Elimination of Methylene Blue and Reactive Black 5 from Aqueous Solution Using HKUST-1

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Abstract—The HKUST-1 copper metal organic framework (MOF) is one of the most studied MOFs because it has high pore volume, a large surface area, high chemical stability and also the ability to bind water, among other molecules, by coordinating to the unsaturated Cu(II) sites. In this study we propose two strategies for the elimination of two dyes from aqueous solution employing HKUST-1: methylene blue, MB, (with a initial concentration of 200 ppm) and reactive black 5, RB5, (with a initial concentration of 100 ppm). The first strategy involves in-situ (IS) adsorption where MB or RB5 are added to the HKIST-1 synthesis precursors and the porous structure is formed including MB or RB5 molecules. The second strategy corresponds to post-synthesis (PS) elimination. HKUST-1 is obtained by stirring at room temperature and pretreated at 100 ℃ during 12 h. Finally, MB or RB5 was incorporated into the HKUST-1 structure by contact solution. MOFs were characterized by XDR, FTIR, TGA and UV-Vis, in order to compare both methods and for identifying the physicochemical properties of the obtained materials. XRD results corroborate that all synthesized materials correspond to the cubic HKUST-1 structure, with different reticular parameters. The UV-Vis results show that the IS adsorption of MB and RB5 in HKUST-1, produced a guest loading of 58.11 % and 82.68 %, respectively. Whereas, the PS method reached a dye loading of 93.57 % and 75.01 % for MB and RB5, respectively.

Index Terms—HKUST-1, MOF, methylene blue, reactive black 5, adsorption.

I. INTRODUCTION

Dyes are used in many industries such as in textiles, plastics, food, cosmetics, carpets, paper, pharmaceuticals, among others [1]. The contamination of water by these dyes generates important environmental problems, due to the incomplete and slow degradation of the dyes. Some degradation processes eliminate the color of wastewater but some times generate more toxic products than the initial dyes [2], [3]. For this reason, porous materials are good candidates for eliminating dyes from wastewater. Dye adsorption using porous materials is by far the most simple and effective technique owing to advantages of being a fast adsorption, high absorbent capacities, weak interaction with dye molecules, easy regeneration, the possibility of desorbing dye molecules and the low-cost of porous materials. Also, the adsorbent can be designed with specific physicochemical properties such as: well defined pore size, high surface area, high thermal stability, low-cost synthesis, nanometric particle size, among others [4]-[6].

Methylene blue (MB) and reactive black 5 (RB5) are the typical dyes (Fig. 1), and have been widely used in textile, food, cosmetic, pharmaceutical industries. MB is also employed in aquariums due to its antifungal properties [7]-[9]. These dyes have been previously adsorbed in porous materials such as: kaolinite, activated charcoal and MOF, among others. Table I summarizes the principal adsorbents used, the maximum retention percentage and the adsorption conditions [10]-[22].
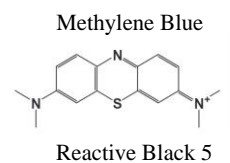
Fig. 1. Molecular structure of methylene blue (MB) and reactive black 5 (RB5).

The advanced and expensive water treatment technology cannot eliminate completely all dyes present in wastewater [3]. A recent invention of crystalline materials, formed by organic ligands and a metal center, has generated interest because of their various applications including drug retention, catalysis, guest adsorption (molecular recognition), optical applications, sensor technologies, dyes adsorption and gas storage [23]-[28]. These materials are metal organic frameworks (MOFs), they have the ability to store compounds in its porous structure or on their surface, due to the 3D structure. Both, the metal centers and the organic ligands, can be chosen depending on the field of application.

The main structural feature of HKUST-1 is a monomeric unit containing a dicopper cluster with a copper–copper distance of 2.63 A. The space group of HKUST-1 is a face centered crystal lattice with Fm-3m symmetry which possesses a 3D channel system with a bimodal pore size distribution, a cell parameter and cell volume of 26.34 A and 18.28 A^3, respectively [29]. Ever since the synthesis of HKUST-1 was reported by Chui, et al. [29] this material has been synthesized many times [30], [31]. The HKUST-1 we employed in the present study is different to others since our synthesis method is carried out stirring at room temperature, by the one-pot metathesis method [31]. A few articles about

dyes adsorption on HKUST-1 are already reported, nevertheless, to our knowledge, no papers about RB5 adsorption on HKUST-1 have been reported [12]-[14].

