

Kinetics and Thermodynamics Adsorption of Phenolic Compounds on Organic-Inorganic Hybrid Mesoporous Material

Makhlouf Mourad, Messabih Sidi Mohamed, Bouchher Omar, Houali Farida, Benrachedi Khaled

Abstract—Mesoporous materials are very commonly used as adsorbent materials for removing phenolic compounds. However, the adsorption mechanism of these compounds is still poorly controlled. However, understanding the interactions mesoporous materials/adsorbed molecules is very important in order to optimize the processes of liquid phase adsorption. The difficulty of synthesis is to keep an orderly and cubic pore structure and achieve a homogeneous surface modification. The grafting of $\text{Si}(\text{CH}_3)_3$ was chosen, to transform hydrophilic surfaces hydrophobic surfaces. The aim of this work is to study the kinetics and thermodynamics of two volatile organic compounds VOC phenol (PhOH) and P hydroxy benzoic acid (4AHB) on a mesoporous material of type MCM-48 grafted with an organosilane of the Trimethylchlorosilane (TMCS) type, the material thus grafted or functionalized (hereinafter referred to as MCM-48-G). In a first step, the kinetic and thermodynamic study of the adsorption isotherms of each of the VOCs in mono-solution was carried out. In a second step, a similar study was carried out on a mixture of these two compounds. Kinetic models (pseudo-first order, pseudo-second order) were used to determine kinetic adsorption parameters. The thermodynamic parameters of the adsorption isotherms were determined by the adsorption models (Langmuir, Freundlich). The comparative study of adsorption of PhOH and 4AHB proved that MCM-48-G had a high adsorption capacity for PhOH and 4AHB; this may be related to the hydrophobicity created by the organic function of TMCS in MCM-48-G. The adsorption results for the two compounds using the Freundlich and Langmuir models show that the adsorption of 4AHB was higher than PhOH. The values obtained by the adsorption thermodynamics show that the adsorption interactions for our sample with the phenol and 4AHB are of a physical nature. The adsorption of our VOCs on the MCM-48 (G) is a spontaneous and exothermic process.

Keywords—Adsorption, kinetics, isotherm, mesoporous materials, TMCS, phenol, P-hydroxy benzoic acid.

I. INTRODUCTION

SINCE 1992, when they were discovered, new mesoporous materials (called MTS), comparable to zeolites (important catalysts in petrochemicals), have attracted interest from many laboratories. These materials, for the most part silicates or aluminosilicates, have a high surface area and a perfectly

controlled porosity. They are distinguished from zeolites by significantly larger pores (from 1.8 to 10 nm compared to a maximum of 1.3 nm for zeolites). These materials thus offer the possibility of enlarging large molecules heterogeneous catalysis or separation, to serve as nanoreactors, to verify physical theories such as adsorption models, quantum confinement, etc. [1]. MSTs are silicates or aluminosilicates formed by cooperatively assembling a mineral phase around an organic phase of micelles of surfactants. STDs are formed by condensing silica around organic surface-active compounds, which will then be removed to give room to pores, which may be the site of controlled chemical or physical reactions. The training process is complex. The phases obtained can be, depending on the case, lamellar, hexagonal or cubic [2]. It is also possible to graft organic functions into the pores by covalent bonding, the purpose of which is to obtain a more hydrophobic surface without changing the structure of the material and to improve the activity, selectivity, and stability in a large number of sorption catalytic reactions and processes [3]. These materials have in particular been tested for optical applications and for the absorption of volatile organic compounds. Certain organic compounds, most often aromatic of the phenol type, present in these industrial effluents cannot be treated by the conventional purification plants because their toxicity disrupts the treatment by biological route. This work is part of the first step of synthesizing and functionalizing an MCM-48 type material and testing them in an environmental application which consists in studying the competitive adsorption of these aromatic compounds, p-hydroxy benzoic acid.

