923	0.0131	5.457	0.9966
10AlHAp	7.07	0.0179	3.783	0.9210	0.0137	7.716	0.9982
20AlHAp	9.30	0.0306	3.890	0.8705	0.0180	9.774	0.9994

Sorption isotherms are shown in [Figure 4](#), showing that the adsorption process is largely dependent on the Al content associated with apatite. For wAlHAp composites and at high initial concentrations of phenol involved, there was no real evidence of a plateau-saturation and the maximum sorption capacity did not seem to be determined. For this, we considered only the highest concentration of

100 mg/L. As previously described, this increase does not depend directly on the specific surface area, but on the chemical nature of alumina where Al^{3+} ions bind better to the phenol species at neutral or alkaline pH. In fact, 5AlHAp has a higher surface area ($206 \text{ m}^2 \text{ g}^{-1}$) with a sorption capacity (30 mg g^{-1}) lower than that of 20AlHAp (42 mg g^{-1}) but greater than that of HAp (5.6 mg g^{-1}). Therefore, these data reflect the low affinity of phenol with apatite due to the electrostatic repulsion with phosphate and hydroxyl groups, while the presence of Al^{3+} cations at composite surface attracts the phenolic species better. Attempts were made to fit the experimental data with the Langmuir and Freundlich models (Table SI.1). For pure HAp, the experimental capacity could be suitably reproduced with Langmuir equation with R^2 value close to 0.99 while for wAlHAp composites a suitable fitting of the experimental data was achieved with Freundlich model ($R^2=0.999$). It should be noted the overall accurate fitting of sorption data by both models is not surprising, because the Langmuir model is adapted to homogeneous surfaces as for HAp through low phenol sorption capacity of 5.6 mg g^{-1} while Freundlich is adapted to heterogeneous surfaces as in wAlHAp composites within high solute concentration between 20-42 mg g^{-1} . These characteristics are in good agreement with assumptions of two models. Results indicate that pure HAp is less favorable for phenol uptake, whereas its association with alumina is effectiveness. In this concept, apatite associated with the alumina can help to eliminate the both organic and inorganic species.

Fig. 4

To get additional information on the adsorption mechanism, the evolution of the equilibrium pH of the phenolic solution was measured (Fig. 5).

Fig. 5

By taking the initial pH of the aqueous solution close to 6 and in the absence of phenol, the equilibrium pH of H₂O/HAp system is close to pH 8. In the presence of phenol, an increase in

equilibrium pH in the presence of the composite was observed unlike HAp. This suggests that the adsorption process takes place in two stages, the first involving a strong interaction between the 20AlHAp surface and phenol molecules, causing the protonation of aluminol groups and then the solution becomes alkaline pH 8.7 for “phenol/20AlHAp” system. Since, the pH of the point of zero charge (PZC) of the alumina is 9.0 and the equilibrium pH is around this value under this experimental condition, the protonated aluminol groups ($-\text{AlOH}_2^+$) must be present with unprotonated AlOH groups: $\text{AlOH} + \text{H}_2\text{O} \rightarrow \text{AlOH}_2^+ + \text{OH}^-$. It can therefore be supposed that different types of interactions between alumina distributed onto wAlHAp surface and phenolate anions may be assumed if the pH of equilibrium solution is close to pH 9. The figure 6 schematize the interaction of the partially negatively charged oxygen atoms of the different OH groups of carbon of phenol with the protonated aluminol groups ($-\text{AlOH}_2^+$) of wAlHAp surface by electrostatic forces or by hydrogen bonding resulting in the adsorbed amount of phenol onto wAlHAp surfaces:

Fig. 6

In addition, different chemical groups of HAp surface may interact with phenol, but lead to low sorption of 5.6 mg g^{-1} at pH 7-8 probably corresponding to the apatite pH point of zero charge (pH_{PZC}) such as mentioned elsewhere [31, 32]. In this case, the interaction modes of phenol with apatite surface may be dependent on the overall apatite surface charge. Below pH_{PZC} , the apatite surface becomes positive and the acid-base Bronsted reaction between an oxygen atom of phenol

and Ca^{2+} occurs, while above pH_{PZC} the negatively charged surface via P-O^- interacts with hydroxyl groups of phenol. Some of the previous studies in the literature [33, 34] have shown that the sorption of phenol by natural sorbents required acidic conditions to create the optimal conditions for elimination of phenolic compounds while others a neutral pH is suggested for adsorption of phenols on fly ash beads and chitosan-calcium alginate [35].

For better economical operation of the water treatment, regeneration of the adsorbents is highly desirable. This was performed by thermally treating the wAlHAp composites at 500°C , despite a slight decrease in their specific surface area. In fact, after the adsorption of phenol on wAlHAp composites, the mixture is filtered, dried at 100°C and the powder obtained is calcined at 500°C for 6h to burn off the fixed organic matter. We limited this study to three cycles of “adsorption-desorption” using only an initial phenol concentration of 20 ppm and 2 g L^{-1} as sorbent dose at pH 6 and at room temperature. Only about 10% reduction was observed in removal efficiency up to third cycles. Based on the used method by using phosphate rock in the presence of Al^{3+} ions, the cost analysis of these composites has shown that it is less expensive than some of the widely used natural or synthetic adsorbents [36-38].

