

Adsorption of Phenol and 4-Hydroxybenzoic Acid onto Functional Materials

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Abstract—The objective of this study was to investigate the removal of two organic pollutants; 4-hydroxybenzoic acid (p-hydroxybenzoic acid) and phenol from synthetic wastewater by the adsorption on mesoporous materials. In this context, the aim of this work is to study the adsorption of organic compounds phenol and 4AHB on MCM-41 and FSM-16 non-grafted (NG) and other grafted (G) by trimethylchlorosilane (TMCS). The results of phenol and 4AHB adsorption in aqueous solution show that the adsorption capacity tends to increase after grafting in relation to the increase in hydrophobicity. The materials are distinguished by a higher adsorption capacity to the other NG materials. The difference in the phenol is 14.43% (MCM-41), 14.55% (FSM-16), and 16.72% (MCM-41), 13.57% (FSM-16) in the 4AHB. Our adsorption results show that the grafted materials by TMCS are good adsorbent at 25 °C.

Keywords—MCM-41, FSM-16, TMCS, phenol, 4AHB.

I. INTRODUCTION

ENVIRONMENTAL pollution control has been a concerned issue in many countries. The most concerned environmental pollution is air pollution and wastewater pollution. Air pollution usually comes from open burning, especially the forest and vehicles combustion, while wastewater pollution comes from the industrial effluent and also from the domestic sewage.

The clay has improved the adsorption of organic substances in aqueous solutions because of its lower cost and greater adsorption capacity [1].

Coal has a high adsorption capacity for organic pollutants because of a large specific surface, a good pore size distribution, and a high mechanical strength [2]. It also has the advantage of being burned or regenerated by pyrolysis. Adsorption is an effective way to treat wastewater containing small amounts of phenol. For the reasons of cost of activated carbon, this technique cannot be used to treat wastewater or industrial effluent containing high concentrations of phenol [3].

The adsorption of organic compounds on silicic materials was considered by many researchers [4]. The porous silicic materials such as zeolite and mesoporous materials are widespread in the adsorption of organic pollutants.

II. PREPARATION OF SAMPLES

The MCM-41 type material is synthesized according to the following stoichiometric composition: 1 SiO₂; 0.6 CTABr; 0.5

TEAOH; 3.9 H₂O [5]. This material is formed by a type of colloidal silica solution condensation (Ludox 40%) around organic surface-active compounds cetyltrimethylammonium bromide CH₃ (CH₂)₁₅N (CH₃)₃Br (CTABr 98.5%) which is then removed to liberate the porosity of this material.

The type of material or FSM (FoldSheetMaterials) is a material whose structure is hexagonal resembling that of MCM-41. It was synthesized from kanemite as silica source for the first time by a Japanese group [6]. The kanemite was prepared by dissolving in water a source of silica (sodium silicate) with stirring for few hours. Then, the mixture is brought in an oven at 100 °C until the water evaporates. Then, it is calcined at 700 °C for 6h.

The kanemite obtained will be crushed and mixed with a quantity of water with stirring for several hours. The filtrate was filtered and placed in a cetyltrimethylammonium chloride solution (CTACl) under reflux for 3h at 70 °C. The mixture was heated under reflux for 3h in a solution of pH 8.5 by 2M HCl solution. The FSM-16 obtained is dried at 100 °C.

Finally, the materials MCM-41 and FSM-2 16 are calcined at 550 °C for 12h to release the porosity.

III. GRAFTING OF TRIMETHYLCHLOROSILANE (TMCS) BY POST-SYNTHESIS

After the synthesis of materials, we adopted the silylation with TMCS and covalently attached to the silanol group of the surface of the material [7]. Thermal pretreatment of 2 g of material at a temperature of 723 K for 3h allows especially removing a portion of water that is bound by hydrogen bonding to the surface silanol group.

The silylation reaction is carried out by stirring the materials with a silicic TMCS solution in toluene (1 g: 50 ml) at 343 K for 3h. After this reaction, the material is rinsed with two solvents, acetone and toluene, to eliminate all products that exist on the surface and were not grafted. Finally, the material is dried at 323 K.

IV. PHYSICOCHEMICAL CHARACTERIZATION

Organic - inorganic hybrid materials prepared under this study are characterized in great detail. For this, a combination of physicochemical techniques and complementary spectroscopic is used. The X-ray diffraction (XRD) provides information on the mesostructure, infrared characterization is used to confirm the grafting of the organic function on the material surface, and the nitrogen adsorption at 77 K (BET) informs us about the parameters of solid texture.