II. PREPARATION OF SAMPLES

The MCM-48 is synthesized from the stoichiometric composition described by Shen et al. [4]: 1 SiO_2 ; 0.65 CTABr; 0.5 NaOH; 60 H_2O . This material is formed by condensation of tetraethylorthosilicate (TEOS) silica, around cetyltrimethylammonium bromide (CTABr), which will then be removed to give place to pores, which may be the site of chemical reactions or physical controls.

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

In order to obtain a more hydrophobic surface without changing the structure of the material, we adopted silylation with Trimethylchlorosilane (TMCS), which is thus covalently

Makhlouf Mourad is with the Laboratory of Food Technology. Faculty of engineering sciences, University of M'hamed Bougarra, Boumerdès, Algeria and Military Academy of Cherchell, Tipaza, Algeria (e-mail: makhlouf.amia@gmail.com).

Messabih Sidi Mohamed, Bouchher Omar and Benrachedi Khaled are with the Laboratory of Food Technology, Faculty of Engineering Sciences, University of M'hamed Bougarra, Boumerdès, Algeria.

Houali Farida is with the Military Academy of Cherchell. Tipaza, Algeria.

attached to the silanol group of the surface of the material (Fig. 1). The silylation reaction is given above:

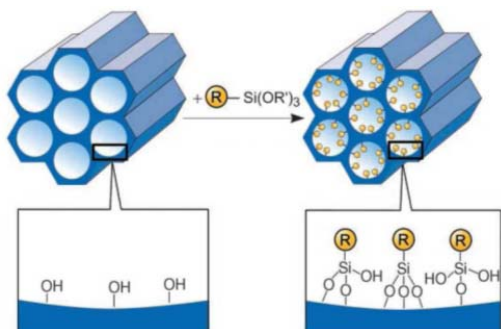
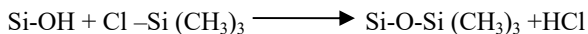


Fig. 1 Post-synthetic grafting of organo-silicic functional [groups 5]

For the grafting of our material, we have followed the silylation protocol described by Zhao et al. [5] which consists of the following steps:

After synthesizing the material, 2 g of material is pretreated for 3 h. This pretreatment makes it possible above all to remove part of the water which is bounded by hydrogen bonding to the surface silanol groups. This is possible only under the condition of the choice of the so-called optimum temperature of dehydration 723 K.

The silylation reaction is carried out by stirring the silicic materials with a solution of TMCS in toluene (1g: 50ml) at 343 K for 3 h.

After the silylation reaction, the material obtained is rinsed with two solvents, toluene and then acetone, in order to remove all the products which exist on the surface and which have not been grafted. Finally, the powder is dried at 323 K.

IV. PHYSICOCHEMICAL CHARACTERIZATION

A. Characterization by X-Ray Powder

The diffractogram of the synthesized material is presented (Fig. 2). The appearance indicates reflections that easily indent in a three-dimensional cubic mesh of the pores (symmetry group (1a3d)). It indicates the appearance of an intense peak attributed to reflection (211) and a lower intensity peak due to reflection (220), as well as two distinct peaks of relatively low intensity corresponding to reflections (420) and (332).

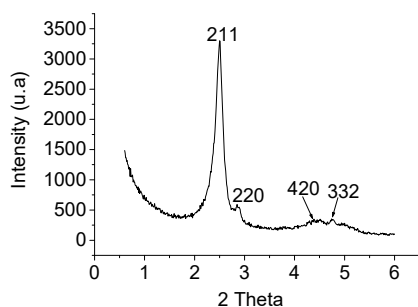


Fig. 2 RX diffractogram of MCM-48

B. Characterization by Nitrogen Adsorption at 77 K (BET Analysis)

The adsorption-desorption curve of N_2 in the MCM-48 (Fig. 3) is superimposable. The adsorption of the nitrogen molecules takes place at the same relative pressures as desorption. For low pressures, the adsorption isotherm results in the appearance of a film of liquid nitrogen at the surface of the pores to form the mono-multilayers.

