Adsorption of phenylalanine on layered double hydroxides: effect of temperature and ionic strength

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Abstract In this work we report the adsorption of phenylalanine (Phe) on Magnesium Aluminum Layered Double Hydroxides (Mg–Al–CO$_3$-LDH) at two different temperatures (298 and 310 K) and under two distinct ionic strength conditions (with and without the addition 0.1 M of NaCl). The adsorption isotherms exhibit the same profile in all conditions, and they only differ in the amount of removed Phe. At lower ionic strength, the isotherms are almost identical at both temperatures, except for the last points, where the increase in temperature causes a decrease in the amount of adsorbed Phe. An increase in ionic strength results in a decrease in Phe adsorption. The electrokinetic potential decreases as the amount of adsorbed Phe increases, and only positive values are observed. This indicates that the surface of the adsorbent is not totally neutralized and suggests that more Phe could be removed by adsorption. The presence of Phe on the solid is confirmed by FTIR spectra, which present the specific bands assigned to Phe. The hydrophobicity of the amino acid probably contributes to its extraction, thus enabling the removal of a great amount of Phe. In conclusion, LDH is potentially applicable in the removal of Phe from wastewater.

Introduction

Phenylalanine (Phe) is an amino acid that is widely used in many fields, such as food, chemical, pharmaceutical, agricultural, medicine, and cosmetic industries [1–4]. To improve the efficiency of recovery, separation, and purification of amino acids from wastewaters coming from fermentations broths, several techniques have been employed [5, 6]. In this way, many studies have been reported in the literature for adsorption of amino acids on various materials including activated carbon, silica, ion exchangers, alumina, and polymeric resins [7–11]. Amino acids have several active functional groups with very different acidities and could thus exhibit complex adsorption behavior due to their different intermolecular interactions, including van der Waals forces, hydrogen bonding, coulombic interactions, and the influence of different molecule–adsorbent interactions.

Layered Double Hydroxides (LDH) are a class of materials originated from the isomorphous substitution of divalent cations, such as Mg^{2+}, by trivalent ones, like Al^{3+}, in a planar brucite-like structure. Such substitution gives rise to a positive residual charge that can be balanced by intercalation of anionic species together with water molecules, stacked in such a way that the hydrotalcite-like structure that presents the general formula: $\left[M^{2+}_{1-x}M^{3+}_{x}(OH)_2\right]^{x+}A^{m-}_{x/m} \cdot nH_2O$, with M^{2+} as a divalent cation, M^{3+} as a trivalent one, and A^{m-} as the intercalated anion with an m$^-$ charge. These materials can present different properties by varying the di- and tri-valent cations and their ratio, the interlamellar anion, and they can remove anionic species from aqueous solution by three different processes: (i) adsorption (surface interaction); (ii) anion exchange (intercalation); and (iii) sorption, a combination of intercalation and adsorption that is more likely to take place in the regeneration of a calcined precursor (*"memory effect"*) [12–19]. When the LDH is intercalated with an anion that is very difficult to undergo exchange (like CO$_3^{2-}$ anions), only the adsorption process is expected

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to occur. In this case, the most important adsorbent/adsorbate interaction occurs on the external surface of the LDH.

Removal of organic species from aqueous solutions is a process of great economic, technological, and industrial interest, and this process has received increasing attention recently. In this sense, natural or synthetic LDH have large importance due to their properties and applications as adsorbents and sorbents, and bi-dimensional matrices [20–27].

In this work, our objective was to study the removal of Phe from aqueous solutions by adsorption on Mg–Al–CO$_3$-LDH, as well as investigate how variables like temperature and ionic strength effect such process. We also compare the results we obtained with those of similar systems, with different adsorbents reported in the literature.

Experimental

The adsorbent, Mg–Al–CO$_3$-LDH, was prepared according to the coprecipitation method proposed by Reichle [28]; all reactants were acquired from Merck (>99% assay). The prepared LDH and the adsorbed solids were characterized by several techniques, such as Powder X-Ray Diffraction (PXRD), Fourrier-Transform Infrared Spectroscopy (FTIR), Scanning Electronic Microscopy (SEM), and Specific Surface Area (S$_{BET}$).

The adsorbate, Phe, was acquired from Acros (99.5% assay) and used without previous purification. All solutions used in the experiments were prepared with deionized water (MilliQ®), and the initial pH was adjusted to 10 by addition of NaOH.

