Fluoride adsorption on stable amino acid functionalized HKUST-1

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ABSTRACT

Fluoride contamination in water due to natural and human activities has become a significant problem worldwide due to the diseases caused by this pollutant, such as dental and skeletal fluorosis caused by constant exposure concentrations above 1 ppm. It is possible to design materials that efficiently absorb fluoride from water, one possibility being metal–organic frameworks (MOFs). The HKUST-1 is a copper-based MOF with a high surface area; however, this framework is unstable in an aqueous solution. In this work, we studied the functionalization of HKUST-1, using five amino acids (tyrosine, serine, histidine, proline, and cysteine) to stabilize the 3D structure in an aqueous medium and evaluate its fluoride adsorption capacity—the X-ray diffraction patterns of functionalized MOF with 5 and 20 wt.% amino acids show the same structure of HKUST-1 for all materials. The amount of amino acid present in each MOF was determined by the relative intensities of the diffraction peaks, and Fourier-transform infrared spectroscopy identified the characteristic bands of the N–H bond. The samples functionalized with 20 wt.% increased the hydrophobic nature, increasing thermal stability to 110°C (proline). The maximum fluoride adsorption was 0.44 mg·g^{-1} (40% for 5 wt.% cysteine-MOF) and 0.55 mg·g^{-1} (50% for 20 wt.% histidine-MOF). The MOF structure is stable after fluoride adsorption when functionalized with 5% of serine, proline, and cysteine and 20% of tyrosine, proline, histidine, and cysteine.

Keywords: Fluoride; Metal–organic frameworks; Amino acids; Post-synthetic modification (PSM); Adsorption

1. Introduction

The importance of materials for their role in everyday life and their effect on the future of technology is decisive [1]. One class of materials that have come to the fore in recent years is metal–organic frameworks (MOFs), composed of clusters of metal oxides connected by organic linkers [2]. MOFs are a class of inorganic–organic hybrid composites. The organic linkers are considered secondary building units that act as "struts", and the metal centers are considered secondary units that act as "joints" in MOF structures. The three most relevant MOF components are the structure topology, the inorganic metal centers, and the organic linker. Properly selecting the reagents can produce high chemical and thermal stability and highly porous materials. The structures formed by MOFs allow higher porosity compared to various zeolites and some other porous materials [3]. MOFs have come to be used for the adsorption of water contaminants such as fluoride, arsenic, etc. Among other water pollutants due to their relevant properties. Some of the most important characteristics of this type of material are the following: high internal surface area, various functionalities, and diversity in the range of porosity from microporous to mesoporous region, in addition to the possibility of design and post-synthesis modification [4].

HKUST-1 was first reported in 1999 [5]; this compound is formed by organic ligands of benzene-1,3,5-tricarboxylic acid (BTC), which are coordinated copper ions in a

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cubic lattice (Fm-3m). This has a three-dimensional system of intersecting large square-shaped pores. In the HKUST-1 network, Cu(II) ions form dimers, in which each copper atom is bonded by four oxygens of the organic ligand and water molecules [6]. The coordinately unsaturated copper sites are reachable only from the larger pore, resulting in higher hydrophobicity than the smaller pores, which are accompanied by benzene rings [7].

The curve obtained from an adsorption isotherm can give us essential information about the strength and kind of interactions between an adsorbed molecule and the surface of the adsorbent material [7]. Wang et al. [8] published the first water adsorption isotherm for HKUST-1. This MOF obtained a water isotherm that adequately matches the type I form. The open metal sites adsorb water mainly within the larger hydrophilic pore at a low relative pressure (P/P_0), and the material finally reaches a saturation loading of around Schoenecker et al. [9], reported that nitrogen adsorption analysis showed that HKUST-1 exposed to water loses about 50% of its original surface area. It has been corroborated that HKUST-1 can retain its structure at a maximum water content of 0.5 mol equivalent relative to copper, but degradation occurs at water contents above this value [7].

In previous work, Rani et al. [10] reported the synthesis and functionalization of HKUST-1 using cysteine, tyrosine, lysine, and glycine. The synthesis was carried out by post-synthesis modification. The results showed that the crystallinity and morphology of the HKUST-1 are preserved after functionalization with amino acids in the case of tyrosine, lysine, and glycine. As a result of the functionalization with amino acids, the MOF changed from a hydrophilic to a hydrophobic character. Making the MOF much more hydrothermally stable. The lack of publications reporting the adsorption of fluoride in solution by MOF HKUST-1 is one of the motivations to report the adsorption capacity obtained from HKUST-1 pristine and for amino acid functionalized MOF samples. It should be noted that there are no previous works on the adsorption of fluoride in HKUST-1 functionalized with amino acids.

Therefore, in this paper, the functionalization of the HKUST-1 was carried out by using different amino acids to improve the stability and evaluate its efficiency in the adsorption of fluoride ions in water. In addition, the complete physico-chemical characterization of the obtained materials was carried out by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA).

