

Dyes Adsorption on $\text{Cu}_3(\text{BTC})_2$ Metal-Organic Framework

S. Loera-Serna*, J. Garcia-Ortiz*, and E. Ortiz*

*Departamento de Ciencias Básicas, DCBI, Universidad Autónoma Metropolitana Azcapotzalco, Av. San Pablo 180, Col. Reynosa Tamaulipas, Azcapotzalco, Ciudad de México, 02200, Mexico, sls@azc.aum.mx

ABSTRACT

The typical highly porous metal organic framework (MOF) based on copper benzenetricarboxylate ($\text{Cu}_3(\text{BTC})_2$) was used for the adsorptive removal of basic fuchsin (BF), crystal violet (CV) and eriochrome black T (EBT). Physicochemical characterization was carried out by XRD, FTIR, SEM and TGA. UV-Vis was used to determine the concentration of dye adsorbed into the MOF framework. The adsorption process was evaluated by two methodologies: post-synthesis process and one-step synthesis.

The results suggest that the adsorption of BF on the MOF in the post-synthesis process was 99.42%, while in the one-step synthesis, when BF is incorporated in the organic solution, was 91.47 %, and when BF is incorporated in the metallic solution was 96.54%. CV adsorption amount was 96.30%, for post-synthesis and 97.61 and 98.12% for the organic solution and metallic solution, respectively. The EBT dye adsorbed was 86.93%, 95.92% and 94.44% for post-synthesis, organic solution and metallic solution, respectively. Based on this study, MOFs can be suggested as potential adsorbents to remove BF, CV and EBT dyes because of their high porosity and facile synthesis.

Keywords: metal organic-frameworks, fuchsin basic, violet crystal, eriocromo black T, adsorption.

1 INTRODUCTION

The textile industry is the largest consumer of synthetic dyes, generating a considerable amount of colored waste water. Some common dyes employed by this industry are azo, anthraquinone, triphenylmethane aniline and flavonoids [1]. Organic compounds with fluorescent chromophore groups imparting color water are usually poorly biodegradable and highly resistant to conventional water treatment processes. The release of these dyes is a serious environmental problem and a concern for public health. In particular, discharges of these effluents into the environment is undesirable not only because of the color imparting water, but also because some dyes and their degradation products are toxic, mutagenic and carcinogenic [1, 2].

The degradation of dye molecules is a complex process as they are very stable to light and oxidation [3]. Some physicochemical processes that are commonly employed for the removal of various types of dyes are coagulation and precipitation; reverse osmosis and ultrafiltration, as well as

treatment by electrolysis, ozone, chlorination and adsorption [4, 5]. The use of such methods is restricted due to its high cost and environmental impact. Regarding the proposed process, removal of dyes by adsorption technologies represents a competitive alternative as they do not need a high operation temperature, the adsorbent can be reused, and several coloring materials can be removed simultaneously.

Another possible alternative to improve efficiency and reduce costs is the use of porous metal organic frameworks (MOFs) for the retention of dyes. The MOFs are chemical compounds consisting of metal ions coordinated to organic linker, highly porous to guest molecules, with an adsorption capacity that is greater than zeolite and carbon activated. MOFs are especially interesting in the field of adsorption, separation, and storage of gases and vapors [6-10]. One of the most cited MOF is $\text{Cu}_3(\text{BTC})_2$ (copper 1,3,5-benzenetricarboxylate).

Basic fuchsin (BF), crystal violet (CV), and eriochrome black T (EBT) are well-known dyes widely used in textile, printing, paper, food, and pharmaceutical industries, as well as in research laboratories. Several adsorbents, including modified activated carbon, metallic nanoparticles, nanocomposites, silica, activated and charcoal, have been studied for the removal of BF, CV and EBT dyes [11-17].

However, there has been few reports of the use of MOFs including $\text{Cu}_3(\text{BTC})_2$ in the removal of dye materials. This work reports, for the first time, the results of the adsorption of basic fuchsin, crystal violet and eriochrome black T using MOFs, especially the well-studied $\text{Cu}_3(\text{BTC})_2$, in order to understand the characteristics of adsorption and the further possibilities of using MOFs as adsorbents for the removal of dye materials from waste water. The adsorption process was carried out by two working methods; post-synthesis process and one-step synthesis, adding dye solution a concentration of 50 ppm. The material obtained was characterized by powder X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FT-IR), thermogravimetric analyses (TGA), scanning electron microscope (SEM) and ultraviolet-visible spectroscopy (UV-Vis).