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A. Characterization by X-Ray Powder

The XRD on powders at room temperature is generally intended to identify the crystal phases, evaluate the crystallinity of samples, and calculate the parameters of the crystal lattice. The ordered mesoporous materials consist of amorphous silica (walls) but have a regular pore network and pore arrangement, which is 2D hexagonal (P6mm) for MCM-41 and FSM-16. Therefore, these materials can diffract X-rays, but most of the reflections are towards the small angles (2θ less than 10°).

The diffractogram of the synthesized materials are shown in Figs. 1 and 2. The peak indicates reflections that are indexed easily in a hexagonal mesh for MCM-41 and FSM-16. The diffractogram of these spectra confirms that the structure is well-ordered with the presence of a peak attributed to the reflection (100) and three weak peaks attributed to reflections (110) (200) (210).

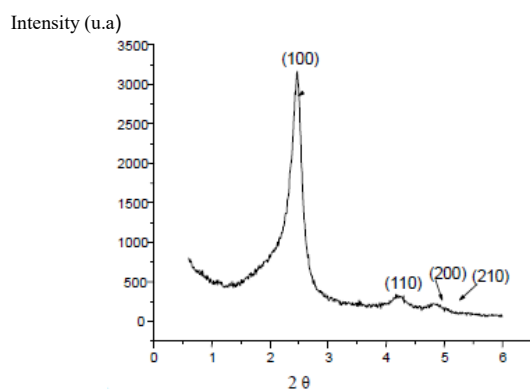


Fig. 1 RX diffractogram of MCM-41

The diffraction patterns at small angles are used to verify the 2D hexagonal pore arrangement (P6mm group symmetry) of these materials; the intensity and width of the peaks characterize the degree of order. It can be calculated from the

formula of Bragg and the geometric parameters of the distance between the mesh pores centers.

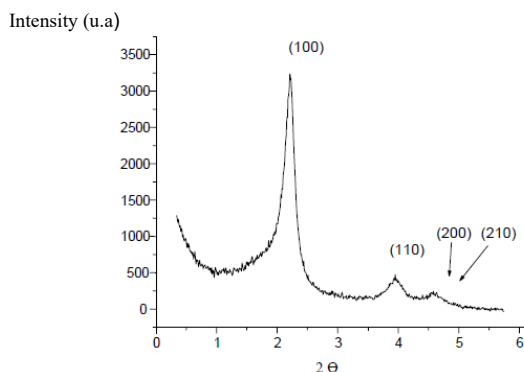


Fig. 2 RX diffractogram of FSM-16

B. Characterization by FTIR Spectroscopy

The examination of these spectra indicates the presence of the characteristic bands of the silicate network (Figs. 3 and 4). The absorption bands observed at $1500\text{--}2000\text{ cm}^{-1}$ and $3200\text{--}3800\text{ cm}^{-1}$ could be assigned to the Si-OH vibrational mode of silanol group. The bands at 468 cm^{-1} are due to the Si-O-Si bending mode.

The calcination process or the degassing, however, has the drawback of condensation of the surface silanol, and therefore a decrease in the overall density of Si-OH. The surface being partially silylated, the trimethylsilyl groups ($-\text{Si}(\text{CH}_3)_3$) grafted contribute to the overall rate of silicon. To clarify this point, we note Si-org silicon atoms contributed by the organic functions grafted. Similarly, Si-inorg designate the silicon atoms present in the inorganic matrix.

The intensity of the band at 960 cm^{-1} decreases after silylation by replacing the Si-Si inorg-org. The appearance of the C-H band between 2900 and 2960 cm^{-1} confirms the presence of the organic groups (TMCS) on the surface of the graft material (Figs. 5 and 6).

