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ORIGINAL ARTICLE

Interaction of some essential amino acids with synthesized poorly crystalline hydroxyapatite

A. El Rhilassi *, M. Mourabet, M. Bennani-Ziatni, R. El Hamri, A. Taitai

Chemistry and Valorization of Inorganic Phosphates, Department of Chemistry, Faculty of Sciences, 13000 Kenitra, Morocco

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Medium composition;
Electrostatic interaction

Abstract This study focused on the release of two essential amino acids, L-lysine and DL-leucine, previously adsorbed onto poorly crystalline hydroxyapatite of Ca/P = 1.59, synthesis by precipitation methods. The composition of the calcium-deficient hydroxyapatite (CDHA) is chemically and structurally similar to the bone mineral. Their surface reactivity is indeed linked to the existence of hydrated surface particles (HPO_4^{2-} and Ca^{2+}). The adsorption kinetics is very fast while the release kinetics is relatively slow. The adsorption rate reached approximately 70%, but the release rate did not exceed 12%. The chemical composition of solution has an influence on the release processes. The presence of phosphate ions favored the release of amino acids, while the calcium ions inhibited it. Also, the release process is slightly influenced by Ra (ml/mg) ratio and incubation temperature of the medium. The charged $–COO^-$ and NH_3^+ of amino acids are the strongest groups that interact with the surface of hydroxyapatite, the adsorption is mainly due to the electrostatic interaction between the groups $–COO^-$ of amino acids and calcium Ca^{2+} ions of the hydroxyapatite. DL-Leucine (non-polar) and L-Lysine (polar–basic) interact with the hydroxyapatite surface in the zwitterionic and cationic forms, respectively. The study of interactions between amino acids and hydroxyapatite is carried out in vitro by using UV–vis and infrared spectroscopy IR techniques.

1. Introduction

The study of the interactions between biomolecules and biomaterials has received much attention in recent years because of the potentiality of nanotechnology applied to biotechnological processes and in biomedical applications (De et al., 2008; Gray, 2004; Vallet-Regí et al., 2004; Vo-Dinh, 2007). The adsorption and release at the apatite-solution interface are the result of the various interactions between and within the system components which include the solid surface, the adsorbate, the solvent and other solutes present. Among various biomaterials, calcium hydroxyapatite, has been widely considered as one of the most important inorganic materials for medical and dental applications such as dental implants, alveolar bridge augmentation, orthopaedics, maxillofacial surgery and drug delivery systems due to its biocompatibility, chemical and biological affinity with bone tissue (Burg et al.,

* Corresponding author. Address: Department of Chemistry, Ibn Tofail University, Faculty of Science, 13000 Kenitra, Morocco. Tel.: +212 662 13 13 72.
E-mail address: aelrhilassi@gmail.com (A. El Rhilassi).
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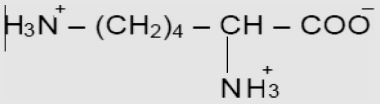
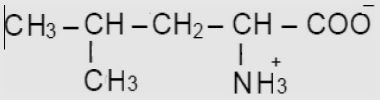
Table 1 Characteristics and properties of L-Lysine and DL-Leucine.

Amino acid	L-Lysine	DL-leucine
Chemical structure		
Molecular formula	$C_6H_{14}N_2O_2$	$C_6H_{13}NO_2$
Other names	2,6-diaminohexanoic	2-amino-4-méthylpentanoic
Hydrophobicity	Strongly basic and hydrophilic	Very hydrophobic (non polar)
Acidity (pK_a)	2,18 (carboxyl), 8,95 (amino), 10.53 (side chain)	2.36 (carboxyl), 9.60 (amino)
Molecular weight (g/mol)	146.19	131.17
Isoelectric point (pI)	9.74	6.04
Solubility in water at 25 °C (g/L)	1500	24

2000; Dash and Cudworth, 1998; Suchanek and Yoshimura, 1998; Zhou and Lee, 2011). Their availability structure, ionic exchange property, adsorption affinity, and their characteristic to establish bonds with organic molecules of different sizes have conferred to this material to be often used as a reference to study biomolecule/biocompatible surface interactions (Jones, 2001; Ratner et al., 2004). Multiple techniques have been used for the preparation of hydroxyapatite powders, as reviewed in several works (Aoki, 1991). Depending upon the technique, materials with various morphologies, stoichiometries, and levels of crystallinity can be obtained. In the present work, the poorly crystalline hydroxyapatite was prepared in an aqueous medium by rapid precipitation at room temperature and at neutral pH. The fixation/release process of low-crystalline calcium phosphate apatite is dependent on the composition of the hydrated surface layer and the surrounding environments (El Rhilassi et al., 2011, 2012a).