2 EXPERIMENTAL SECTION

2.1 Materials

Benzene-1,3,5-tricarboxylic acid (BTC, 95% purity), copper nitrate (99-99% grade), basic fuchsin (>88%), crystal violet (>90%) and eriochrome® black T (ASC reagent) were purchased from Sigma-Aldrich. Anhydrous

ethanol (99% of purity, Aldrich) and deionized water were used as solvents.

2.2 Post-synthesis process

$\text{Cu}_3(\text{BTC})_2$ was prepared using the procedure reported by Loera-Serna et al. [6] BTC, 2.38 mmol, was dissolved in 150 ml of deionized water. Then, a solution containing 3.57 mmol of copper nitrate trihydrate and 40 ml of ethanol was added drop by drop. The synthetic mixture was stirred at room temperature for 12 h. The resulting $\text{Cu}_3(\text{BTC})_2$ product was isolated by centrifugation and dried at 323K for 2 h. Before adsorption, the solid was dried overnight at 373K and 10^{-3} Torr. An amount of 0.5 g of the as-synthesized dry MOF was added in 50 ml of 50 ppm dye solution and the mixture was stirred at room temperature for 1 h. The solids were separated by centrifugation and dried at 323K for 2 h.

2.3 One-step synthesis

The same procedure as in the post-synthesis process was carried out, with the difference that the dye solution (50 ppm) is added in the BTC solution (organic solution) or copper nitrate solution (metallic solution). The synthetic mixture was stirred at room temperature for 12 h. The resulting product was isolated by centrifugation and dried at 323K for 2 h. The as-obtained solids and liquid separated by centrifugation were stored for further characterization.

2.4 Characterization

Materials were characterized by X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FT-IR), thermogravimetric analyses (TGA), scanning electron microscope (SEM) and ultraviolet-visible spectroscopy (UV-Vis). XRD patterns were collected on a powder diffractometer (Philips X'PERT PRO) coupled to a copper anode X-ray tube used to identify the crystalline structure of each sample. The Cu $K\alpha$ radiation (45 kV, 40 mA, $k = 1.5406 \text{ \AA}$) was selected with a diffracted beam monochromator, with a step size of 0.01° , and a time per step of 0.9 s. The FT-IR spectra ($4000\text{--}650 \text{ cm}^{-1}$) were obtained with a resolution of 2 cm^{-1} at room temperature on a Bruker Tensor-27 spectrometer, fitted with a DTGS detector. The FT-IR spectra were recorded through the ATR technique. The TGA experiments were performed under N_2 atmosphere at a rate of $5^\circ\text{C}/\text{min}$ with a TA TGA Q500 (TA Instruments, USA). The samples were heated from room temperature to 500°C . The micrographs were acquired in a scanning electron microscope model Supra 55VP, with field emission cathode, in high vacuum. UV-Vis spectrophotometric analysis was performed using a Shimadzu Pharm Spec UV-VIS spectrometer ($200\text{--}800 \text{ nm}$).

3 RESULTS AND DISCUSSION

Figure 1 compares XRD diffraction of dyes contained samples and $\text{Cu}_3(\text{BTC})_2$. All diffractograms correspond to $\text{Cu}_3(\text{BTC})_2$ structure, additional peaks were observed in CV-M, corresponding to CV molecules. The cell parameters were 26.25, 26.20, 26.21, 26.19, 26.13, 26.17, 26.20, 26.17 and 26.19 \AA for BF-Post, BF-M, BF-O, CV-Post, CV-M, CV-O, EBT-Post, EBT-M and EBT-O, respectively. Reference sample ($\text{Cu}_3(\text{BTC})_2$) have a cell parameter of 26.68 \AA . The decrease in the cell parameter can be attributed to the replacement of solvent molecules from the dye molecules. Indeed, dye molecules can generate interactions with the pores of the MOF, which decreases the cell.