2. Experimental section

2.1. Materials

MOF HKUST-1 powders were synthesized using as precursors: copper(II) nitrate trihydrate (99%+), benzene-1,3,5-tricarboxylic acid (95%), sodium bicarbonate (99%+), sodium hydroxide (98%), ethanol absolute (99%+). As for the amino acids used for post-synthesis functionalization, they were as follows: L-proline (99%+), L-tyrosine (98%+), L-serine (>99%), L-histidine (99%), L-cysteine (>98%). All precursors were supplied for Sigma-Aldrich (Massachusetts, United States) and were used without prior purification.

2.2. Synthesis of HKUST-1

The synthesis method used to obtain HKUST-1 was carried out in the following way by a previously reported procedure [11,12]. A solution was prepared with 2 mmol of the organic linker benzene-1,3,5-tricarboxylic acid (BTC) and 80 mL of deionized water, stirred until complete dissolution. In a second solution, 3 mmol of copper nitrate ($Cu(NO_3)_2$) and 100 mL of ethanol were added. Once the second solution was dissolved, it was added dropwise to the first solution, and the mixture was kept stirred for 12 h until a blue solid was formed. Subsequently, the mixture was placed in centrifuge tubes at 6,000 rpm for 30 min. Once the components were separated, the solid was dried in an oven at 70°C for 4 h. The solid obtained was stored for subsequent characterization, and the experiments were performed in triplicate.

2.3. HKUST-1 functionalization

The functionalization methodology was performed in a post-synthesis process, as reported by Rani et al. [10], where 0.3 g of HKUST-1 was put in contact with 5% and 20% (in weight) of dilution of each amino acid (L-proline, L-cysteine, L-histidine, L-serine, or L-tyrosine), additionally each dilution contained dissolved NaOH to aid the proper dissolution of all amino acids employed. After this time, the solid was separated from the liquid by centrifugation at 6,000 rpm for 30 min.

2.4. Characterization

The crystallographic parameters (lattice parameter and crystal size) and the characterization of the materials obtained were carried out by X-ray diffraction, using a Philips X'Pert (United States) model equipment with a copper anode (CuKα = 1.5406 Å). The obtained samples were analyzed at a high angle, between 4–50 (2θ), with a step size of 0.02° and step time of 0.04 s. FTIR spectroscopy was used to determine the functional groups in the crystal structure. A Frontier model infrared spectrophotometer (PerkinElmer, United States) equipped with an attenuated total reflectance (ATR) accessory was used. The spectra obtained were reported in the range of 400–500 cm^{-1}. SEM studies were performed in a Zeiss electron microscope with a voltage of 2.0 kV. For the preparation of the powdered sample, these were obtained from the synthesis method, which was at least 10 mg. Thermogravimetric analysis (TGA) was used to determine the thermal stability of the MOFs and the dehydration temperature. The materials were analyzed using a TA Instruments SDT Q600 (New Castle, Delaware, United States) model. The study was carried out with a temperature increase of 15°C per min until the decomposition of the sample at 600°C was reached.

For the fluoride adsorption tests, 0.1 g of the MOF was placed in contact with 10 mL of the fluoride solution while stirring for 1 h, and the maximum adsorption capacity at equilibrium was corroborated by measuring the fluoride concentration. The mixture was placed in centrifuge tubes at 60 rpm for 20 min to separate the solid from the liquid. The remaining fluoride was measured with a

high-range fluoride colorimeter (0–20 mg·L⁻¹) of the Hanna Brand (Checker HC, Woonsocket, RI, United States) with a 0.01 mg·L⁻¹ resolution.

3. Results and discussion

3.1. Physico-chemical properties of HKUST-1 and amino acid functionalized MOFs

The study of the structure of the synthesized MOF was carried out using the powder XRD technique. Fig. 1 shows the indexed diffraction pattern for the HKUST-1 synthesized by stirring at room temperature, in this, it can be observed that the diffraction planes possess definition and belong to the cubic structure reported for this MOF [5]. Indeed HKUST-1 has a cubic three-dimensional crystal structure; it was feasible to determine the lattice parameter a_0 using Bragg's law [13]. The plane through which the calculation was performed was (731), from the interplanar distance (d_{hkl}). The crystal size was calculated from the (222) plane using the Scherrer equation. The crystal size

of HKUST-1 corresponds to a nanometer scale material of 30.54 nm, with a lattice parameter of 26.04 Å.

Fig. 2 shows the diffraction patterns obtained for the HKUST-1 samples, functionalized with the amino acids: proline, tyrosine, cysteine, serine, and histidine, using 5% (Fig. 2a) and 20% (Fig. 2b). It can be observed that the diffraction patterns possess the same reflections characteristic of HKUST-1, which means that the MOF structure is preserved after functionalization with the amino acids. Since the aggregate concentration of 20 wt.% is high, different characteristic peaks corresponding to the amino acids are expected to be observed in the diffractograms. However, they are only perceived in some diffractograms. This may occur possibly due to (1) the functionalization of the materials was performed, and the amino acid is part of the MOF structure but with a concentration lower than 20%, which prevents the amino acid peaks from being observed in the pattern, or (2) the amino acid is not incorporated in the MOF structure and therefore the MOF structure is maintained. To corroborate either hypothesis, crystallographic parameter calculations, and other characterization techniques were performed and are presented in the following sections.