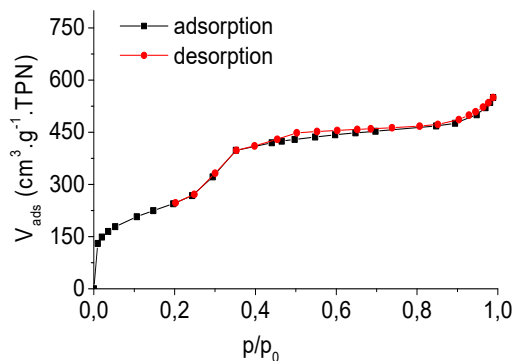


Fig. 3 Adsorption isotherms of MCM-48

	a_0 (Å)	S (BET) (m^2g^{-1})	V meso (cm^3g^{-1})	Dp (Å)	Ep (Å)
MCM-48	86.51	925	0.65	33.30	9.82

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

V. COMPETITIVE ADSORPTION OF P-HYDROXYBENZOIC-PHENOL ACID IN AQUEOUS PHASE

The first stage of our work was the adsorption of a single component (phenol or 4AHB). The remainder of this study is devoted to the adsorption of the initial binary equimolar mixture of these two phenolic compounds.

The approach adopted is the same as for the study of the constituents alone: follow-up of the adsorption dynamics of the two constituents at ambient temperature to determine the equilibrium time, establishment of the adsorption isotherms at ambient temperature.

A. Estimation of the Equilibrium Time for an Equimolar Mixture of 4-Hydroxybenzoic Acid and Phenol on MCM-48 Grafted at Room Temperature

The adsorption dynamics of phenol and 4AHB obtained in competition for an equimolar mixture show differences in amplified behavior compared to pure products. The adsorption dynamics of 4AHB-phenol equimolar mixtures and those of each adsorbate only is shown in Fig. 4.

The equilibrium is reached much more rapidly for phenol (less than 30 minutes versus 60 minutes pure phenol) than for 4AHB (more than 120 minutes). At equilibrium, there remains in solution more phenol than 4AHB (0.25/0.05): in competition in an equimolar mixture, the 4AHB adsorbs very preferentially.

B. Isotherms for the Adsorption of Pollutants in Equimolar Proportions

Isotherms for the adsorption of pollutants in equimolar proportions (Fig. 5), which represent the evolution of the adsorbed quantity as a function of time, make it possible to compare the adsorption isotherms of an equimolar mixture (phenol 4AHB) on grafted MCM-48. The adsorption kinetics of the two pollutants exhibit the same patterns characterized by strong adsorption of (phenol 4AHB) on MCM-48 (G) from the first minutes of contact, followed by a slow increase until reaching a state of balanced. The rapid kinetics of adsorption during the first minutes of reaction can be interpreted by the fact that, at the beginning of adsorption, the number of active sites available on the surface of the adsorbent material is much greater than that of the sites remaining after a certain time [6].

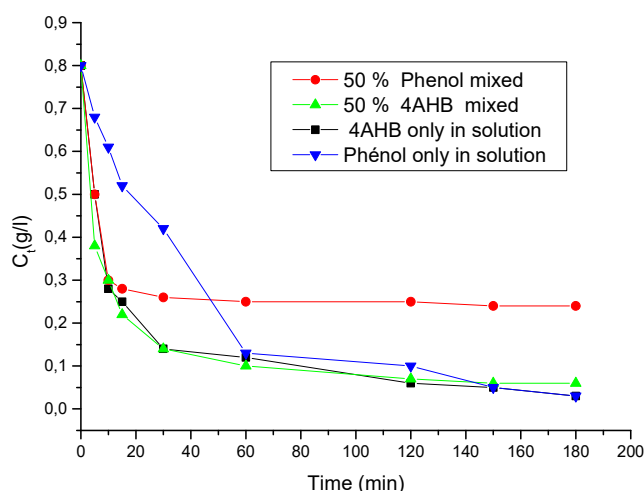


Fig. 4 Comparison of the adsorption of an equimolar 4AHB-phenol mixed with those of 4AHB and phenol, only in solution