The adsorption isotherms were obtained by the batch method, at two different temperatures (298 and 310 K), and under two distinct ionic strength conditions (with and without addition 0.1 mol dm^{-3} NaCl, in this case only at 298 K). Samples of the adsorbent LDH (constant mass

500 mg) previously dried under vacuum at room temperature were added to 25 cm^{-3} aliquots of Phe solutions at different initial concentrations (in the range 6.0×10^{-4}–0.15 mol dm^{-3}), all of them initially at pH = 10, contained in erlenmeyers equipped with a stopper. The resulting suspensions were submitted to ultra-sonication for 10 min, in order to homogenize particle size. Then the samples were kept in a thermostatic bath at temperature ($T \pm 0.5$ K) with orbital shaking for 70 h, to ensure that the adsorption equilibrium was reached. After this period, each sample was divided into two parts: one was centrifuged at 10,000g for 20 min, separating the supernatant (where the amount of Phe was quantified by UV–vis spectroscopy—ninidrin method [29]) from the solid (which was dried and characterized); the other part of the sample was kept in aqueous suspension, for determination of the electrokinetic potential, which was performed after a decanting time of 10 min, at the same temperature of the adsorption experiments.

Results and discussion

The LDH prepared to be used as adsorbent in this work can be represented by the empirical formula, $[Mg_{0.7}Al_{0.3}(OH)_2]^{0.3+}(CO_3)^{2-}_{0.15} \cdot 0.7\,H_2O$, calculated from elemental and TG analyses data. The Mg/Al ratio of 2.5:1 leads to charge density, which is extremely important for the adsorption process.

All the isotherms obtained for the adsorption of Phe on the present LDH under the three different conditions used in this work are shown in Fig. 1. Comparing the results obtained at the same ionic strength (without addition of NaCl), we can note that an increase in temperature from 298–310 K does not affect the adsorption up to a Phe equilibrium concentration close to 0.13 mol dm^{-3}. Above this value, the amount of removed Phe decreases with increasing temperature. Moreover, both isotherms give

Fig. 1 Adsorption of Phe. (a) isotherms, (b) electrokinetic potential
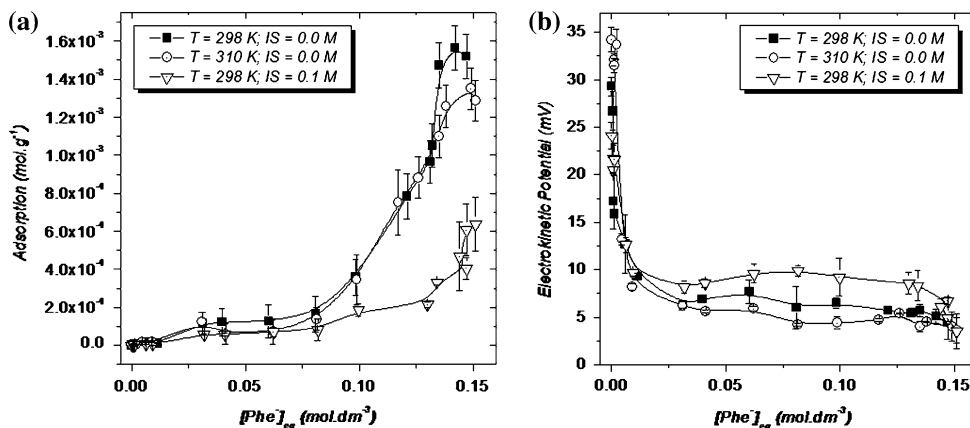
evidence of the saturation of the adsorption sites in the last points of the curves, as can be seen from the change in their respective angular coefficients. The adsorption isotherms obtained at higher ionic strength (by addition of NaCl) indicate there is a reduction in the amount of removed Phe at equilibrium concentrations above 0.08 mol dm^{-3}, if compared with the two others conditions. No tendency to saturation is observed for the highest Phe equilibrium concentration used in this ionic strength condition, which suggests that the amount of adsorbed Phe should increase if a higher concentration, limited by the solubility product, could be used.

The decrease in adsorption with increasing temperature can be explained by considering that the adsorption process is thermodynamically governed by both an entropic and an enthalpic factor. So, when $\Delta S < 0$, a positive entropic contribution to the negative Gibb's free energy ($\Delta G = \Delta H - T\Delta S$) of the process, governed by the negative enthalpy, should increase with the temperature of the system, thus leading to a decrease in the amount of adsorbed Phe. Therefore, this entropic contribution should overcome the negative enthalpy above some amount of adsorbed Phe close to the equilibrium concentration of 0.13 mol dm^{-3} Phe. The same behavior has been reported for several systems involving the adsorption of surfactants on mineral oxides [15, 16, 30–32].