The sample functionalized with 20% of serine presents a pattern that lacks peaks, which indicates that the 3D network of HKUST-1 is destroyed. The solid obtained does not have a crystalline structure that XRD can identify. The functionalization of the amino acids may depend on the acidity they present in the solution to analyze the possible effects they generate; some physico-chemical data are shown in Table 1 [14,15]. It is observed that the amino acids used have similar pKa values; this is an acid dissociation constant used to describe the acidity of a specific molecule, in this case, of the amino acids used. Its value is closely related to the structure of the compound.

Furthermore, by using NaOH to dissolve the amino acids in water, the pH of this solution was basic between 9 and 12; it has also been reported that amino acids generally possess a high-water solubility, as presented in Table 1. Still, when working with them experimentally, only most of the amino acids were dissolved when using powdered NaOH, especially in the case of the MOF with
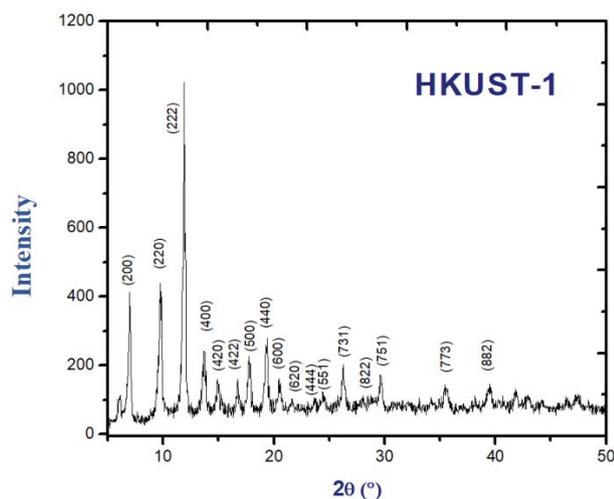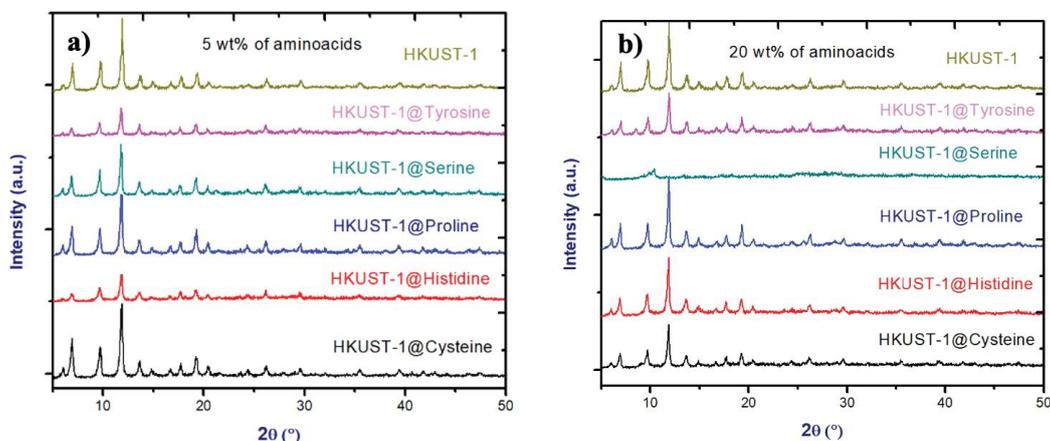

Fig. 1. X-ray diffraction pattern of pristine HKUST-1.

Fig. 2. Powder X-ray diffraction patterns were obtained for samples of HKUST-1 functionalized with (a) 5 wt.% and (b) 20 wt.% of amino acids.

serine, which could only dissolve correctly for post-synthesis functionalization with 5% by weight.

Table 2 shows the crystallographic parameters (lattice parameter and crystal size) calculated for the MOF functionalized with each amino acid. The crystal size (D) of the materials obtained corresponds to nanometer-scale materials between 30–33 nm. It was possible to observe "D" increased with the number of amino acids used for all the samples obtained, with the crystals of the samples functionalized with 20 wt.% larger. This result indicates that the amino acids generate interactions between the particles, which produces an association and an increase in the size of the crystals.

In addition, an average lattice parameter of 26 Å was obtained for the functionalized samples; in the case of the 5% samples, this increased by about 0.1 Å, and for the 20% samples, in the case of histidine, it increased by 0.04 Å and for cysteine by 0.13 Å. This could be attributed mainly to incorporating amino acids into the HKUST-1 structure.

The amino acid molecules could adsorb in the pores and on the surface of the MOF crystals. They could also incorporate into the structure because no additional evidence of other crystalline or amorphous materials was observed. This could have occurred due to physical incorporation/substitution of the solvent molecules or even by molecular substitution at the copper coordination sites causing a displacement associated with a change in the lattice parameter.

Using these calculations, it was possible to demonstrate that the structure of HKUST-1 has slight variations in the functionalized samples where the structure is maintained, which could modify the fluoride adsorption capacity. For HKUST-1, functionalized with 20% serine, the data are not presented because, as mentioned above, it was impossible to obtain the material in this composition.