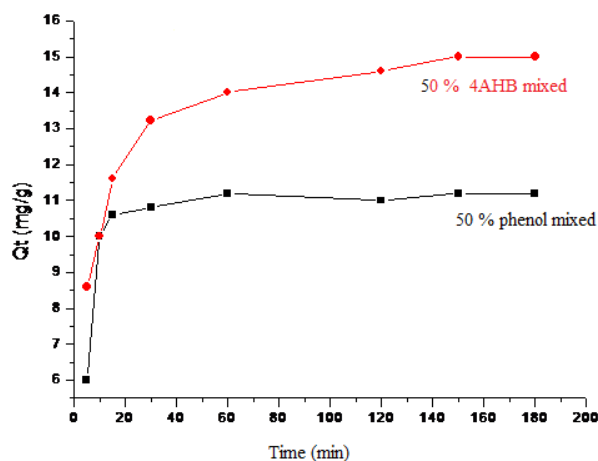


Fig. 5 Adsorption kinetics of phenol and 4AHB in an equimolar mixture ($V_{\text{solution}} = 0.01\text{L}$, $M_{\text{MCM-48 (G)}} = 0.05\text{ g}$)

Then, the higher the concentration, the more the adsorption of 4AHB takes precedence over that of phenol: the amount of adsorbed phenol decreases (almost saturated). On the same adsorption site, when phenol and 4AHB compete, 4AHB is

preferentially adsorbed. The preferential adsorption of 4AHB is mainly due to the difference in solubility of the two molecules. 4AHB is about 19 times less soluble in water than phenol. According to the literature, this phenomenon is particularly marked at high concentrations near the solubility limits of the less soluble species, 4AHB [7]. The electron-attracting character of the $-\text{COOH}$ group increases the strength of the interactions between the surface of the MCM-48 (G) and the aromatic nucleus. It is interesting to note that relatively small differences in the maximum adsorption capacities of phenol and 4AHB alone in solution do not reflect the very large difference in adsorption in competition. It is rather the parameter K_L , the adsorption constant (0.044 for 4AHB and 0.036 for phenol), which translates the affinity of a species for the adsorbent.

C. Kinetics of Adsorption of Pollutants in Equimolar Proportions

The first-order adsorption rate constant is deduced from the model established by Lagergren [8]. In order to approximate the real reaction mechanism as much as possible, Ho and McKay [9], [10] have opted instead for a kinetic model of order 2. These mathematical models were chosen on the one hand for its simplicity and d on the other hand, by its application in the field of adsorption of organic compounds on the various adsorbents.

For the first order: the rate constant k is given by the following relation: $\ln(q_e - q_t)/q_e = -Kt$

For the second order, the rate constant is given by the following relation: $t/q_t = 1/2K'q_e^2 + t/q_e$

With: q_e : Amount of equilibrium adsorbate per gram of adsorbent (mg/g), t : the contact time (min), k and K' : Adsorption speed constants respectively for the first order (min^{-1}), the pseudo second order (g min/mg).

The adsorption velocity constants of the pollutants on the MCM-48 (G) for the first and the second order pseudo are determined graphically (Figs. 6 and 7). For each pollutant, we computed the velocity constants for the first and pseudo second orders from the obtained straight lines.