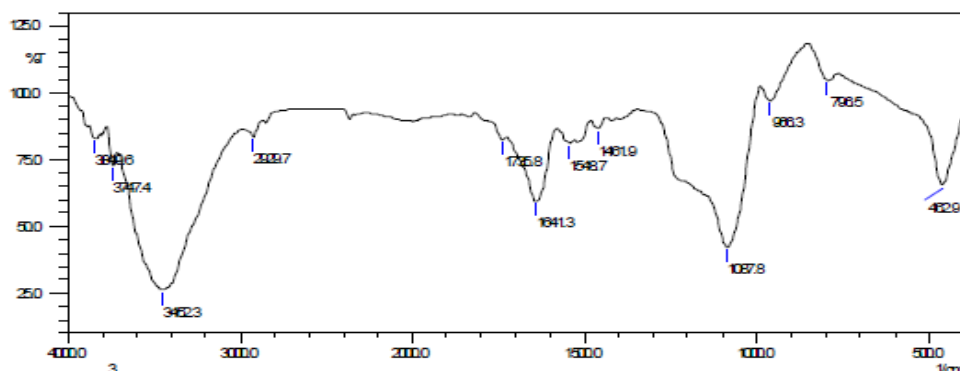


Fig. 3 FTIR spectra of MCM-41

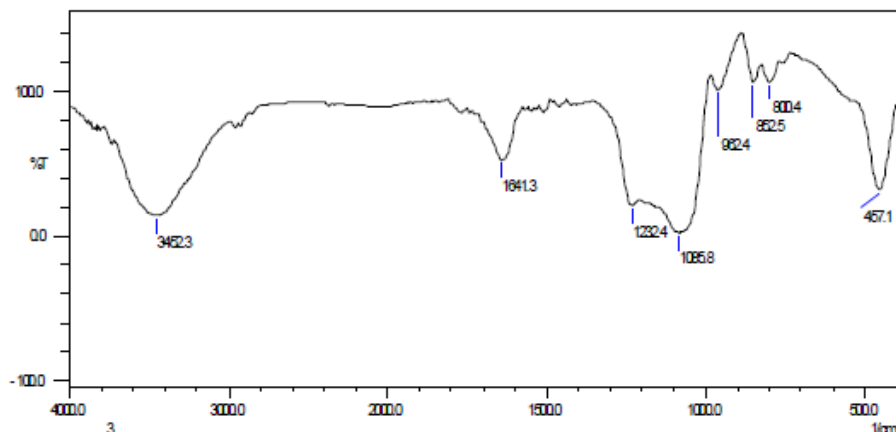


Fig. 4 FTIR spectra of FSM-16

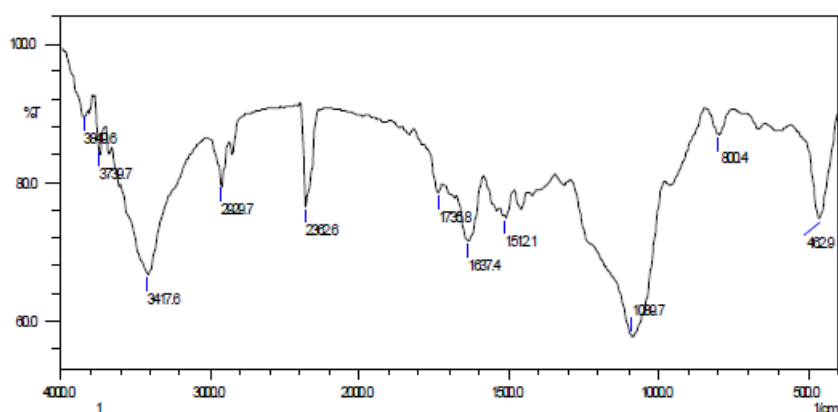


Fig. 5 FTIR spectra of MCM-41(G)

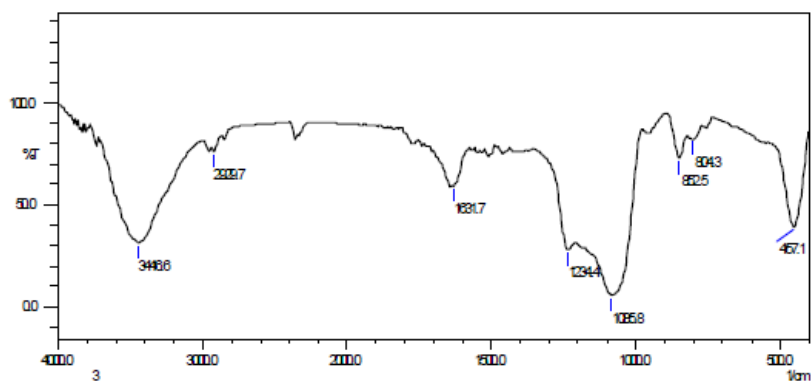


Fig. 6 FTIR spectra of FSM-16(G)

C. Characterization by Nitrogen Adsorption-Desorption at 77 K (BET Analysis)

Isothermal adsorption-desorption of nitrogen at 77 K can characterize the textural properties of the mesoporous materials, i.e. the pore size, surface area, and pore volume. The isotherms are obtained for the MCM-41 materials, and FSM-16 is the type IV according to the classification of IUPAC (Figs. 7 and 8). This includes various isothermal

partial pressure zones corresponding to the following phenomena:

For low pressures, the adsorption isotherm is reflected by the appearance of a film of liquid nitrogen to the surface of the pores to form the mono-layered. A variation of the isotherm between 0.2 and 0.4 w/p_0 indicates a capillary condensation phenomenon in the pores and a final deck with a small inclination at high relative pressures, corresponding to adsorption on the outer surface.