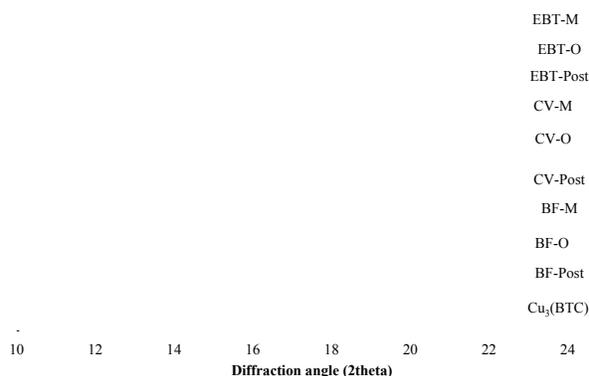


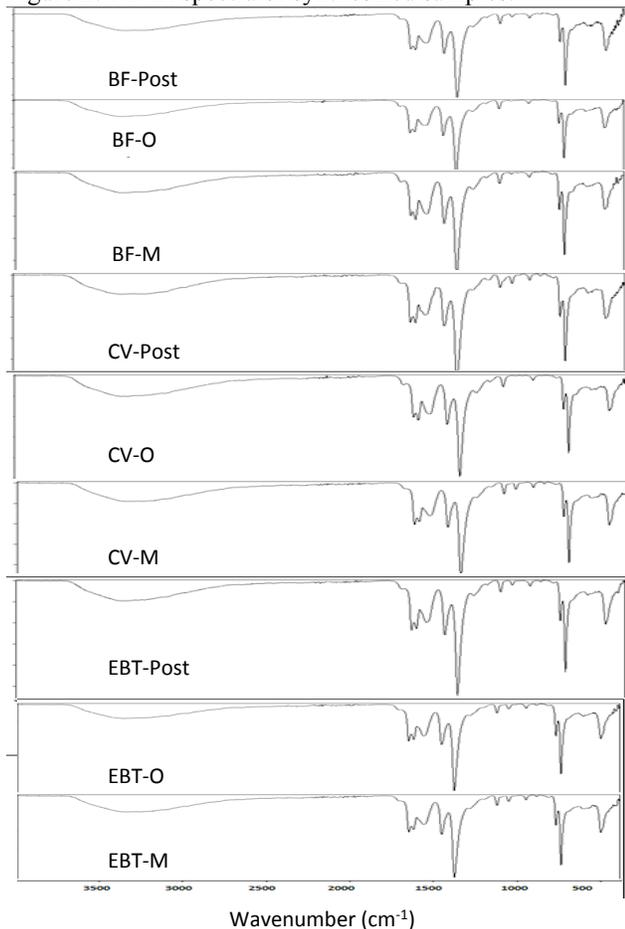
Figure 1: Diffractograms of synthesized samples.

Figure 2 shows the IR spectra of the synthesized samples. All spectra are characteristics of $\text{Cu}_3(\text{BTC})_2$ structure. Bands at $1701.51, 1643.55, 1615.06, 1548.80, 1445.21, 1371.08, 1114.48, 759.31, 728.89$ and 580.88 cm^{-1} , correspond to trisubstituted aromatic group and the band at 938.26 cm^{-1} corresponds to the carboxylate [7]. The BF-Post show presents additional bands at 1643.55 and 1615.06 cm^{-1} attributed to chloride ion and primary and secondary amine functional groups of the dye. The BF-O spectrum presents additional bands at: 1643.06 and 1615.27 cm^{-1} ; BF-M presents these bands at 1625.63 and 1643.62 cm^{-1} , corresponding to BF dye. The CV samples have bands at 1644.46 and 1614.96 cm^{-1} , corresponding to chloride ion and primary and secondary amines of the functional groups of the dye. The EBT samples exhibit bands to $1446.31, 1370.95$ and 596.41 cm^{-1} , corresponding to the covalent sulfate, nitrate, sulfonamides, sulfones, and sulfoxides, present in the EBT molecule.

Table 1 shows the results of thermogravimetric analysis, the weight loss at 100°C corresponds to the temperature at which the solvent molecules presented in the pores of the network are eliminated. MOF loss corresponds to 31.08%, being the highest value reported. This result indicates that the dye molecules replace solvent molecules within the pores of MOF, so that the weight loss at 100°C of solids containing colorant are lower.

The degradation temperature of encapsulated dye depends on the network, the BF destabilizes the structure resulting in a degradation temperature lower than the reference MOF. The solid generating CV is more thermally stable than the reference MOF, while the dye EBT generates a thermally stable solid when the dye is incorporated in the post-synthesis process, but when incorporated during synthesis processes the solids obtained stumps lower thermal stability than the reference MOF. The results can be inferred based on the interactions of dyes generated with the MOF, it could suggest that the dye CV generates a greater amount of interaction, whereas other dyes have many interactions [18].

