Tests of Adsorption of Amino-Acids on the Natural Phosphate of the El Hadba layer, Djebel Onk, Algeria

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Adsorption tests were carried out in static mode, on natural phosphate samples both in a raw state and after processing. Various techniques of analyses were used (i) to characterize the material adsorbing on the granulo-chemical and thermo-mineralogical levels, (ii) to evaluate the performances of the process of adsorption used in relation to the existing mineralogical species, in phosphatic and gangue elements, (iii) to evaluate incubation condition in ions PO_4^{3-}, carboxylate grouping and steric obstruction effect on lateral chains of adsorbates. This effect is significantly affected by the composition of the incubation medium. Thus, the fractions low in phosphate ions appeared definitely more effective. The adsorption isotherms highlight a good correlation between experimental points and values predicted by Temkin model, confirming the influence of interactive effects on the used adsorbates. Study of the mechanisms of adsorption and the transfer mode of matter was carried out using the linear shape of the isotherm models, their respective correlation coefficients, the speed constants and the diffusion coefficients for the kinetic models based on reaction and diffusion.

1. Introduction

The Djebel Onk mine, southeast of Algeria, contains the most important phosphate layers in the country, in terms of reserves, exploitation and accessibility. However, the use of this material is generally limited to the manufacturing of manures and of phosphoric acid, thus involving large quantities of effluents near the treatment unit. The latter contain certain organic and mineral pollutants and micro-pollutants whose environmental impact is considerable. In this context, our study which relates to the determination of the adsorbing power of this material, could provide a new approach to valorization and exploitation of the natural phosphate. The phosphate ores of Djebel Onk are carbonated calcium phosphates belonging to the apatite group. This group constitutes the major mineral phase of hard fabrics of the vertebrae and presents a great aptitude for structural distortions, enabling them to admit in substitution a very large number of chemical species. Many studies have shown that the osseous mineral consists mainly of a carbonated apatite. It plays an important role in the bone tissue metabolism because of its capacities for adsorbing proteins, peptides, amino-acids and other organic molecules. Within this framework, we are interested in the investigation of adsorption of two amino-acids: alanine and aspartic acid by natural calcium carbonated phosphates, whether they are raw or processed. Physico-chemical studies related to solid-liquid interfaces were carried out to make it possible to better develop this kind of material and consequently to propose the most suitable processes of adsorption which may contribute to elimination of commonest pollutants in waste waters

resulting from various industries. Our goal is to highlight a number of methodologies and a synthesis regarding the parameters influencing the adsorption process. Adsorption tests for the various types of phosphates were carried out on two model adsorbates: alanine or α-amino acid and aspartic acid. The choice of these organic molecules is dependent on their hydrophobicity and on their chemical structure. This should help study their performances in the relevant adsorption processes.