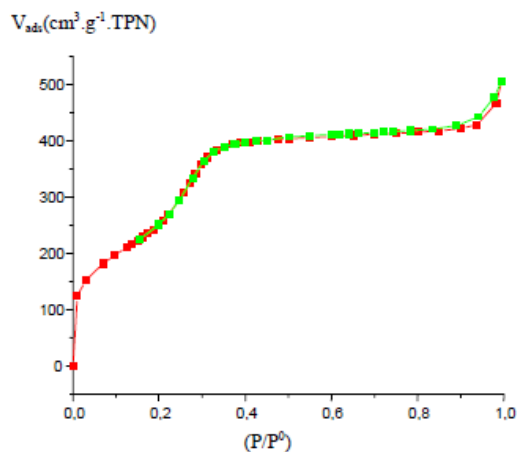


Fig. 7 Adsorption-desorption isotherms for MCM-41

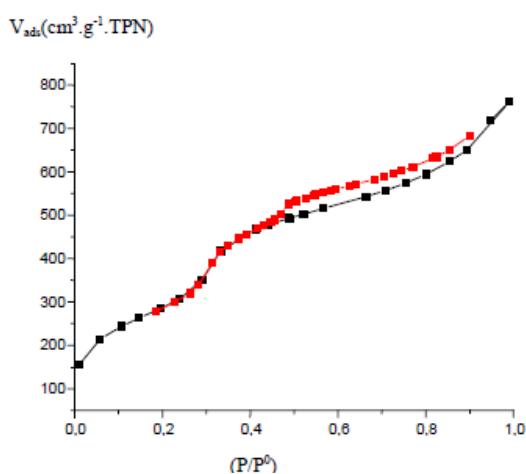


Fig. 8 Adsorption-desorption isotherms for FSM-16

The adsorption isotherm in the FSM-16 is the type (IV), but the adsorption-desorption curves are not identical in comparison with MCM-41. The nitrogen adsorption of molecules is not made to the same pressures for desorption.

TABLE I
TEXTURAL PROPERTIES OF OUR MATERIALS

| | a_0 (Å) | $S^{(BET)}$ ($m^2.g^{-1}$) | V_{meso} ($cm^3.g^{-1}$) | Dp (Å) | Ep (Å) |
|--------|-----------|------------------------------|------------------------------|--------|--------|
| MCM-41 | 32.29 | 1100 | 0.65 | 22.91 | 10.53 |
| FSM-16 | 35.54 | 1071 | 0.75 | 26.81 | 10.07 |

a_0 : lattice parameter, S (BET): surface area, V meso: volume of the pore, Dp: pore diameter, Ep: wall thickness.

The step of capillary condensation is not entirely clear and it is at low relative pressures and almost associated with the step of forming the mono-multilayer. These results are in favor of a heterogeneous distribution of pore size.

The textural properties determined after operating data on the nitrogen adsorption analysis are reported in Table I.

V. THE ADSORPTION OF PHENOL/4AHB ON MESOPOROUS MATERIALS MCM-41/MCM-41 (G) AND FSM-16/FSM-16 (G)

The reagents used are marketed by Sigma Aldrich. In Table II, some physicochemical properties of phenol 4-hydroxy benzoic acid (4AHB) are grouped.

TABLE II
PHYSICO-CHEMICAL PROPERTIES OF PHENOL 4-HYDROXY BENZOIC ACID

| | 4AHB | Phenol |
|--|-------------|-----------|
| Brute formula | $C_7H_6O_3$ | C_6H_6O |
| Molecular weight ($g.mol^{-1}$) | 138.12 | 94.11 |
| Melting point ($^{\circ}C$) | 214 | 41 |
| Solubility in water at 25 $^{\circ}C$ ($g.L^{-1}$) | 5 | 95 |

For the adsorption of phenol and 4AHB by these different materials, we followed the protocol described by Qadeer et al. [8]. Mesoporous materials MCM-41 and NG FSM16 and other graft (G) by TMCS are dried in an oven at 110 $^{\circ}C$ for 24h to remove all the water molecules. In vials, a mass $m = 0.05$ g of each material is placed with phenol solution of 0,01 L 0.014 g/l and pH between 5 and 6.