It is interesting to note that the composition of the phosphocalcic hydroxyapatite may vary in the domain in which the Ca/P atomic ratio is between 1.5 and 1.67. In fact, only the hydroxyapatite of ratio 1.67 is stoichiometric [$Ca_{10}(PO4)_6(OH)_2$], the other apatites are called calcium-deficient hydroxyapatites (CDHA). Several chemical formulas have been proposed for calcium-deficient hydroxyapatite (Dorozhkin, 2009; Elliott, 1994; Posner et al., 1960). An example of a proposed formula is: Ca_{10-x} $(PO_4)_{6-x}$ $(HPO_4)_x$ $(OH)_{2-x}$ $(0 < x < 1)$.

In the case $x = 1$ (the boundary condition with Ca/P = 1.5), the chemical formula of CDHA looks as follows: Ca_9 (HPO_4) $(PO_4)_5$ (OH).

The purpose of the present work is to study the adsorption and release process of amino acids L-lysine and DL-leucine onto poorly crystalline hydroxyapatite (CDHA) under physiological conditions. We propose to analyze the solution after release, and study the influence of calcium and phosphate ions,

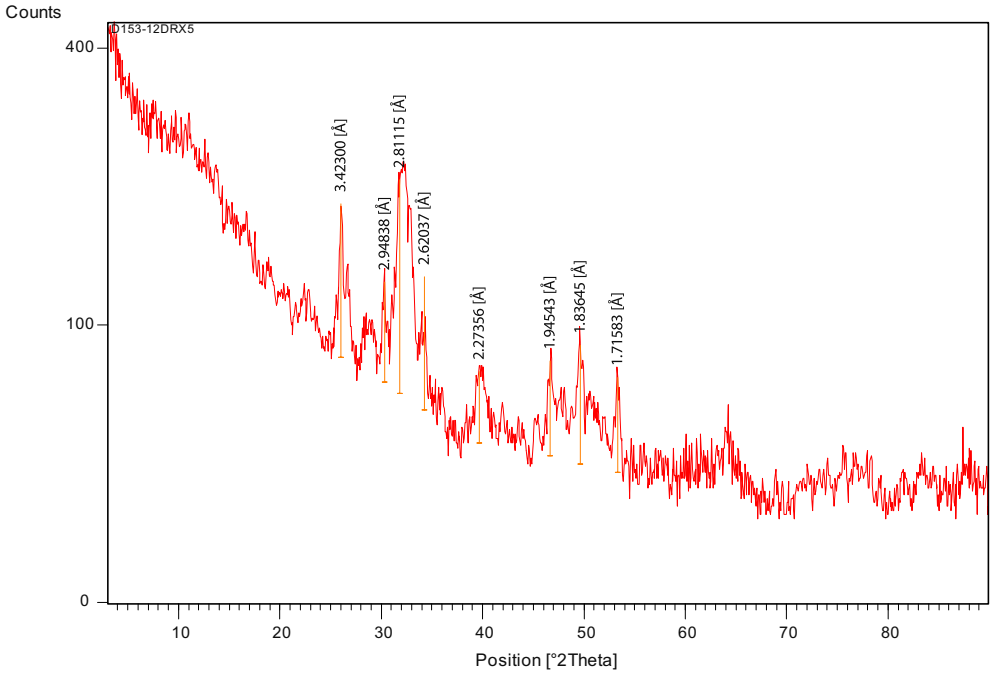


Figure 1 XRD patterns of poorly crystalline hydroxyapatite (CDHA).