Figure 2: FT-IR spectra of synthesized samples.



SEM micrographs of the synthesized samples are presented in Figure 3. BF-Post presents some agglomerated particles with spherical form of size c.a. to 0.5 μm and 1 micron and others without apparent shape, joint form an amorphous structure that measures approximately 16 microns long and 10 μm wide. The sample BF-O is made up of polyhedral particles with size of 2 μm , and some sheets of 1 μm . The BFM sample consisted of polyhedral particles with sizes ranging from 4 to 2 μm . Irregular particles with size less than 1 μm are present for CV-Post. Polyhedral porous particles with size of 4 and 1 μm , are

observed for CV-O and CV-M, respectively. The EBT-Post sample also presents shaped morphology with porous polyhedral particles size of 1 μm . Well-defined polyhedral particles were obtained in the EBT-O sample with size of 1-2 μm , while the EBT-M sample exhibits morphology similar to BF-M with particle size less than 1 μm . Generally, the morphology of the material do not depends on the methodology studied or the encapsulated dye. However, a larger particle size is obtained in samples where the dye is added into the organic solution (O).

Sample	Weight loss at 100 °C (%)	Degradation temperature (°C)
MOF-Ref	31.08	320.00
BF-Post	21.77	311.63
BF-O	29.97	313.56
BF-M	23.75	316.15
CV-Post	16.21	333.13
CV-O	19.61	322.16
CV-M	26.57	329.78
EBT-Post	20.08	330.01
EBT-O	24.08	309.00
EBT-M	27.44	315.93

Table 1: TGA results of synthesized samples.

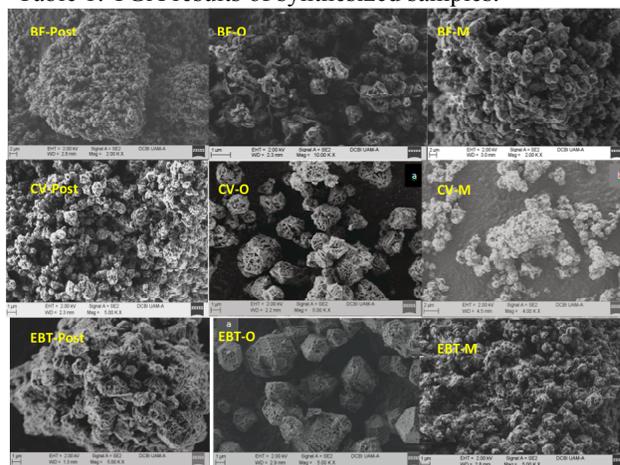


Figure 3: SEM micrographs of synthesized samples.

Table 2 presents the results of the adsorption of certain dye by UV-Vis. All dyes are absorbed into a greater than 86%. The post-synthesis methodology was the most efficient to absorb BF, this result suggests that the dye molecules can diffuse into the structure of the MOF. Additionally, some molecules can be on the surface and interact strongly with the network, increasing the dye adsorption.

Lower adsorption occurs in the post-synthesis methodology for CV and EBT dyes, is likely to steric effects are present to prevent the spread of the dyes molecules into the framework. The one-step methodology allows greater adsorption of CV and EBT on $\text{Cu}_3(\text{BTC})_2$.

Sample	Dye adsorption (%)
BF-Post	99.42
BF-O	91.47
BF-M	96.54
CV-Post	96.30
CV-O	97.61
CV-M	98.18
EBT-Post	86.93
EBT-O	95.92
EBT-M	94.44

Table 2: Amount of dye adsorption into MOF.

4 CONCLUSIONS

We synthesize the porous crystalline structure of $\text{Cu}_3(\text{BTC})_2$ MOF. The material characterization was performed to determine the physicochemical properties by XRD, IR, TGA and SEM. It managed to absorb basic fuchsin, crystal violet, and eriochrome black T dyes, using two methodologies: post-synthesis and one-step synthesis. The results indicated that percent retention of BF in the post-synthesis process was 99.42%, while in the process of one-step, when the dye is incorporated in the organic solution (BF-O), was 91.47 %, and when BF was incorporated into the metallic solution the adsorption was 96.54%. CV dye in the post-synthesis process managed to retain 96.30%, in the second approach the percentages were 97.61 and 98.12% for CV-O and CV-M, respectively. The EBT dye adsorption was 86.93, 95.92 and 94.44% for post-synthesis, organic solution, and metallic solution, respectively.