These vials are then tightly closed and placed on a horizontal plane (table) and shaken manually every 10 min for 2h and left for a total contact time of 24h after which the balance between the different phases is assumed reached.

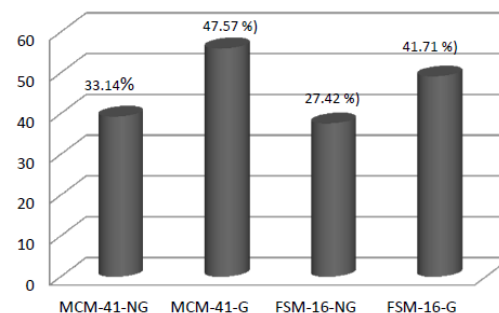


Fig. 9 Histogram of adsorption performance of phenol at room temperature

Adsorption study of phenol in aqueous solution shows that the mesoporous materials have different adsorption capacities. The comparative study of these six materials shows that MCM-41 (G) has a high adsorption rate (47.57%) for an average concentration of 0.014 (g/l). The FSM-16 (G) is the second with an adsorption rate (41.71% of). Non-silyl materials are less adsorbent materials.

The adsorption study (4AHB) in aqueous solution on the different mesoporous materials shows that they have an adsorption capacity slightly higher than adsorption of phenol. The comparative study of these documents shows that the MCM-41 (G) has a high adsorption rate (56%). The FSM-16 (G) is the second with an adsorption rate (from 49.14%). The NG materials are less adsorbent than the graft materials.

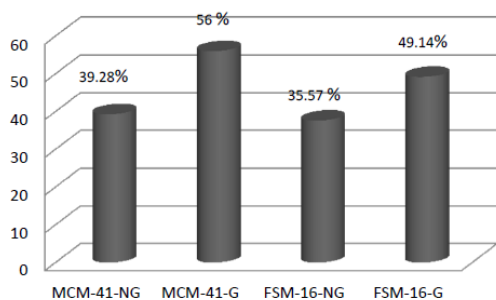


Fig. 10 Histogram of adsorption performance of 4AHB at room temperature

MCM-41 and FSM-16 is characterized by higher adsorption capacity to the other NG materials in the case of adsorption (phenol and 4AHB) especially after grafting. For MCM-41, a difference of 14.43% (phenol) and 16.72% (4AHB) and for the FSM-16 a difference of 14.29% (phenol) and 13.57% (4AHB)

The adsorption rate obtained shows that the amount adsorbed is limited by the porosity of the material. These results show both the influence of the geometric nature of the mesoporous materials of the adsorbed molecule and the hydrophobicity of the surface thereof.

The adsorption experiments of phenol and 4AHB show that the grafted materials by TMCS are good adsorbents at 25 °C.

It is worth remembering that by grafting organosilane by post-synthesis method on these materials, an assembly is obtained from an inorganic part (silica) and an organic part (TMCS) which increases the hydrophobicity of the surface, therefore its ability to adsorb organic molecules.

VI. CONCLUSION

Our results indicate that the method of graft modification of TMCS on the surfaces of these mesoporous materials enhances the activity of these materials by increasing their hydrophobicity. The adsorbent properties of the material are essentially related to the adsorption surface and the pore structure, which facilitates the diffusion of molecules and trapped in the cavities.

The adsorption of phenol and 4-hydroxy benzoic acid on different mesoporous materials MCM-41 and FSM-16 grafts or not the by TMCS, brings many data in response to the different needs of our study. The species adsorb similarly with very similar adsorption capacities, showing a slight superiority for the acid.

REFERENCES

- [1] Shu H-T., Li D., Scala A.A., Ma Y.H. Separation and Purification Technology 11, 27-36- 1997.
- [2] Perrich, J. R. "Activated carbon adsorption for wastewater treatment." (CRC press)-1981.
- [3] Banat, F. A., Al-Bashir. Environmental Pollution 107, 391-398-2000.
- [4] Jia, Q, Lua, A. C. Journal of Analytical and Applied Pyrolysis, 83, 175-179-2008.
- [5] R. Mokaya.; W. Jones, Chem .Commun, 1839-1998.
- [6] S. Inagaki, Y. Fukushima, K. Kuroda, J. Chem. Soc. Chem. Commun, 680-682-1993.

- [7] X. S. Zhao and G. Q. Lu. J. Phys. Chem. B, 102, 1556-1561-1998.
- [8] R. Qadeer, A. H. Rehan. Turk J Chem 26 .357-361-2002.