These results are in good correlation with the structural and morphological properties of wAlHAp powders, in particular the specific surface area of the adsorbents. Their adsorption capacities are significantly higher than those reported with other sorbents (Table 3), but sometimes slightly lower, depending on the cost of the synthesis method and the precursors used. This new synthesis procedure using natural resources used in this work makes it possible to produce porous adsorbents containing numerous interesting functions.

Table 3.

Adsorbents	pH	Capacity (mg/g)	Reference
Zeolite X/activated carbon composite	6.5	37.92	[39]
SDS-alumina	6.7	6.6	[40]
Bentonite	5.0	1.7	[41]
Commercial activated carbon	-	49.72	[42]
Modified activated carbon	-	144.93	[43]
Chitosan-calcium alginate blended beads	7.0	51	[32]
HFAU Zeolites	6.0	160	[44]
Magnetic Hydroxyapatite	7.0	18.0	[45]
Natural phosphate Morocco	6.0	3.9	[11]
Converted HAp from natural phosphate	6.0	6.5	[11]
Porous hydroxyapatite	6.0	8.2	[12]
5AlHAp	5.6	33.79	This study
10AlHAp	5.6	46.57	This study
20AlHAp	5.6	56.43	This study

Conclusion

Alumina-hydroxyapatite composites were prepared using the selected wet method, avoiding the formation of the aluminum phosphate phases often reported in the literature, leading to the stabilization of the Al_2O_3 phase upon heating. The adsorption performance of the resulting wAlHAp composites was evaluated for phenol removal from aqueous solutions. The studied eco-friendly composites resulting from a soft chemistry approach with low-cost natural phosphate show promising properties in terms of surface affinity for organic pollutants.

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Tables Captions

Table 1. Chemical analysis, specific surface area (S_{BET}), porous volume (V) and average pore size (D_p) of pure HAp and wAlHAp composites.

Table 2. Kinetic rate constants (k_i) and adsorption capacities ($q_{e,i}$) as obtained for different models for the phenol removal by wAlHAp composites ($C_0 = 20 \text{ mg L}^{-1}$, dose = 2 g L^{-1} , pH=6).

Table 3. Comparative adsorption capacities of phenol by known adsorbents

Caption of supplementary Table

Table SI.1. Maximum experimental capacity ($q_{e,exp}$) and constants obtained from the modeling of the phenol sorption isotherms using Langmuir and Freundlich equations.

Figures captions

Fig. 1. XRD patterns of wAlHAp composite powders (a) dried at 100°C and (b) calcined at 800°C .

Fig. 2. (a) N_2 -sorption isotherms and (b) pore size distribution from BJH analysis of wAlHAp composites.

Fig. 3. Effect of contact time on the adsorption of phenol on the wAlHAp composites. Plain lines correspond to the fitting curves obtained using the Lagergren pseudo-second-order equation.

Fig. 4. Variation of sorbed phenol content (q_e) with phenol concentration at equilibrium on the wAlHAp composites compared to the pure HAp.

Fig. 5. pH monitoring with time t during phenol adsorption on 20AlHAp composite compared to that of HAp.

Fig. 6. Schema of electrostatic interactions between phenol and wAlHAp surface.

Caption of supplementary figures

Fig.SI.1. Infrared spectra of (a) dried wAlHAp and (b) heated at 800°C compared to the pure HAp.

Fig.SI.2. (a) Scanning electron microscope images of as-received wAlHAp composites dried at 100°C as well as HAp and (b) their EDX analyses.

Table SI.1. Maximum experimental capacity ($q_{e,exp}$) and constants obtained from the modeling of the phenol sorption isotherms using Langmuir and Freundlich equations.

	$q_{e,exp}$	Langmuir equation			Freundlich equation		
	(mg g ⁻¹)	q_L (mg g ⁻¹)	β (L.mg ⁻¹)	R ²	log K _f	1/n	R ²
HAp	5.6	6.88	0.047	0.9987	1.84	0.60	0.9517
5AlHAp	20	33.79	0.0239	0.9671	1.37	0.67	0.9922
10AlHAp	25	46.57	0.0325	0.9708	1.05	0.99	0.9708
20AlHAp	42	56.43	0.0767	0.6068	1.16	1.38	0.9418

Fig.SI.1. Infrared spectra of (a) dried wAlHAp and (b) heated at 800°C compared to the pure HAp.

Fig.SI.2. (a) Scanning electron microscope images of as-received wAlHAp composites dried at 100°C as well as HAp and (b) their EDX analyses.