For all the cases studied here, we can consider that a large amount of Phe has been removed if we bear in mind that at the pH used in the experiments (pH = 10), the charge density on the LDH surface is small due to the larger interaction of the positive residual charge on the LDH with the OH^{-} anions from the solution. The amino acid Phe has a hydrophobic part, which favors its adsorption on the LDH surface. Moreover, we have to consider the possibility that bi-layers are formed by π–π type interactions between the aromatic rings of the Phe molecules. These amino acid properties, allied with the properties of the LDH surface, can account for the large amount of adsorbed Phe without saturation being reached.

The Phe extraction rate by the LDH was calculated, and it can be shown that this adsorbent is highly capable of removing this species, especially when one considers that the LDH had not been pre-calcined and that saturation was not achieved under the conditions used here. At low initial Phe concentrations (near 0.65 mmol dm^{-3}), approximately 6% of the amino acid is removed, whereas the extraction rate is as high as 17% in the last points of the isotherms, without addition of NaCl. It must be borne in mind that at these points, the initial Phe concentration is in the limit of its solubility product, which is close to 0.16 mol dm^{-3}. We calculated the loading capacity (LC) for the adsorption and these values are reported in Table 1. By comparing these results with others reported in the literature using different

Table 1 Loading capacities for the adsorption of Phe on LDH under different conditions

Condition imposed	Loading capacity (mol kg)
298 K, IS = 0.0 M	1.52
313 K, IS = 0.0 M	1.29
298 K, IS = 0.1 M	0.64

adsorbent systems, like zeolites (LC 0.26 mol kg^{-1}) [33], polymeric (LC 1.42 mol kg^{-1}) [34], and cation-exchange resins (LC 5.4 mol kg^{-1}) [35], we found that the LDH is potentially useful in the treatment of wastewaters containing Phe.

The electrokinetic potential curves present similar profiles, which are all compatible with their respective isotherms (see Fig. 1b). These curves lead to higher and more positive values at low equilibrium concentrations. These values decrease quickly as the Phe concentration increases, converging to small (but still positive) values close to 5 mV. These positive values have led us to believe that the adsorption sites are not completely occupied, as indicated by the absence of a plateau.

These results are very interesting, especially because the LDH allows the removal of large amounts of Phe at a high pH value. The other adsorbents mentioned here present LC similar to that of the LDH at lower pH values. Considering that the LDH adsorption is directly related to the residual charge at its surface, we believe that the LC can increase at lower (but alkaline) pH values.

A variation in the pH value of the supernatant solutions obtained after the contact between the adsorbent and the Phe solution (Fig. 2) was observed, and the profile of this variation was the same in all conditions studied here. After the adsorption equilibrium, the observed pH value was lower than the one of the initial solution, being close to 8.5. The pH values increased with increasing Phe concentrations, until they stabilized at the initial value (10.0). This behavior may be due to the fact that, at pH 10, the concentration of OH^{-} ions is high enough to promote a competition between the OH^{-} and Phe^{-} anions for the LDH adsorption sites at lower amino acid concentrations. As the Phe concentration increases, the adsorption equilibrium is shifted favoring Phe adsorption. In other words, the higher the Phe concentration, the smaller the effect of pH values on the adsorption process.

The PXRD pattern of the pure LDH adsorbent and those of the solids corresponding to the last points in the isotherms are shown in Fig. 3. All the diffractograms present a basal spacing of 7.6 Å, which corresponds to the intercalation of carbonate anions and confirms that the adsorption does not change the intercalated anions. The FTIR spectra (Fig. 3) of the adsorbed solids display bands
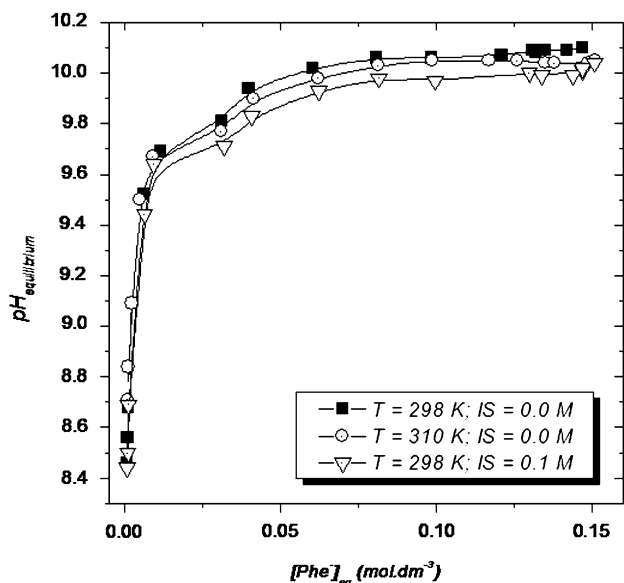
Fig. 2 Variation in the pH value of the supernatant solutions after the contact between the adsorbent and the Phe solution under several conditions