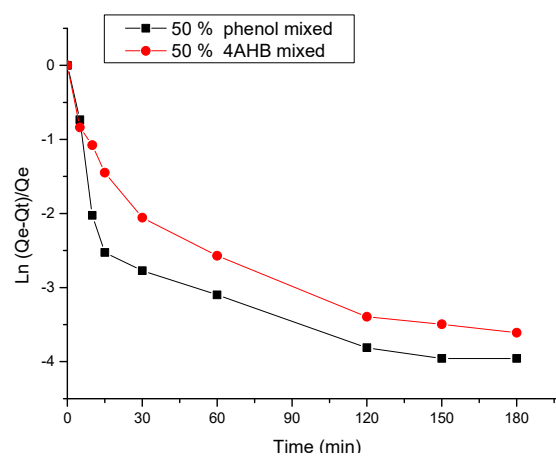


Fig. 6 Determination of the first-order rate constants of the (4AHB) phenol by the MCM-48 (G)

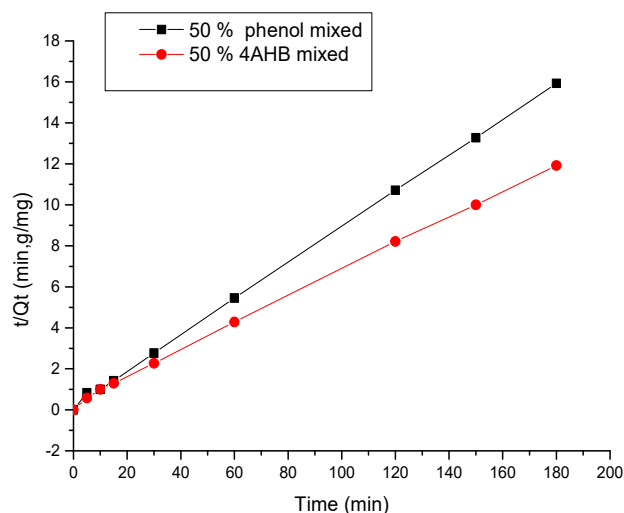


Fig. 7 Determination of velocity constants of the pseudo-second order of adsorption of (phenol 4AHB) by MCM-48 (G)

first order rate constants		pseudo-second order rate constants		
K (min ⁻¹)	R ²	K' (min ⁻¹ .g/mg)	R ²	Qe (mg/g)
1.469	0.408	0.02	0.998	12.5

first order rate constants		pseudo-second order rate constants		
K (min ⁻¹)	R ²	K' (min ⁻¹ .g/mg)	R ²	Qe (mg/g)
0.016	0.687	0.008	0.999	15.384

From the results obtained in Tables II and III, we note that the pseudo-second order model is more suitable for determining the order of the adsorption kinetics of the two pollutants by the MCM-48 (G). Indeed, a good correlation coefficient ($R^2 = 0.998$ for phenol and $R^2 = 0.999$ for 4AHB).

The MCM-48 (G) used in this work showed a clear efficiency in the reduction of water pollution. Experiments have shown that the two pollutants studied are adsorbed on TMCS-grafted MCM-48. The adsorption kinetics of phenol and 4-hydroxybenzoic acid (4AHB) on the grafted MCM-48 are both pseudo-second order.

D.Adsorption Thermodynamics

The adsorption of the atoms of a gas or of a liquid will have the consequence of decreasing the surface energy of the material. The adsorption experiments of phenol and p-hydroxybenzoic acid were carried out under static conditions.

It is possible to determine the heat of adsorption ΔH_{ads} by: $\ln K_{ad} = -\Delta H_{ads} / RT + \ln K_0$ where K_{ad} is the equilibrium adsorption constant with $K_c = C_e / (C_i - C_e)$, R the perfect gas constant (usual value) $R = 8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$ and T is the absolute temperature.

The global variation of free energy ΔG_{ads} and adsorption entropy ΔS_{ads} resulting therefrom can be calculated according to: $\Delta G_{ads} = RT \ln K_{ads}$; $\Delta S_{ads} = (\Delta H_{ads} - \Delta G_{ads}) / T$.

The heat of adsorption Q_{ads} is defined as being the opposite

of the enthalpy variation: ΔH_{ads} soit: $Q_{ads} = -\Delta H_{ads}$
The experimental data are grouped in Table IV.