Fig. 3 shows the micrographs obtained (x1,000 magnification); according to the histograms performed, the particle size distribution has an average size between 4.5 and 5.9 μm, which are attached to some larger particles. In the images obtained, the classical morphology of HKUST-1 corresponding to octahedral particles was not observed, it was noted that particles with varied shapes form the material. Table 3 shows the data obtained for the average sizes for each sample functionalized with 20% by weight.

Fig. 4 presents the micrographs obtained for the same samples with 20% by weight of amino acids at higher magnification (x20,000). For the samples functionalized with histidine, tyrosine, and serine, some needle-shaped crystals different from the HKUST-1 matrix were observed. The formation of rod-like structures or microstructural changes is due to the chemical interactions generated by the functional groups added in the functionalization. As with the band shift in FTIR, the research group observed this microstructural effect when dyes are adsorbed [16]. The following is an example of a microstructural effect observed by the research group in the past.

Fig. 5 shows the FTIR spectra obtained for pristine HKUST-1 and the FTIR spectra obtained for the amino acid functionalized samples with 5 wt.% (Fig. 5a) and 20 wt.% (Fig. 5b) of amino acids, respectively. It was possible to determine that the bands related to the (–OH) vibrations around 3,250 cm^{-1} correspond to the water or ethanol molecules in the MOFs. The characteristic bands of the HKUST-1 crystals are mainly in the range of 500–1,800 cm^{-1}. One can observe that the distinctive band at 1,370 cm^{-1} is related to the C–O of BTC, and the bands at 1,448 and 1,549 cm^{-1} were assigned to the C=O of BTC. The band around 1,113 cm^{-1} was assigned to the stretching vibration band of the C=O and the bending vibration band of the C–H bond at 939 cm^{-1}. Also, the bond-related bands (Cu–O) are observed at approximately 750 cm^{-1}. Finally, the small band at 1,705 cm^{-1} indicates the existence of the BTC, the results agree with those reported previously [17].

Due to the presence of the amino acids in the HKUST-1 network, the bands corresponding to the organic ligand (benzene-1,3,5-tricarboxylic acid) associated with the C–O bonds at 1,370 cm^{-1}, C=O 1,549 cm^{-1} and COO = 1,613 cm^{-1} present in the spectra a shift towards higher wavenumbers for all the samples functionalized with amino acids by 5% and 20% by weight, concerning the bands of pristine HKUST-1. For the other bands, no significant shift was observed. Fig. 6 shows the FTIR spectra of the samples functionalized with 20 wt.% amino acids, showing the shift of the characteristic bands of the organic binder concerning the pristine HKUST-1.

Thermogravimetric analysis (TGA) was performed to corroborate the thermal stability of the obtained MOFs. The TGA curve of the pristine HKUST-1 and the functionalized samples with 20 wt.% amino acids are presented in Fig. 7. Three main stages of weight loss were observed in the synthesized HKUST-1. First, solvent molecules (H_2O and EtOH) were removed from the MOF up to 120°C. After solvent removal, a stable plateau was observed up to 315°C. In the case of the amino acid functionalized samples, a small

Table 1
Reported pKa values of the amino acids used and basic pH obtained for each solution

Amino acid	pKa$_1$, pKa$_2$	pH at 5 wt.%	pH at 20 wt.%	Solubility (g·L^{-1})
Proline	1.99, 10.60	9	10	162
Tyrosine	2.09, 9.11	10	10	0.479
Serine	2.21, 9.15	10	12	425
Histidine	1.82, 9.17	11	10	45.6
Cysteine	1.96, 8.18	7	10	277

Table 2
Values of lattice parameter and crystal size for functionalized MOF

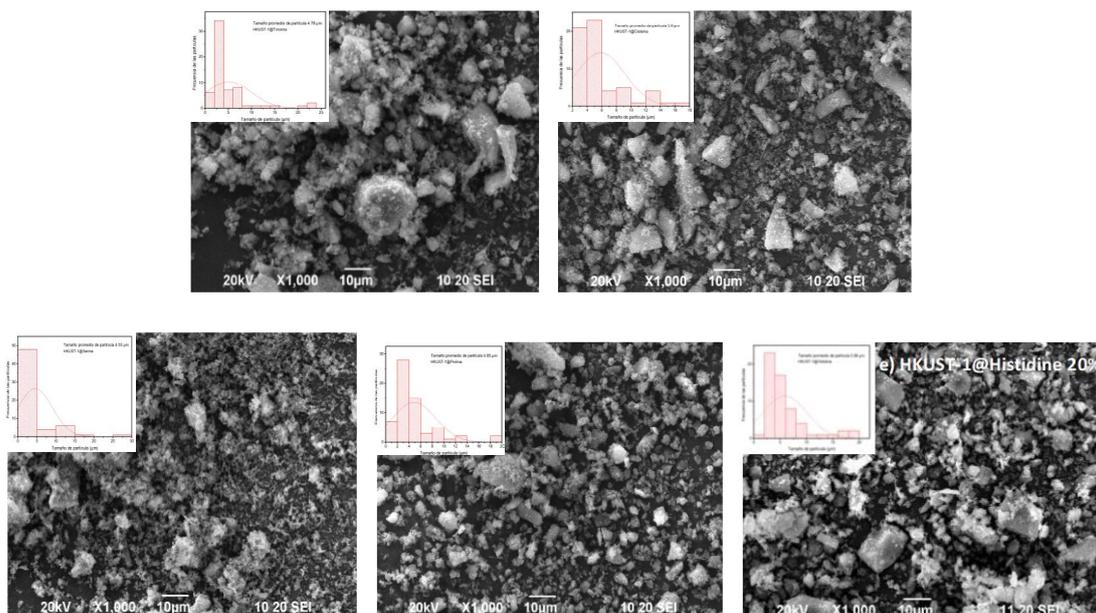| MOF amino acid functionalized	5 wt.%		20 wt.%	
	a_0 (Å)	D (nm)$_{(222)}$	a_0 (Å)	D (nm)$_{(222)}$
Proline	26.14	29.87	26.01	32.21
Tyrosine	26.14	30.75	26.08	33.09
Serine	26.17	31.20	26.17	33.07
Histidine	26.14	29.06	26.14	29.06
Cysteine	26.08	28.13	26.08	28.13