that give evidence of the presence of Phe on the material. The wide band observed between 3,600 and 3,000 cm^{-1} is due to both the stretching of the O–H groups into the vertexes of the octahedra layer and the interlayer water; at 3,030 and 2,900 cm^{-1} one can see the absorption bands corresponding to the N–H and C–H stretchings, respectively. At 1,590 cm^{-1}, there is an overlap of the absorption bands due to the C=C bonds of the aromatic ring, the N–H

symmetric stretching, and the C=O stretching. In the region below 900 cm^{-1} there are bands due to the vibrational modes of the lattice, attributed to the M–O and O–M–O bonds [36–38].

The average particle size of the materials was calculated from the PXRD data by the Debye–Scherer method [39], and the results are shown in Table 2. The average particle sizes of the adsorbed solids are larger than that of pure LDH, and they increase proportionally with increasing amount of adsorbed Phe. The surface areas of the solids adsorbed with Phe, determined by BET isotherms, are larger than that of the clean LDH. The total pore volumes, as determined by BJH isotherms, are also larger than that of the clean LDH. This significant increase on the BET surface area and pore volumes after adsorption of Phe on the LDH indicates that the amino acid molecules are not located inside the pores. The adsorption process should produce a very organized agglomeration of the small LDH particles, thus resulting in aggregates with larger sizes. This process is enhanced by the adsorption of Phe molecules, thus producing a more porous surface.

The SEM images of the solids containing the largest amounts of adsorbed Phe, shown in Fig. 4, are very different from that of the clean LDH. In all cases, large aggregates can be observed on the surface, and they are better organized for the solids adsorbed at 298 K. The solids adsorbed at 310 K contain similar aggregates, but in smaller quantity. The addition of NaCl produces adsorbed solids with less ordered aggregates, which is in agreement with the interpretation of the isotherms.

Fig. 3 Left: PXRD, Right: FTIR of the LDH containing adsorbed Phe under several conditions. (**a**) Clean LDH, (**b**) Phe adsorbed at 298 K, (**c**) Phe adsorbed at 310 K, and (**d**) Phe adsorbed at 298 K (with addition of NaCl)
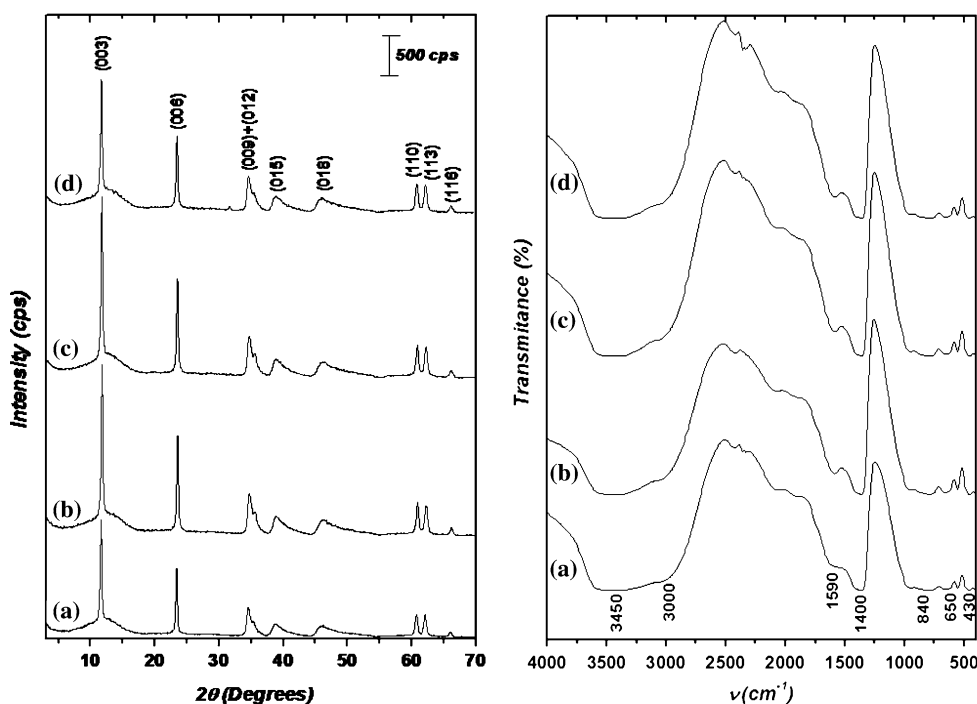
Table 2 General parameters observed for the pure LDH and the LDH obtained after adsorption of Phe under different conditions