TABLE I: ADSORBENTS OF MB AND RB5: MAXIMUM AMOUNT AND CONDITIONS

Dye	Adsorbent	Adsorption conditions	Maximum retention percentage	Reference
MB	HKUST-1	C_0= 1.0 μmol L^{-1} to 10 μmol L^{-1}, T= 298, 308 and 318 K.	15.28 μmol g^{-1} (298 K) 11.79 μmol g^{-1} (308 K) 11.10 μmol g^{-1} (318 K)	[12]
	MOF-235	5 mg of MOF C_0= 100 ppm T=298, 308 and 318 K	187 mg g^{-1} (298 K) 230 mg g^{-1} (308 K) 252 mg g^{-1} (318 K)	[13]
	MIL-68 (Al)	C_0= 0.3 to 5 mg L^{-1}	67 mg g^{-1} (pH=7.96) 60 mg g^{-1} (pH=6.50)	[14]
	cotton stalk (CS) sulphuric acid treated CS (SCS) phosphoric acid treated CS (PCS)	T= 308 ±2 K t=120 min	25.65 mg g^{-1} (C_0=825 mg L^{-1} of CS), 646.12 mg g^{-1}(C_0=1415 mg L^{-1} of SCS), 105.38 mg g^{-1} (C_0=1415 mg L^{-1} of PSC)	[15]
	hazelnut shell	pH=4.1–4.5, SS= 200 rpm, PS= 0–75μm, C_0= 1×10^{-4} mol L^{-1},t=40min, T =303 K	ca.15 mol g^{-1}	[16]
	USM-chitin	C_0=of 50 mg L^{-1}, T= 298 K, SS= 150 rpm, t= 6 h	26.69 mg g^{-1}	[17]
	garlic peel	C_0= 25–200mg L^{-1}, pH=4–12, T=303, 313 and 323 K	82.64 mg g^{-1} (303 K), 123.45 mg g^{-1} (313 K), and 142.86 mg g^{-1} (323 K)	[18]
	bamboo-based activated carbon	T=303 K 0.2g, PS=150μm, t= 48 h	454.2 mg/g	[19]
	Graphene	C_0= 1000 mg L^{-1}, T=293 K	153.85 mg·g^{-1}	[20]
	humic acid-coated Fe$_3$O$_4$ nanoparticle	C_0= 1 mg L^{-1}, T= 298 K T=7min	0.291 mmol g^{-1}	[22]
RB5	Activated carbon (PAC) Afsin-Elbistan fly ash (AE)	C_0=50 mg/L, SS= 200 rpm.	58.823 mg g^{-1} (PAC) and 7.936 mg g^{-1} (AE)	[11]

The dyes adsorption was carried out employing two methodologies: *in-situ* (IS) adsorption, where MB and RB5 are added to the HKUST-1 synthesis, and *post-synthesis* (PS) retention. In order to determine the physicochemical properties of the synthesized MOF we report DRX, IR, TGA and nitrogen adsorption characterization. UV-Vis spectroscopy was employed to quantify the amount of dyes adsorbed.

II. EXPERIMENTAL PROCEDURE

A. Reagents and Materials

Benzene-1,3,5-tricarboxylic acid (BTC, 95% purity), copper nitrate (99.99% grade), methylene blue (3,7-bis(Dimethylamino)phenazathionium chloride, Basic Blue 9, Tetramethylthionine chloride) and reactive black 5 (Remazol Black B, >50%) were acquired from Sigma-Aldrich. Ethanol anhydrous (99% of purity, Aldrich) and deionized water were used as solvents. All the chemicals were used as received.

B. Synthesis Procedure

***In-situ* elimination**. 2.0 mmol of benzene-1,3,5-tricarboxylic acid were dissolved in 100 mL of distilled water. 50 mL of dye solution (200 and 100 ppm for MB and RB5, respectively) was added first solution. A second solution prepared with 3.0 mmol of copper nitrate in 40 mL of ethanol anhydrous was gradually added to the previous solution. The mixture was stirred at room temperature for 12 h. The resulting product was isolated by centrifugation and dried at 323 K for 2 h. Solid and liquid

obtained were stored for further characterization.