2. Outline on materials used: adsorbents and adsorbates

The phosphates of the Djebel Onk area belong to a vast whole of phosphatic layers formed at the end of Cretaceous-Eocene. They are in the shape of grains, sandy (pseudoolites and pellets), often with organic support (diatoms and radiolarians, mainly), whose granulometry generally belongs to the class of arenites, more rarely to that of rudites. The facies are homogeneous, with fine grains (200 to 300 μm), or heterogeneous, with fine and coarse grains (up to 2-3 mm); they are pulverulent to stratified, and cement can be argillaceous, calcitic or dolomitic. As far as compactness is concerned, they are soft with friable elements, seldom hard. Except for the phosphate grains, instances of other elements are rare (grains of quartz and glauconite, mainly). We note the importance of diatoms and radiolarians in the development of the phosphated pseudoolites, whereas other types of micro-organisms seem to be lacking. The adsorption tests on various types of phosphates were carried out on two model adsorbates: alanine and aspartic acid. Alanine, or acid α-amino-propionic ($C_4H_7O_4N$), is the higher counterpart of wisteria. It is a very widespread amino-acid which accounts for approximately 6% of the amino-acids of proteins of our organism. Its radical is reduced to a methyl, conferring to it slightly non-polar and hydrophobic properties. It is thus prevented from taking part in chemical reactions. The radical of the aspartic acid ($C_3H_7O_2N$) is a chain of two carbons carrying a carboxylic acid function. This function is almost entirely ionized with the physiological pH, the pKa being of 4.0. Aspartate plays a significant role in certain proteins. This molecule accounts for approximately 6 % of the amino-acids of the proteins of our organism. The negative charge makes this molecule a very polar and adsorbent radical. It creates electrovalent connections with positive electric charges of other amino-acids, contributing to the tertiary and quaternary structure of protein. The study was carried out on a series of five phosphate samples in a raw state (PB), treated by calcination (PC) and classified according to particle shapes: fine PF (<80 μm), intermediate PI (80-125 μm) and coarse PG (>280 μm). Phosphate extracted from the quarry with a dimension of ~0-15 mm underwent a mechanical treatment to reduce the fragments of the exploited rock to 0-4 mm (PB). The mechanical preparation is carried out successively by crushing, homogenizing, quartering and sifting, to release the mineralogical components and define the suitable granulometry interval. These samples were subjected to physico-chemical tests of characterization by various methods of qualitative and quantitative analyses (Figure 1). The series of phosphates that were studied by the previous various techniques, revealed appreciable differences on granulometric, chemical, thermal, mineralogical and structural levels. The dimensional classification carried out by sifting showed that the major part of the raw ore mass is represented by the particle-size class of dimensions 180-250 μm (69 %). It thus constitutes the mesh of optimal release of the phosphatic elements. The particle shapes: fine (< 80 μm), and coarse (> 280 μm) recorded small quantities, 9 and 8 % respectively (Figure 1a). In addition, laser granulometry highlighted a unimodal curve for the raw ore (PB), indicating homogeneity of the grains. On the chemical level (Figure 1b), the best contents of P_2O_5 and MgO are located in the slice which may undergo beneficiation 90 to 250 μm, where the mesh of release of the phosphatic elements is located. The reduction in the frequency in these elements results in strong contents of MgO which are reflected on P_2O_5 outputs. TGA analyses (Figure 1c) show three principal losses of masses, attributed successively at the beginning to moisture water, boiler feed water, and organic matter such as decomposition of carbonates (500 °C < T < 900 °C). Decarbonation really starts from 650 C and develops between 750°C and 800°C. Apatitic CO2 is affected towards 850°C; its elimination is slow and continues beyond 900 °C. DSC with sweeping highlighted three endothermic peaks attributed to reactions of vaporization of moisture water, of constitution water and organic matter as well as to decarbonation (Figure 1d). The mineral phases identified by XRD (Figure 1e) are mainly: apatite at a fluctuating rate of substitution out of F-, OH- and CO32-, dolomite as well as other minerals in small quantities such as quartz, calcite and silicates. The microscopic examinations with the SEM and the

polarizing microscope (Figure 1f,g) and the analyses with the microprobe show that the phosphatic phase consists of grains with circular (oolites), rectangular (coprolites) and ovoid (pellets) section, having a compact structure, in the range 50-500 μm, cemented by carbonated aggregates, and a little clay and quartz. In addition, inclusions of carbonated endogangue inside the oolites, derived from decomposition of micro-organisms with carbonated shell, are also well expressed.
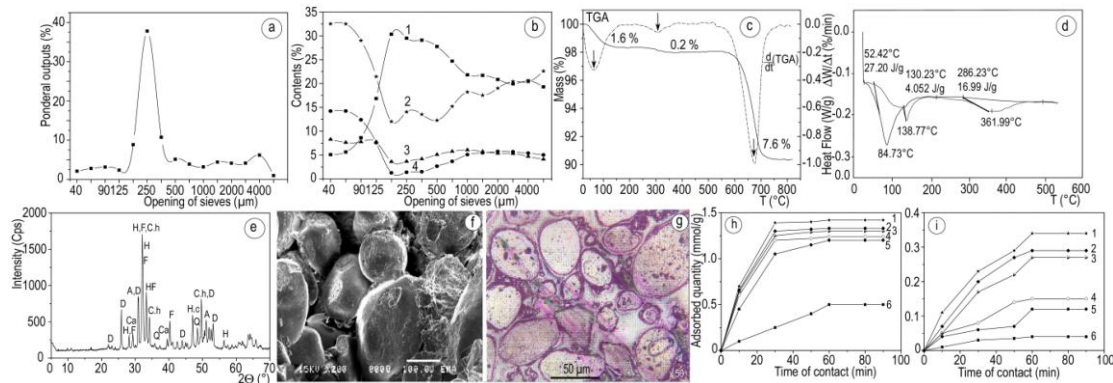

Figure 1: (a) Laser granulometry, (b) FX Chemical, (c) TGA, (d) DSC, (e) XRD Diffractogram, (f) SEM micrography and (g) Polarized micrography analyses of PB. (1) P_2O_5, (2) loss by combustion (PF), (3) SiO_2, (4) MgO. A: Ankerite, Ca: Calcite, D: Dolomite, C.h: Carbonates hydroxyapatite, F: Fluorapatite, H: hydroxyapatite, Q: quartz. Effect of time of contact for the adsorption of (h) alanine and (i) aspartic acid on various adsorbents. (1) PB, (2) PG, (3) PD, (4) PF, (5) PI, (6) PC.