Overall, the dye adsorption amount was higher with the one-step synthesis. The difference in the percentages obtained is attributed to the interactions generated between the dye and the $\text{Cu}_3(\text{BTC})_2$, and steric effects, which prevent the diffusion of dye molecules into the structure.

This process can be implemented to remove more efficiently the dye in waste water treatment of textiles, after the coloring process of the fabric. It is noteworthy that the synthesis of $\text{Cu}_3(\text{BTC})_2$ does not need high toxicity or carcinogenic solvents, preventing any environmental problems, and does not need high temperatures and washing, which tends to increase the cost of the synthesis.

REFERENCES

- [1] G. Crini, *Bioresour. Technol.* 97 1061–1085, 2006.
- [2] A. Mittal, A. Malviya, D. Kaur, J. Mittal, L. Kurup, *J. Hazard. Mater.* 148, 229–240, 2007.
- [3] S. Chen, J. Zhang, C. Zhang, Q. Yue, Y. Li, C. Li, *Desalination* 252, 149–156, 2010.
- [4] V. Camargo, E. Ortiz, H. Solís, C. M. Cortés-Romero, S. Loera-Serna, C. J. Pérez, *J. Environmental Protection*, 5, 1342-1351, 2014.
- [5] E. Haquea, J. E. Leea, I. T. Jangb, Y. K. Hwangb, J.-S. Changb, J. Jegalc, S. H. Jhunga, *Journal of Hazardous Materials* 181, 535–542, 2010.
- [6] S. Loera-Serna, L. López- Núñez, J. Flores, R. López- Simeon, H. I. Beltrán, *RSC Advances*, 3, 10962-10972, 2013.
- [7] S. Loera-Serna, M. A. Oliver-Tolentino, M. L. López-Núñez, A. Santana-Cruz, A. Guzmán-Vargas, R. Cabrera-Sierra, Hiram I. Beltrán, *J. Flores. J. Alloys and Compounds*, 540, 113-120, 2012.
- [8] S. Bourrelly, B. Moulin, A. Rivera, G. Maurin, S. Devautour-Vinot, C. Serre, T. Devic, P. Horcajada, A. Vimont, G. Clet, M. Daturi, J.-C. Lavalley, R. Denoyel, P. Llewellyn, Ge. Férey, S. Loera-Serna. *J. Am. Chem. Soc.*, 132, 9488-9498, 2010.
- [9] P. L. Llewellyn, P. Horcajada, G. Maurin, T. Devic, N. Rosenbach, S. Bourrelly, C. Serre, S. Loera-Serna, D. Vincent, Y. Filinchuk, G. Férey. *J. Am. Chem. Soc.*, 131, 13002-13008, 2009.
- [10] T. Khuong Trung, P. Trens, N. Tanchoux, S. Bourrelly, P. L. Llewellyn, S. Loera-Serna, Christian Serre, T. Loiseau, F. Fajula, G. Férey. *J. Am. Chem. Soc.*, 130, 16926-16932, 2008.
- [11] V.K. Gupta, A. Mittal, V. Gajbe, J. Mittal. *J. Colloid Inter. Science*, 319, 30-39, 2008.
- [12] B. Zargar, H. Parham, A. Hatamie. *Talanta*, 77, 1328-1331, 2009.
- [13] L. Huang, J. Kong, W. Wang, C. Zhang, S. Niuc, B.Y. Gao. *Desalination*, 286, 268-276, 2012.
- [14] A. Mittal, J. Mittal, A. Malviya, D. Kaur, V.K. Gupt. *J. Colloid Inter. Science*, 343,463-473, 2010.
- [15] S. Senthilkumaar, P. Kalaamani, C.V. Subburaam. *J. Hazardous Mater.* 136, 800-808, 2006.
- [16] M. D. G. de Luna, E. D. Flores, D. A. D. Genuino, C. M. Futralan, M.-W. Wanc. *J. Taiwan Institute Chem. Eng.*, 44, 646-653, 2013.
- [17] M. J. Iqbal, M. N. Ashiq. *J. Hazardous Mater.* 139, 57-66, 2007.
- [18] M. Tong, D. Liu, Q. Yang, S. Devautour-Vinot, G. Maurin, C. Zhonga. *J. Mater. Chem. A*, 1, 8534-8537, 2013.