***Post-synthesis* elimination.** HKUST-1 was prepared using the reported procedure by Loera-Serna *et al*. [31] The quantity of 2.38 mmol of 1,3,5-benzenetricarboxylic acid was dissolved in 100 mL of distilled water. Then, a solution containing the quantity of 3.57 mmol of copper nitrate trihydrate and 40 mL of ethanol was added drop by drop. The synthetic mixture was stirring at room temperature during 12 h. The resulting HKUST-1 product was isolated by centrifugation and dried at 323 K for 2 h. Before adsorption, the HKUST-1 was dried overnight at 373 K and 10^{-3} Torr. The ratio of adsorbent/dye was 0.5g /50 mL (200 and 100 ppm for MB and RB5, respectively).

C. Characterization

1) Powder X-ray diffraction

The MOFs were characterized by X-ray diffraction (XRD) analysis. A powder diffractometer (Philips X'PERT PRO) coupled to a copper anode X-ray tube was used for the identification of compounds present in each sample. The Ka1 radiation (45 kV, 40 mA, k = 1.5406 Å) was selected with a diffracted beam monochromator and with a step size of 0.01" and a time per step of 0.9 s.

2) Fourier transform infrared spectroscopy

The FT–IR spectra (4000–650 cm^{-1}) were obtained with a 2 cm^{-1} resolution at room temperature on a Bruker Tensor-27 spectrometer, fitted with a DTGS detector. The samples were previously prepared as KBr mixtures and recorded via the ATR technique.

3) Thermogravimetric analyses

The experiments were preformed under N$_2$ atmosphere at a

heating rate of 5 ℃/min with a TA TGA Q500 (TA Instruments, USA). The samples were heated from room temperature to 500 ℃.

4) Nitrogen adsorption

All adsorption measurements were conducted using a BELSORP-max (BELL Japan Inc.) system at -196 ℃. Samples were degassed under dynamic conditions (extra-dry air flow) over 24 h at 100 ℃ prior to adsorption measurements. BET specific surface areas were calculated from the N_2 adsorption isotherms.

5) Ultraviolet-visible spectroscopy

Spectrophotometric analysis was performed using a Shimadzu Pharm Spec UV-VIS spectrometer.

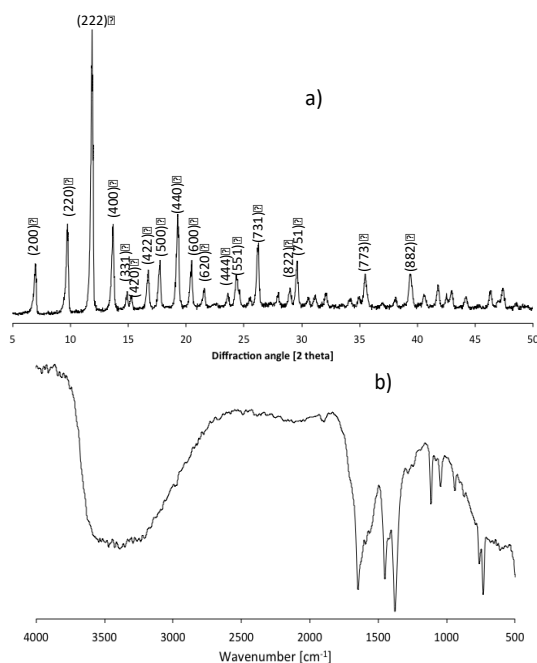## III. RESULTS AND DISCUSSION

A. The HKUST-1 Sample

Fig. 2. a) XRD and b) FTIR of HKUST-1 sample.

Diffraction peaks in Fig. 2a are readily indexed as the cubic structure of the copper metal organic framework, known as HKUST-1 or $Cu_3(BTC)_2$ [29]. The cell parameter is 26.11 Å and the crystal size of 115 nm. The FTIR spectrum of HKUST-1 (Fig. 2b) evidenced an almost isobidentate behavior of the -COO moiety since bands at 1645, 1620, 1570, 1550, 1450 and 1378 cm^{-1} are characteristic of this coordination mode. The latter due to the fact that iso- and aniso-bidentate dicopper (II) carboxylate, type of monomeric clusters are present within the HKUST-1 frame. Additionally, the thermal stability of HKUST-1 was determined by TGA, finding the structure is decomposed at 337 ℃. The HKUST-1 sample exhibited a continuous mass loss of 20.1 %, up to a temperature of 100 ℃ due to the loss of ethanol and water. After decomposition, at 336.9 ℃, 23.5 % of the starting weight remains, and this residual material could correspond to the formation of copper oxides, metallic copper or residual carbon [32]. The HKUST-1 synthesized by stirring at room temperature generates a 3D structure with BET and Langmuir specific surface area of 1345.9 and 1637.6 m^{2}g^{-1}, respectively. Such values indicate a considerably a high area for this type of MOF [31].