3. Adsorption kinetics and isotherms : experimental protocol and models

The study of the influence of time of contact is carried out starting from adsorbent materials having various particle shapes: coarse (PG), intermediate (PI), raw (PB) and fine (PF) and those treated by calcination (PC) and scrubbing (PD) resulting from the main layer of the Djebel Onk ore deposit. The samples are dried previously for 24 h at 105 °C to eliminate the physically absorbed water molecules. The kinetic study relating to the evolution of the quantity adsorbed according to the time of contact, was carried out by putting 1 g of each adsorbent into a solution of alanine (2.9 g/L) and of aspartic acid (3.9 g/L). The suspension is maintained under moderated magnetic agitation and at room temperature. The pH of the reactional medium is alkaline (pH = 8) by addition of concentrated weld. At the times given, the solid is separated from the solution by filtration, then dried at 105 °C for 24 h. The quantity of amino-acid adsorbed by various phosphates adsorbents vs. time was given from the initial concentration in amino-acid and of that with the balance of adsorption according to the equation (Akiko et al., 2006): $Qa = \dfrac{(C_0 - C_e).V}{m}$, with Qa : Quantity of acid adsorbed at equilibrium (mmol/g), C0: Initial concentration of the amino-acid (mol/L), Ce: Concentration at equilibrium of the amino-acid (mol/g), V: Volume of the solution (mL), m: Mass of the phosphate sample put in suspension (g). The concentrations at equilibrium were determined by colorimetric proportioning using a UV/Visible spectrometer to 570 nm.

Many mathematical models in empirical form describe the graphic relations of the adsorption kinetics. A special mention may be made of:

3.1 Models based on the reaction

This approach assumes that resistance to the transfer of external and internal matter is low. This means that the process of adsorption is limited by the reaction speed of the molecule of adsorbate and by an active site of the adsorbent. Thus, this reaction can be modelled according to kinetics of the 1st or 2nd order. The basic models are those of the pseudo-first (Aroguz et al., 2007) and pseudo-second (Kumer et al., 2007) order as follows:

Model of the pseudo-balance of 1st order: $\dfrac{dQ_a(t)}{dt}=k_1(Q_e-Q_a(t))$, with K_1 (l/min): constant speed of 1st order, $Q_a(t)$ (mmol/g): quantity adsorbed at moment t, Q_e (mmol/g): quantity adsorbed at equilibrium. After integration and application of the boundary conditions, the following solution is obtained: $\log(Q_e-Q_a(t))=\log Q_e-k_1 t$

Model of the pseudo-balance of 2nd order: $\dfrac{dQ_a(t)}{dt}=k_1(Q_e-Q_a(t))^2$, after integration the following solution is obtained: $\dfrac{1}{Q_e-Q_a(t)}=\dfrac{1}{Q_e}+k_2 t$, with K_2 (mmol/g min): constant speed of 2nd order.

3.2 Models based on the diffusion

External model of diffusion: The concentration on the surface of the material will depend on the diffusion through the boundary layer surrounding the grains of adsorbents. The model is written as follows (Wang et al., 2007): $\log(1-F(t))=-R^e t$, with F(t): ratio of the quantity adsorbed at the moment t and at equilibrium, R^e (1/min): external coefficient of mass transfer. The linearity of this curve will highlight the role of the external mass transfer in the adsorption process.

Model of intraparticule diffusion: Adsorption is entirely controlled by the internal diffusion and the corresponding equation: $Q_a(t)=k_D\sqrt{t}+C$, with K_D: coefficient of intraparticule diffusion. The C constant gives an idea of the thickness of the boundary layer. A high value of C indicates an important effect of boundary layer.

The study of the adsorption isotherms was carried out with an aim of evaluating the parameters at equilibrium such as the ultimate capacities of adsorption and the constants of balances. The adsorption tests were run in vitro, by putting 1 g of previously dried adsorbing material into 30 mL of adsorbate solution at various concentrations, at room temperature and with pH = 8. Agitation causes the homogenization of the solution and the reduction of the boundary layer thickness which surrounds the adsorbent grains, and making it possible to support the contact between adsorbate and adsorbent. In all cases, we chose 2 h of time of contact to make sure the balance of adsorption was reached. The study was applied the series of adsorbent phosphates with and without chemical activation.

Several models in empirical form describe the graphic relations of the adsorption isotherms as for the Freundlich, Langmuir and Temkin Models.