Fig. 3. Micrographs obtained (x1,000 magnification) for HKUST-1 samples functionalized with 20 wt.% of amino acids.
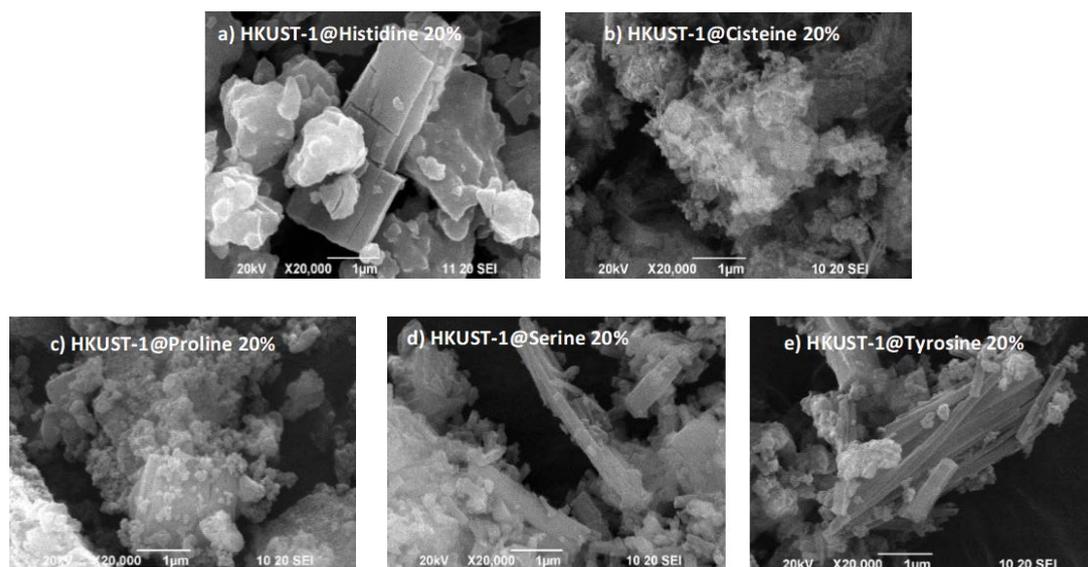

Fig. 4. Micrographs obtained (x20,000 magnification) for HKUST-1 samples functionalized with 20 wt.% of amino acids.

Table 3
Average particle size in the samples functionalized with amino acids at 20 wt.%

HKUST-1 with 20% of each amino acid	Average particle size (μm)
Cysteine	5.81
Histidine	5.88
Proline	4.85
Tyrosine	4.78
Serine	4.53

jump related to a 2° weight loss attributed to the amino acids used was also observed, confirming the interaction of the amino acids with the HKUST-1 network. After 315°C, an abrupt weight loss step was followed due to the degradation of the organic binder (benzene-1,3,5-tricarboxylic acid), resulting in the complete collapse of the pristine HKUST-1 structure. Finally, the last weight loss was attributed to the remaining CuO residue and inorganic carbon traces [18].