Fig. 3 shows the SEM micrographs of HKUST-1. The HKUST-1 particles have a well defined octahedral shape, with a homogenous particle size (2–4 μm). This morphology is characteristic of the HKUST-1 structure [33], but rarely is observed with the present synthesis conditions: stirring at room temperature.
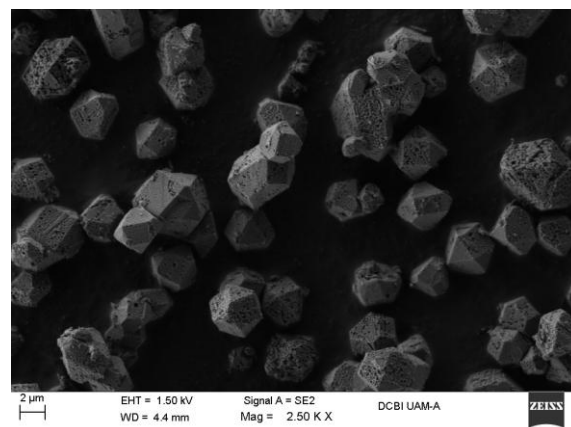

Fig. 3. SEM micrograph of HKUST-1.

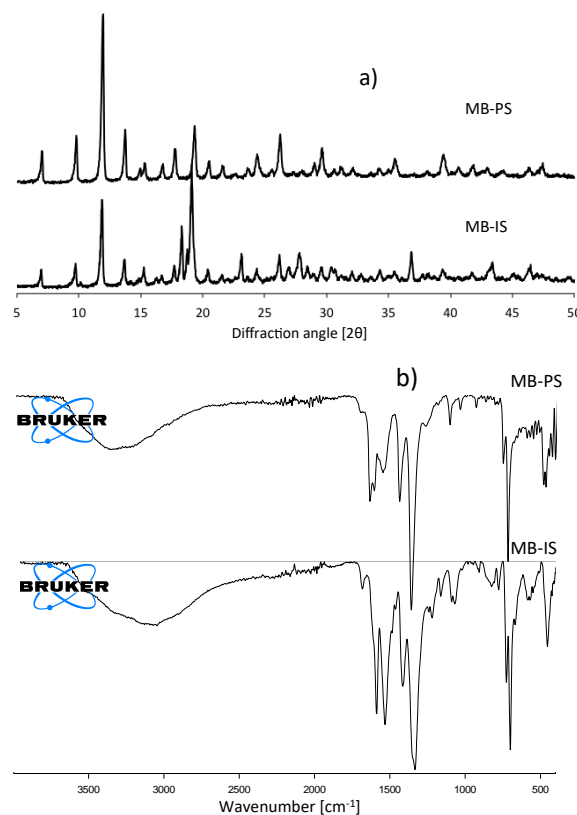### B. MB Eliminated by Adsorption on HKUST-1

Fig. 4. a) XRD and b) FTIR of MB adsorbed in HKUST-1.

Fig. 4a) presents the X-ray diffraction pattern of MB-IS and MB-PS. The diffraction peaks in both diffractograms correspond to the HKUST-1 structure. New peaks at 2θ of 18.3 and 36.8 appear in sample MB-IS, corresponding to an unidentified new crystalline compound, not present in the

HKUST-1 pattern.

When MB was incorporated onto the HKUST-1 structure by the IS procedure, the cell parameter was 26.75 A, bigger than cell parameter of pure HKUST-1 (26.11 Å), for the MB-PS the cell parameter was 26.67 Å. MB molecules can generate interactions inside the HKUST-1 cavities, responsible for increasing of cell parameter; these dye molecules can replace the solvent molecules inside the MOF structure. The crystal size determined by the Scherrer equation [34] was 64 and 97 nm for, MB-IS and MB-PS, respectively.

Fig. 4b compares the FTIR spectra of MB-IS and MB-PS. All main bands correspond to functional groups in the HKUST-1 structure. Additional bands at 1598.67, 1422.34 and 1364.67 cm^{-1}, belong to the functional groups present in the MB molecule, according to the Spectra Data Base of Organic Compounds (SDBS).