4. Discussion and conclusions

The kinetic study of the evolution of the quantity adsorbed vs. time of contact was carried out for the whole series of the studied samples, previously dried for 24 hours at 105°C (*Figure 1h,i*). The evolution of the graphs makes it possible to put forward two behaviours: a linear type, in which the adsorbed quantity increases with the time of contact, ranging up to 60 mn and corresponds to relatively fast kinetics. The second type showed the stage of saturation which corresponds to the establishment of a pseudo-balance between speeds of adsorption and desorption (Ola, 2007). In order to free itself from the kinetically determining stage, the selected tool is the comparison of the correlation coefficients, obtained using least squares of the various adopted kinetic models. The principle of the analysis consists in detecting the kinetic model associated with its mode with transfer or reaction which presents the correlation coefficient nearest to unity. From the selected models for the study of the adsorption mechanisms and the transfer mode of matter, we determined, using linear regression by tracing the linear shape of the models and their respective correlation coefficients, the k_1, k_2 and R^e, k_D for the models based on reaction and diffusion, respectively. k_1 and k_2 are of the same order of magnitude and vary little vs. the adsorbate-adsorbent couple. The lowest correlation coefficients are observed for the models based on reaction, indicating that reactions do not limit their adsorption kinetics. R^e and k_D vary little vs. type of sample as well. R^e increases with the adsorbed quantity, consequently, saturation is reached more quickly. Coefficients of internal diffusion are closest to unity compared to those of external diffusion. The results of the tests of adsorption obtained (Figure 2a-e) show that adsorption isotherms are in every case of the Temkin type whatever the type of adsorbate-adsorbent couple. For a given adsorbent, the quantity adsorbed with saturation for alanine is higher than for aspartic acid. The

maximum quantities adsorbed (Q^∞) at equilibrium for a given adsorbate vary vs. chemical and mineralogical composition of the adsorbent. However, the highest adsorbed quantities are obtained with adsorbents low in phosphate ions. The composition of the medium of incubation in ion shows that these ions obstruct the adsorption processes. The pH of the solution decreases compared to its initial value, because of the protonation of ions OH^- by the amino-acid. Consequently, the molecule of amino-acid in its anion shape can interact, partly with the calcium ions being on the surface of phosphate. The lack of overshoot phenomenon seems to indicate that the competition of water molecules to occupy the sites of adsorption is really negligible (Gupta and Ali, 2000). The raw fraction (PB) seems the most effective adsorbent with a maximum quantity of adsorption (in mmol/g) of 1.45 for alanine and of 0.35 for the molecules of aspartic acid. The calcinated fraction (PC) shows the smallest adsorbed quantities (in mmol/g), i.e. 0.48 for alanine and 0.05 for the aspartic acid, regardless of the used adsorbate. This low reactivity is attributed to the sharp fall of its porosity and its specific surface. Indeed, the specific surface passes from 20.29 m^2/g in a raw state to 1.98 m^2/g after calcination. This is probably due to sintering phenomena. Generally, the quantities adsorbed at equilibrium vary appreciably between the coarse (PG) and fine (PF) fractions which are rich in siliceous and dolomitic matters. They recorded (in mmol/g) 1.40 and 1.30 for alanine and 0.29 and 0.26 for the aspartic acid from the PG and PF fractions, respectively. The intermediate fraction, rich in phosphate ions, presents the low values of the amino-acid quantity. The quantities of aspartic acid adsorbed are lower than those of alanine whatever the type of phosphate sample. This can be explained by the fact that the molecule consists of two carboxylate groupings. It is grafted horizontally on the cation sites of the substrate surface, thus occupying an important surface with fewer molecules (Wong et al., 2004). In addition, the effect of the steric obstruction of the side chain of the aspartic acid influenced negatively the quantity adsorbed at saturation (Li et al., 2007). A chemical activation in acid medium was applied for all the series of adsorbents to evaluate the impact of this treatment on the adsorption output. Activation consists in impregnating 12 g of adsorbent in 500 ml of sulphuric (98%) and hydrochloric (36 %) acid solution. The mixture is heated at 90 °C for 5 h, then washed and filtered. Scrubbing is stopped when the tests with silver nitrate and barium chromate become negative. The adsorbents collected on the filters are dried at 105 °C for 24 h before undergoing an operation of crushing and sifting (< 100 µm). The adsorption tests (Figure 2f,g) were carried out in the same conditions as the non-activated samples. The adsorption tests carried out on the adsorbents activated by acid attack did not show appreciable differences concerning the quantities adsorbed at saturation. Nevertheless, the calcinated fraction (PC) appeared definitely more effective with the hydrochloric acid treatment. Indeed, as Figure 2f,g clearly shows, the increase in the quantity adsorbed at saturation is very important. It can be attributed mainly to the elimination of the lime, which is in a very high proportion in this fraction out of soluble $CaCl_2$ and $CaSO_4$ salts in an aqueous medium. This departure will thus support the formation of porosity in the structure of the adsorbent. From the experimental values of the concentrations and quantities adsorbed at equilibrium, we calculated, using linear regression, the values of the parameters of the models retained in this study. The results show low values of the RMSE recorded for the Temkin model, which seems most representative of the experimental points. However, the highest RMSE values are observed for the Langmuir model which presents a bad correlation. This is especially visible in the important variations recorded between experimental and computed quantities adsorbed. The Freundlich model presents a rather good correlation with values of the intermediate RMSE between those of Temkin and Langmuir. It also presents values of n higher than unity, indicating a favorable adsorption and high values of K_F, pointing to a strong affinity of these amino-acids with respect to the considered adsorbents. This study should allow a new approach to the beneficiation of Algerian phosphates by conferring surface properties to use them in water treatment loaded with pollutants of organic origin. It is a matter of evaluating the effectiveness of retention of both amino-acids (alanine and aspartic acid), in particular the influence of carboxylate grouping (-COO^-), steric obstruction of the side chain of adsorbates and phosphate ions (PO_4^{3-}) of the adsorbent on the adsorption processes. The physico-chemical characterization of the phosphate samples revealed appreciable differences which had a remarkable influence on the performances of the adsorption process of the phosphate amino-acid couple. Adsorption tests revealed that the fixing of the amino-acids on this kind of substrate is appreciably affected by the composition of the incubation medium. Examination of the influence of the composition on this substrate in PO_4^{3-} ions showed that they obstruct the adsorption processes. For