When comparing the thermal stability of pristine HKUST-1 with the samples functionalized with 20 wt.% amino acids, it was observed that the latter possesses much higher thermal stability than the pristine MOF,
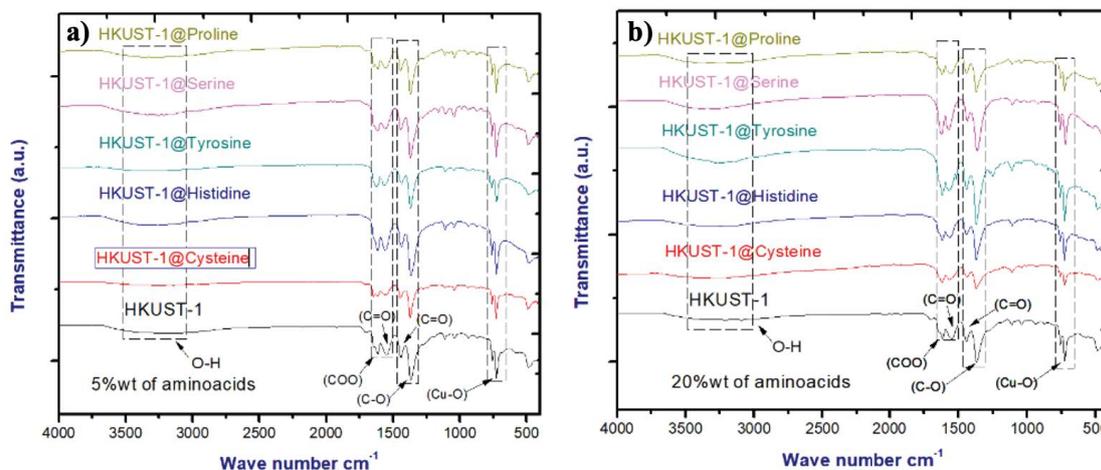
Fig. 5. Fourier-transform infrared spectra were obtained for pristine HKUST-1 and the MOFs samples functionalized with amino acids at (a) 5 wt.% and (b) 20 wt.%.
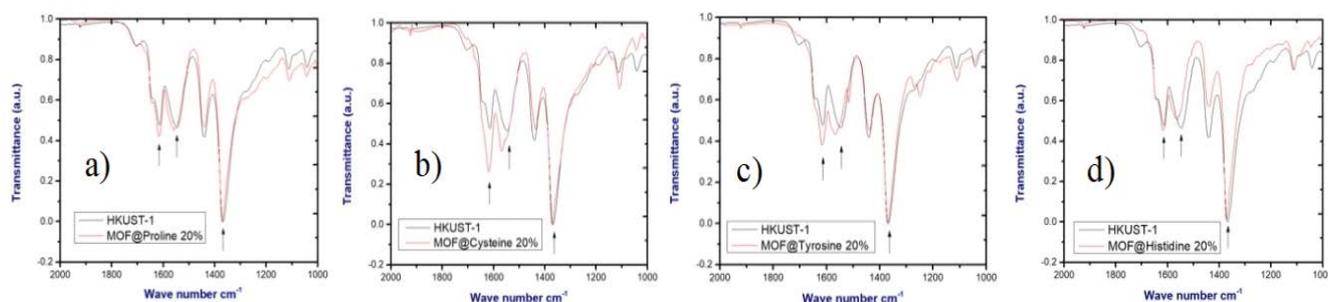

Fig. 6. Fourier-transform infrared spectra of the samples functionalized with amino acids with 20 wt.%, showing the shifts of the bands corresponding to the organic linker.
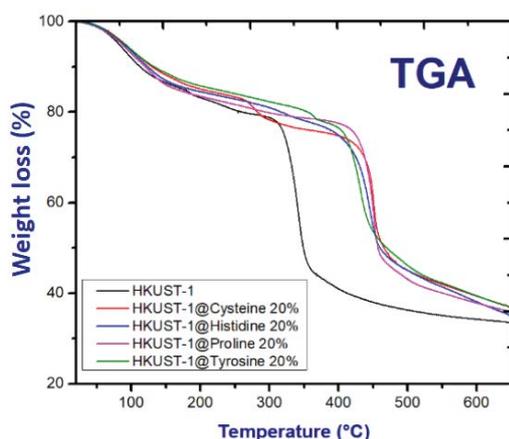

Fig. 7. Thermogravimetric analysis of HKUST-1 and materials functionalized with 20 wt.% of amino acids.

higher in the case of pristine HKUST-1, compared to the samples functionalized with amino acids. Also presented are the values of the second weight loss observed in tiny drops, only present in the functionalized samples, these losses were observed between 286°C and 380°C which are close to the degradation temperatures of the amino acids used cysteine, histidine, proline, serine, and tyrosine 260°C, 287°C, 220°C–222°C, 228°C, and 348°C, respectively.

This leads to the conclusion that the amino acids substituted some of the water molecules (present in the open metal sites of the MOF) that are responsible for the degradation of HKUST-1. Resulting in a much more hydrophobic nature of the samples functionalized with the amino acids [10]. This result agrees with what was observed in the FTIR spectra about the band located at 3,250 cm^{-1}, which was attributed to the (–OH) groups coming from the solvent molecules (H_2O or EtOH) found in the pores of the MOF structure.

3.2. Fluoride adsorption

3.2.1. Fluoride adsorption capacities

Table 5 shows the results obtained for the adsorption capacity for pristine HKUST-1 and MOF samples functionalized with amino acids at 5% and 20% by weight.

increasing its degradation temperature by up to 110°C in the case of the sample with proline. The first weight loss observed in the four samples functionalized with 20 wt.% was attributed to less water than in the matrix.