Table II compares the surface area of the pure HKUST-1 with those belonging to samples containing MB and RB5; as expected, in all samples the surface area decreased when the dye molecules were adsorbed on the MOF structure.

TABLE II: BET AND LANGMUIR SPECIFIC SURFACE AREA OF SYNTHESIZED SAMPLES

Sample	A_{BET} (m^{2}g^{-1})	$A_{Langmuir}$ (m^{2}g^{-1})
HKUST-1	1345.9	1637.6
MB-IS	945.7	1127.6
MB-PS	664.8	825.4
RB5-IS	773.5	903.2
RB5-PS	710.5	854.3

The micrographs obtained by SEM, of MB-IS and MB-PS materials are presented in Fig. 5. The morphological form of MB-IS samples is the same as HKUST-1, a well defined octahedral (2 μm). However, MB-IS particles present small pores on the surface. On the other hand, MB-PS exhibit agglomerated particles with a truncated octahedral shape of about 10 μm particle size.
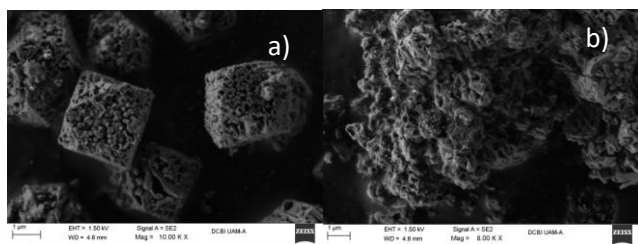

Fig. 5. SEM micrographs of a) MB-IS and MB-PS.

C. RB5 Eliminated by Adsorption on HKUST-1

Powder X-ray diffraction patterns of samples containing RB5 are compared in Fig. 6a. The diffraction peaks in all diffractograms, correspond to the HKUST-1 structure; no additional peaks are present, in an indication that the incorporation of the dye do not modify the structure of HKUST-1 or that the concentration of the dye is small enough for not being detected. The main difference after the adsorption procedure is the relative intensity of some diffraction peaks attributed to the presence of dyes molecules in some crystallographic planes. When RB5 was incorporated into the HKUST-1 structure by in-situ adsorption (RB5-IS) the resultant cell parameter was 26.11

Å, whereas RB 5 was incorporated by post-synthesis methodology (RB5-PS) and the cell parameter was 26.17 Å. The difference, ca. 1%, is relevant and beyond experimental error. The crystal size determined by the Scherrer equation [34] was 63 and 43 nm for RB5-IS and RB5-PS respectively.

Fig. 6b) compares the FTIR spectra of RB5-IS and RB5-PS. All bands belonging to HKUST-1 are present in both spectra. Additional bands at 1446.31, 1370.95 and 596.41 cm^{-1}, corresponding to the azo and sulfonate groups, are present in the RB5 sample, according to the SDBS Data Base.

The thermal stability of RB5-IS and RB5-PS was determined by TGA. Both samples show a continuous mass loss of 15.6 % and 14.8 %, respectively, up to a temperature of 100 ℃ due to the loss of ethanol and water. The thermal degradation of RB5-IS and RB5-PS occurred at 333.9 and 340.6 ℃, respectively. The residual material after the thermal decomposition of HKUST-1 was 25.45 and 29.5 % for RB5-IS and RB5-PS, respectively. These results are higher than the percentage of material remaining in the TGA of the pure HKUST-1 (23.5 %), due to the presence of the dyes molecules.
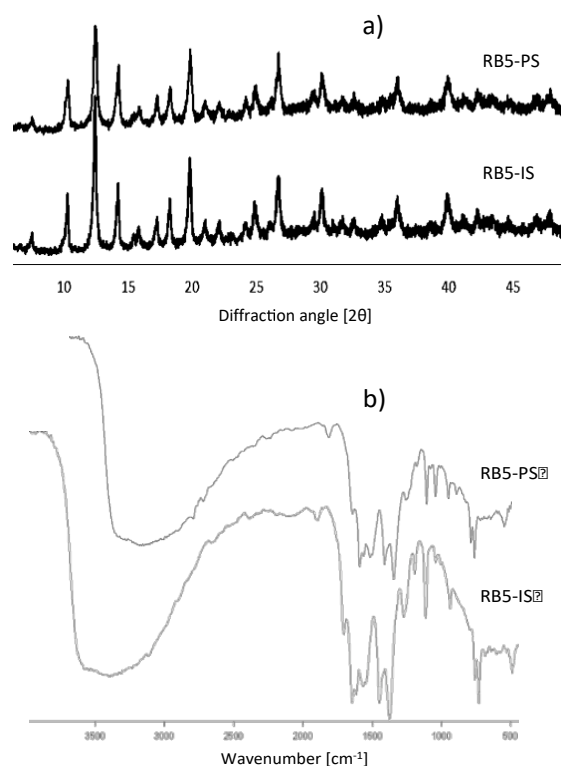

Fig. 6. a) XRD and b) FTIR of RB5 adsorbed in HKUST-1.