TABLE IV
EXPERIMENTAL RESULTS OF THE PHENOL AND 4AHB ADSORPTION THERMODYNAMICS

	T (K)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol K)
Phenol	298		-5.57	-21.34
	308	-11.95	-5.22	-21.78
	318		-5.15	-21.32
4AHB	298		-6.98	-29.96
	308	-15.91	-6.50	-30.55
	318		-6.39	-29.93

The adsorption rates obtained show that the adsorbed amount is limited by the porosity. These results show both the influence of the geometric nature of the mesoporous materials (cubic and hexagonal) and the hydrophobicity of the surface of the latter.

The adsorption experiments of phenol and 4AHB show that MCM-48 (G) grafted with TMCS is a good adsorbent at 25 °C.

The adsorption isotherms show that the adsorption of the two constituents increases with the increase of the concentration at equilibrium. It is worth recalling that the cubic structure facilitates the diffusion of the molecules and their trapping in the cavities. The grafting of the organosilanes by the post-synthesis method on these materials is an assembly of an inorganic part (silica) and an organic part (TMCS) which increases the hydrophobicity of this surface, hence its capacity to absorb the organic molecules.

The adsorption obeys both the Langmuir isotherms and the Freundlich isotherms. In our case, the adsorption is a non-specific adsorption characterized by a low value of adsorption heat of the order of -11.93 kJ/mol for phenol and -15.91 kJ/mol for 4AHB. The values obtained for our sample confirm that the interactions with phenol and 4AHB are physical in nature. The adsorption of our pollutants on the MCM-48 (G) is a spontaneous and exothermic process. The low adsorption heat values confirm that the interactions between these pollutants and the material are of a physical nature.

VI. CONCLUSION

The adsorption of phenol and 4-hydroxybenzoic acid on the MCM-48 mesoporous material grafted by TMCS provides numerous data in response to the different needs of our study. The adsorption isotherms were obtained successively for aqueous solutions of phenol, 4AHB and phenol-4AHB mixture.

The representation of these isotherms is applicable to the Langmuir and Freundlich model with a maximum adsorption capacity.

The two species adsorb in a similar manner with very similar adsorption capacities, showing a slight superiority for the acid.

Competitive adsorption phenol-4AHB demonstrates the clear superiority of 4AHB, so that the isotherm of phenol,

obtained from an equimolecular initial mixture, passes through a fairly marked maximum at very low equilibrium concentration.

The variation of the temperature, from 298 K to 318 K, made it possible to calculate the heat of adsorption of the phenol (-11.95 kJ/mol) and 4AHB (-15.91 kJ/mol) and to confirm that the interactions with phenol and 4AHB are physical in nature.

REFERENCES

- [1] N. Coustel, F. Di Renzo, F. Faj; Chem Commun., 967 (1994)
- [2] A. Cauvel, D. Brunel, F. Di Renzo, F. Fajula; American Institute of Physics, 354, 477 (1996)
- [3] A. Cauvel, D. Brunel, F. Di Renzo, B. Fubini, E. Garrone, Langmuir, 13, 2773 (1997).
- [4] J. L. Shen, Y. C. Lee, Y. L. Liu, C. C. Yu, P. W. Cheng, C. F. Cheng, Microporous and Mesoporous Materials, 64, 135-143. (2003).
- [5] X. S. Zhao and G. Q. Lu. J. Phys. Chem. B, 102, 1556-1561. (1998).
- [6] A. R. Dincer, Y. Gunes, N. Karakaya, Journal of Hazardous Materials 141 -529. (2007).
- [7] Z. Yaneva, B. Koumanova, Journal of Colloid and Interface Science 293 -303. (2006).
- [8] S. Lagergren, S. Vetenskapsakad, Hand. Band. 24 (4) 1. (1898).
- [9] Y. S. Ho, G. Mc Kay, Water Research 34 (3) -735. (2000).
- [10] Y. S. Ho, G. Mc Kay, Process Biochemistry 34 -451. (1996).