Table 4 presents the values of weight loss at 120°C, it can be observed that of these losses at this temperature were

Table 4
Weight losses and degradation temperature for HKUST-1 and samples functionalized with 20 wt.%

Sample	% weight loss at 120°C	2nd weight loss (°C)	Decomposition temperature (°C)	% of the remaining material
HKUST-1	10.95	–	320	33.41
HKUST-1@Cysteine 20%	8.85	286	446	36.60
HKUST-1@Histidine 20%	9.48	328	435	34.61
HKUST-1@Proline 20%	10.00	316	442	35.53
HKUST-1@Tyrosine 20%	8.68	380	428	36.50

Table 5
Fluoride adsorption capacities were obtained using pristine HKUST-1, and MOFs functionalized with 5 and 20 wt.% amino acids

Functionalized MOF	1° fluoride adsorption capacity (mg·g^{-1})	2° fluoride adsorption capacity (mg·g^{-1})	Total adsorption (mg·g^{-1})	% adsorption
HKUST-1	0.28	–	0.28	25.5
MOF@Cysteine 5%	0.20	0.22	0.44	40.0
MOF@Serine 5%	0.06	0.14	0.20	18.1
MOF@Tyrosine 5%	0.10	0.19	0.29	27.3
MOF@Proline 5%	0.13	0.21	0.34	31.0
MOF@Histidine 5%	0.15	0.28	0.43	39.0
MOF@Cysteine 20%	0.22	0.25	0.47	42.7
MOF@Serine 20%	0.1	0.16	0.26	23.6
MOF@Tyrosine 20%	0.15	0.23	0.38	34.5
MOF@Proline 20%	0.21	0.27	0.48	43.6
MOF@Histidine 20%	0.2	0.35	0.55	50.0

The pristine HKUST-1 removed fluoride by adsorbing 2.8 ppm without any additional functionalization. On the other hand, amino acid functionalized MOFs also managed to adsorb fluoride from the prepared solution, the adsorption was performed for the same materials used twice, exceeding the adsorption capacity of pristine HKUST-1 in most cases. The enhanced adsorption capacity of the functionalized MOF samples could be attributed to the fact that the amino acids could have van der Waals interactions because of the functional groups present in their structure and the contaminating fluoride present in the solution.

In addition, the active sites of HKUST-1, such as the copper metal center could have positively influenced fluoride adsorption. Although there is a wide variation in the size of the amino acids used (e.g., the bulkiness and length of the side chain residues, *R*) functionalization with these allowed adsorptions of between 0.20 and 0.55 mg·g^{-1}, removal of fluoride well above the amount in water allowed by international regulations. Indeed, the maximum amount of fluoride in drinking water is 1.5 mg·L^{-1}, according to World Health Organization [19]. In addition, the functionalization significantly increased the chemical and aqueous stability by conferring a hydrophobic character to the MOFs.
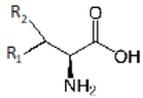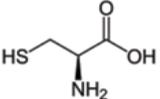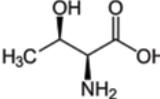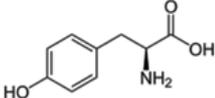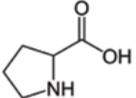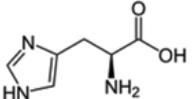
As can be seen in Table 5, the MOF functionalized with amino acids that achieved the highest adsorption of fluoride from the prepared solution were those of 5 and 20 wt.% of histidine, this could be attributed to the fact that observing their corresponding diffraction patterns the structure of the HKUST-1 network is well preserved when observing the characteristic reflections of the Cu MOF and to the amount of reactive functional groups that this amino acid possesses.

As expected, the adsorption capacity was higher when amino acids were incorporated due to the "hydrogen bridge" type bonds that could be formed between the protons bonded to the amino groups of the amino acids and the contaminating fluoride. In addition to probable van der Waals-type interactions to increase the interactions between the adsorbate and the adsorbent material, which could have been present, being strong enough to increase the fluoride adsorption capacity in the functionalized MOFs.

The trend in the fluoride adsorption capacity was cysteine > histidine > proline > tyrosine > serine for 5%, while it was observed that for 20%, the trend was: histidine > proline > cysteine > tyrosine > serine. Table 6 presents the structures of the amino acids and an analysis of the functional groups in each one. It is observed that the amino acids that have electron–donating groups have greater adsorption capacity because they generate attractive forces that make the –NH$_2$ group and the –OH group more willing to form hydrogen bonds, it is expected that the electron–donating groups interact with the metal centers which displaces the water molecules and provides greater stability to the structure of the MOF.

Table 6
Amino acid structures a molecular model including the donating groups

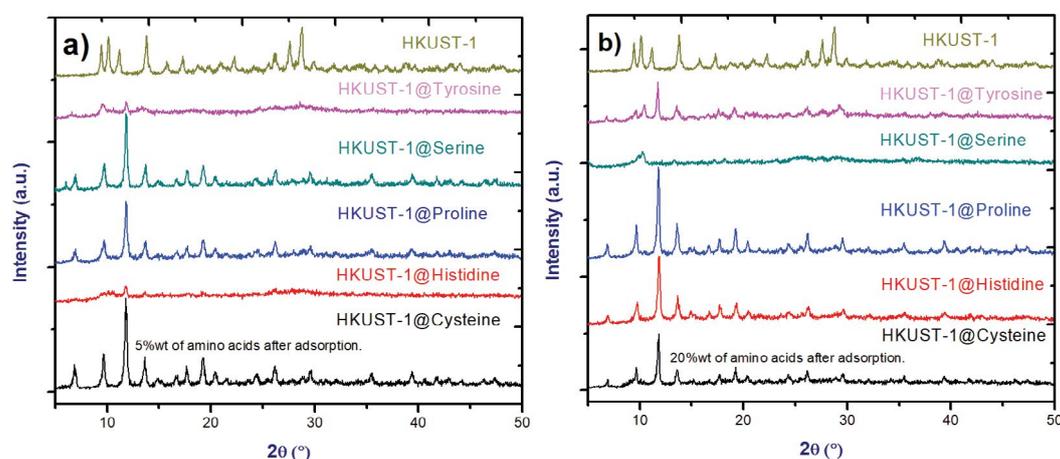| Amino acid	Structure	Molecular model
		(Except proline)
Cysteine		R_1 = HS (electron donating group) R_2 = H
Serine		R_1 = OH (electron donating group) R_2 = CH_3
Tyrosine		R_1 = (–OH electron donating group) R_2 = H
Proline		R_1 = (electron donating group) R_2 = H
Histidine		R_1 = (electron donating group) R_2 = H