Sample	Average particle size (Å)	S_{BET} (m^2 g^{-1})	Pores' total volume (cm^{-3} g^{-1})	Pores' medium diameter (Å)
Pure LDH	507.9	34.5	0.127	147.4
Phe (298 K/IS $\approx$ 0.0 M)	729.7	46.3	0.130	112.0
Phe (310 K/IS $\approx$ 0.0 M)	655.7	42.8	0.199	185.7
Phe (298 K/IS $\approx$ 0.1 M)	597.5	43.6	0.274	217.9

Fig. 4 SEM images of MgAlCO$_3$-LDH containing adsorbed Phe. (**a**) Clean LDH (10.000×), (**b**) 298 K (10.000×), (**c**) 310 K (10.000×), and (**d**) 298 K; IS 0.1 M (10.000×)
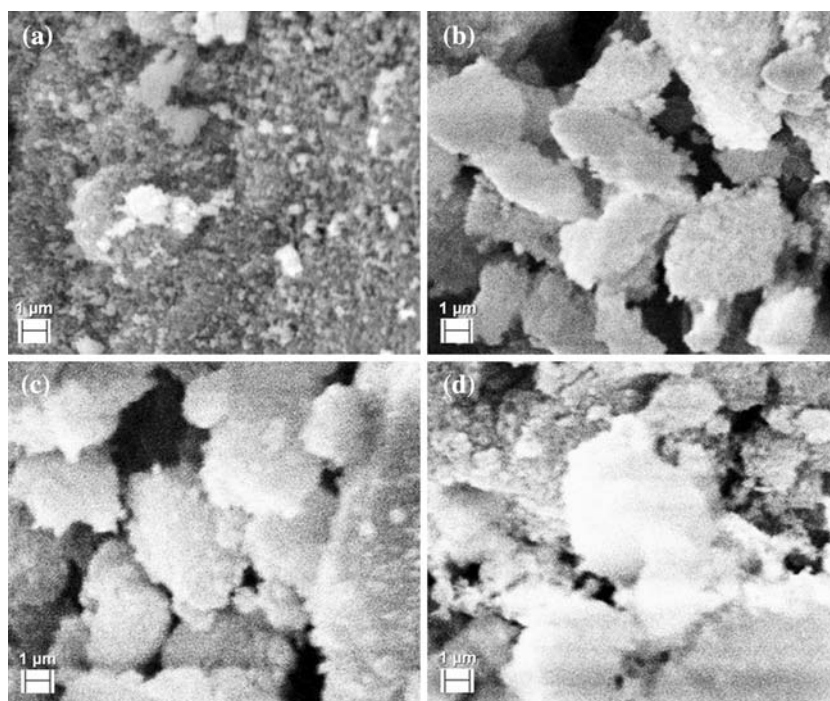
Conclusions

This work presents a new alternative for the Phe removal from aqueous medium. Our results have shown that the Phe adsorption occurs at a very efficient extraction rate, even at higher amino acid concentration, and this removal process is greatly dependent on the variables studied here. The results also suggest that an increase in temperature reduces the amount of Phe removed from the solution, mainly at higher concentrations. An increase in the ionic strength by addition of NaCl results in a decrease in the amount of removed Phe. This effect is probably due to the hydrophobic character of Phe, which makes its adsorption less influenced by the ionic strength, thus reducing the electrostatic character of the adsorption. The adsorption process should be favored by the π–π interactions between the aromatic rings of the Phe molecules, which contribute to the formation of a bi-layer even at lower ionic strength. By comparison with other studies reported in the literature, the LDH seem to be a better adsorbent than those described therein since it can be used at higher pH values, which allows a wider range of applications. This new approach is potentially useful in the treatment of wastewaters coming from industrial processes.

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