The BET and Langmuir specific surface area of RB5-IS and RB5-PS determined by nitrogen adsorption are presented in Table II. As mentioned before, the HKUST-1 surface area decreases because MB molecules can incorporate inside the pores and replace the solvent molecules. On the other hand, RB5 molecules are bigger than MB molecules, and can not access the HKUST-1 pores (9.5 or 13.3 Å size across its diagonal); these molecules interact on the surface structure via Van der Waals interactions.

SEM micrographs of RB5-IS and RB5-PS are compared in Fig. 7. Sample RB5-IS presents a well-defined octahedral shape, as the pure HKUST-1, but with small pores on the

surface. The particle size are in the same order as the pure HKUST-1, between 2 and 4 μm. On the other hand, RB5-PS exhibit agglomerated particles with a truncated octahedral shape of about 6 μm particle size and some smaller particles of around 1−2.5 μm (Fig. 7b).
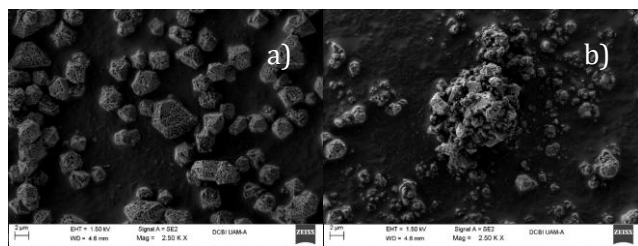

Fig. 7. SEM pictures of a) RB5-Is and b) RB5-PS.

D. Quantification of MB and RB5

The liquids from the filtrate from HKUST-1 and the MB and RB5 solutions were analyzed with UV-Vis spectroscopy. Calibration curves and the quantification of the dyes molecules were carried out using the Beer-Lambert Law; the concentration of the not adsorbed MB and RB5 was also determined (Table III).

TABLE III: PERCENTAGES OF MB AND RB5 RETAINED IN HKUST-1, DETERMINED BY VU-VIS

Sample	% of MB	Sample	% RB5
MB-IS	58.11	RB5-IS	82.68
MB-PS	93.57	RB5-PS	75.01

IV. CONCLUSIONS

The preparation method discussed in this work provides a HKUST-1 MOF with crystalline cubic structure and high surface area. The thermal stability of the material is above 300 ℃. Adsorption of two organic molecules, extensively used as textile dyes was conducted by two different strategies; the first adsorption strategy was during the synthesis of the HKUST-1 (is-situ adsorption) and the second one during the post-synthesis process. 58.11% of methylene blue, MB, was retained by the MOF by in-situ adsorption and 93.57 % by post-synthesis adsorption. Therefore a large proportion of the dye was effectively eliminated from the water effluent when employing the PS method because the dye molecules are able to get inside the MOF's pore suystem. 82.68% of reactive black 5, RB5, was retained by the MOF by in-situ adsorption and 75.01 % by post-synthesis adsorption. Compared to MB, a smaller amount of RB5 was retained by the MOF by the PS method, due to the larger size of the RB5 molecule that makes it more difficult to fit inside the MOF's pore system; nevertheless, the retention of RB5 achieved by the IS method, makes this procedure an attractive alternative for dye removal water treatment. Therefore, the adsorption of dyes on the HKUST-1 MOF depends on the chemical and physicochemical characteristics of the adsorptive molecule, such as the functional groups or the molecule size. A considerable percentage of molecules with even bigger size than the HKUST-1 pore size, can be adsorbed on the external surface framework.

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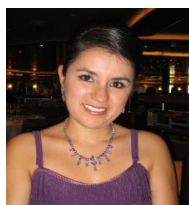
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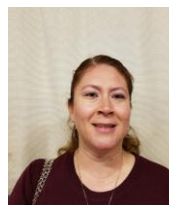
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