Fig. 8. X-ray diffraction patterns obtained after fluoride adsorption from MOFs functionalized with amino acid at, (a) 5% and (b) 20 wt.%.

3.2.2. Evaluation of stability in aqueous media

As mentioned in the background, the applications of the HKUST-1 MOF are limited due to the instability of the 3D network in aqueous media. Due to this, the test was carried out to know if the MOFs had been made more stable by functionalization.

X-ray diffraction patterns (Fig. 8) were performed for each MOF used for fluoride adsorption in the ethanol-water solution, the results can be noticed that the pristine

HKUST-1 structure has practically collapsed due to the presence of diffraction peaks different from those reported, and in various positions in the Bragg angle.

The diffraction patterns obtained for the samples functionalized with 5% and 20% amino acids by weight are also presented. For the samples with 5% by weight of amino acids (Fig. 8a), it was observed that the samples functionalized with serine, proline, and cysteine managed to successfully preserve the HKUST-1 structure due to the presence of the characteristic MOF reflections. While for this same

composition in the case of the samples functionalized with tyrosine and histidine, they did not manage to conserve the HKUST-1 structure after adsorption with fluoride since the reflections corresponding to the MOF were not observed.

As for the samples functionalized with 20% by weight of amino acids (Fig. 8b), the samples with tyrosine, proline, histidine, and cysteine successfully managed to preserve the structure of HKUST-1 by similarly showing the characteristic diffraction peaks for the Cu MOF, confirming the change from a hydrophilic character of HKUST-1 to an entirely hydrophobic one of the functionalized samples. As can be seen in the case of the MOF functionalized with 20% tyrosine, as opposed to the one containing only 5%, this one manages to preserve in a better way the MOF network structure. Only in the case of serine, the characteristic reflections of the material were not observed, because this material was not successfully obtained from the synthesis. As mentioned in Table 1, serine has the highest pKa_1 of the amino acids studied in this work, additionally, with 20% of this amino acid, a pH of 12 is generated in the solution, which is very basic. The structure of HKUST-1 is unstable in an aqueous medium, and it has been shown that at basic pH, it also loses its structure due to the rapid nucleation of the network [20].

4. Conclusions

After the post-synthesis functionalization with the amino acids, the structure of HKUST-1 was preserved by observing the characteristic reflections of the MOF. Only in the case of functionalization using 20 wt.% of serine was this material not obtained due to the lack of solubility of this amino acid at this concentration. The obtaining of the desired materials was also corroborated by FTIR observing the bands associated with the functional groups of pristine HKUST-1.

Scanning electron microscopy allowed observing the morphology of the materials functionalized with 20% by weight of amino acids. A particle size distribution was obtained with an average size between 4.5 and 5.9 μm, these are found attached to certain particles of larger size. The functionalized samples have higher thermal stability than the pristine MOF, increasing the degradation temperature up to 110°C for the MOF with proline. As for fluoride adsorption, the contaminant was successfully eliminated from the prepared solution. For the samples with 5% by weight of amino acids, the fluoride removal varied between 0.20 and 0.43 mg·g⁻¹. In comparison, the amount of adsorbed contaminant increased for the samples with 20% of amino acids, removing between 0.22 and 0.55 mg·g⁻¹. Being the MOF with the highest adsorption capacity, the one functionalized with 20% by weight of histidine, this amino acid has the highest number of functional groups, with five groups in its structure. The effect of amino acids on the adsorption capacity of HKUST-1 is derived from the electron donor groups since these generate interactions with the metal centers, and it is possible that fluoride can interact with electro-deficient functional groups. Due to this, the amino acids histidine, proline, and cysteine are the ones that present greater adsorption of fluoride. It would then be possible to search for other molecules with electron donor groups to functionalize HKUST-1 and thereby further improve the adsorption capacity of F⁻.

Finally, using X-ray diffraction, it was also corroborated that after performing fluoride adsorption with pristine HKUST-1, its structure is practically completely lost since its characteristic diffraction peaks are no longer observed. As for the stability tests in the aqueous medium of the samples functionalized with amino acids at 5 wt.%, the MOFs that lost their structure were tyrosine and histidine, as the reflections corresponding to the framework were not observed. In the case of samples with 20% amino acids, all successfully synthesized MOFs retained their structure, indicating that increasing the amount of amino acid used improved the stability of HKUST-1 in an aqueous solution. This confirms the change from a hydrophilic character of HKUST-1 to a more hydrophobic nature of the functionalized samples.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgments

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