a given adsorbent, the quantity adsorbed at saturation of alanine is higher than that of aspartic acid.
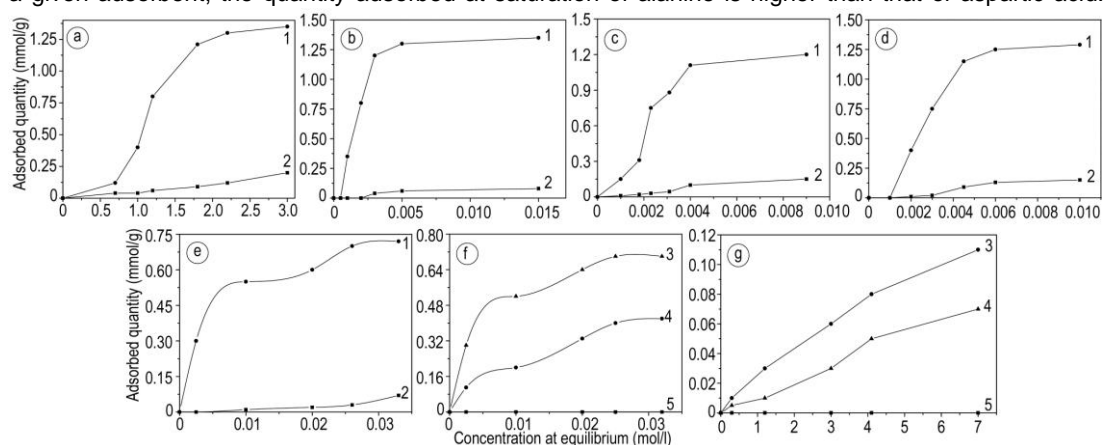

Figure 2: Adsorption isotherms of alanine and aspartic acid by (a) PB, (b) PG, (c) PI, (d) PF, and (e) PC. (1) alanine, (2) aspartic acid. Adsorption isotherms of (f) alanine and (g) aspartic acid by PC. (3) Hydrochloric and (4) sulphuric attacks, (5) without attack.

This is partly related to the steric obstruction of these molecules. The quantity of amino-acid adsorbed at equilibrium is more important for adsorbents low in phosphate ions. Thus, under the experimental conditions used and whatever the type of adsorbate, the adsorbent which adsorbs more (1.45 mmol/g) is the raw phosphate. The phosphate treated by calcination at 900 °C during 20 min involved a considerable drop of the adsorption quantity. This is probably related to specific surface, mineralogical and chemical composition of the used adsorbents, as well as the effect of the steric obstruction of side chains of both amino-acids, particularly aspartic acid. The results obtained also revealed a good correlation between experimental points and values predicted by the Temkin model, compared to the other models. This clearly confirms the influence of interaction effects of adsorbates loaded on the adsorption processes.

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