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Amino functionalized mesoporous silica for drug adsorption

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ABSTRACT/RESUME

Abstract: *The main objective of this work was to synthesize hexagonal mesoporous materials such as MCM-41 from optimized protocols and to test their effectiveness in adsorption of different pharmaceutical pollutants. First, pore size and the specific surface area of the base materials have been modified by incorporation of amino groups in post-synthesis, by selective extraction of the loaded groups and finally by calcination. Subsequently, adsorbent products were characterized by their mesoscopic textures, structures and controls using different methods: X-Ray Diffraction (XRD), Specific Surface Area (BET), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric analyses (TGA/DTA) and Zetametry. Finally, their adsorption capacities were evaluated using several pharmaceutical residues under standard conditions (such as Diclofenac, Cefalexin ...). The results obtained during the adsorption study showed the effectiveness of these materials for the decontamination of aqueous media contaminated with pharmaceutical residues. Kinetic and adsorption isotherm studies were carried out to clarify the method of binding of the selected pharmaceutical pollutants to the tested materials.*

I .Introduction

Over the last twenty years, the chemistry of inorganic nanostructured materials has been greatly expanded with the advent of soft "sol-gel" chemistry [1]. Thus, in the early 1990s, Mobil scientists proposed the first syntheses of mesostructured silicates, ie materials with an organized porous system consisting of mesopores [2-4] Since then, many research groups have patented new families of materials with different structures, pore sizes and modes of synthesis: several methods are needed in the way of manufacturing new organized porous materials "MPO" [5].

Since, a new family of ordered mesoporous solids is widely studied by many researchers from different horizons for various applications including adsorption and catalysis. In the field of catalysis, many studies report information on different methods of synthesis, and characterization, so a wide variety of catalysts based on different mesoporous materials has been implemented and used in different types of catalysis (acidic, basic, chiral) [6].

In the field of adsorption, specifically in an aqueous medium, various mesoporous materials such as: MCM-41, MSU, SBA-15, SBA-16, have been functionalized by various groups for the adsorption of metal ions and various organic pollutants. (pharmaceutical substances) [7-13].

Pharmaceutical substances are active molecules used to induce a favorable effect on health in the animal or human organism (diagnosis, treatment of diseases, etc) [14]. Their large use is therefore at the origin of widespread contamination of aquatic environments by a variety of molecules [15]. It was reported for the first time in the United States in the 1970s following the detection of antibiotics in wastewater [16]. Ten years later, drug residues were detected in Britain. Nevertheless, it was only from

the 1990s that knowledge about this environmental contamination developed. Pharmaceuticals can be considered as persistent and harmful micropollutants because of their continuous release into the environment and sometimes their intrinsic properties (toxic, metabolic, hardly biodegradable etc) [14, 17].

Indeed, studies and analysis techniques have allowed the detection of quantities of the order of µg / l in samples of domestic wastewater and water intended for consumption [13-27]. The contamination of aquatic environments (surface water and those intended for consumption) by pharmaceutical residues has therefore been the subject of increasing studies over the past ten years [13, 15, 17, 28].

The main objective of this work is to synthesize MCM-41 hexagonal mesoporous material, to modify it by: the addition of organic groups, the selective extraction and the calcination, then to evaluate the adsorption capacity of prepared materials on different pharmaceutical pollutants. A kinetic study and that of adsorption isotherms will also be discussed.

II .Synthesis and Characterization

II.1. Materials and reagents

Cetyltrimethylammonium Bromide 99% (CTAB); Smoked Silica (SiO_2) 98%; Tetramethylammonium Hydroxide (TMAOH); Tetraethylorthosilicate 99% (TEOS); N-N, Dimethyl-dodecylamine (DMDDA) 98% ; Ethanol 96%.

II.2. Synthesis methods

MCM-41 Synthesis

The pure silica MCM-41 was prepared according to an optimized protocol [29]. The synthetic gel is initially heated to 100°C for 2 days. TMAOH and CTAB were added to the distilled water under stirring until the solution became clear. The silica source was added to the stirred solution for 2 h. The gel was transverse in a Teflon-coated autoclave, then sealed and placed in the oven at 100°C for 48 h. The product was recovered by vacuum filtration and washed several times with distilled water, then dried at 100 °C to obtain a white powder at the end, which is called "MCM-41/P" parent material.

Functionalization of materials

An amount of MCM-41/P is added to an emulsion consisting of water and NN-Dimethyl-dodecylamine (DMDDA) stirred previously for 5 min. This mixture is left under agitation for 30 min, then transferred to a Teflon reactor and placed in an oven set at 120°C for 3 days. The resulting material is filtered and washed several times with distilled water and then dried at room temperature (20°C): it is the amino material "DMDDA-41/A" [29].

Other modifications can also be made: the material MCM-41/P is calcined directly at 550°C for 7 hours, resulting in a parent/calcined material "MCM-41-P/C". Then, the selective extraction of the amine DMDDA is done using a specific solvent which is ethanol using a soxhlet gives us the deaminated material "DMDDA-41/B". And at the end, the calcination of the material A and/or B at 550°C for 7 h at a heating rate of 1°C/min gives the calcined material "DMDDA-41/C".

II.3. Characterization techniques

This characterization aims in a very detailed way, the study and identification of the textural, structural and surface properties, as well as the electrochemical properties of the surface of the materials obtained. A combination of physico-chemical (X-ray diffraction, BET, ATG/ATD and Zetametry) and spectroscopic (FTIR) techniques is performed and their understanding could allow a good exploitation of these materials for specific applications.

III .Results and discussions

III.1. Characterization

Low angle X-ray diffraction is used to demonstrate the arrangement of channels created by surfactant micelles.

Fig 1 shows the diffractograms measured from 0.5 to 6 degrees (2θ) of the materials DMDDA-41/A, DMDDA-41/B and DMDDA-41/C. These three materials are compared to MCM-41/P-C which is the base material. For each of the materials, there is a very intense main peak of about 2.2° [hkl plane (100)] followed by three other low intensity peaks. These peaks are similar and characterize a preserved and well-ordered mesoporous structure with a hexagonal symmetry of pores P6 mm [2, 4, 30].

Maximum slip (MCM-41/P-C and DMDDA-41/B) is observed at higher diffraction angles [23, 31] resulting in smaller interplanar distances as shown in Table 1.

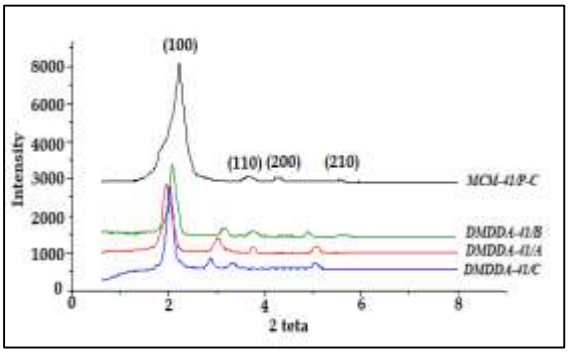

Figure 1. *Difractograms of materials (parent, amino, deaminated and calcined)*

The adsorption-desorption isotherms of the parent MCM-41 and these modified forms are illustrated in Fig 2. This is type IV according to the IUPAC classification and hysteresis H1 which is representative of structured mesopores [32- 33].

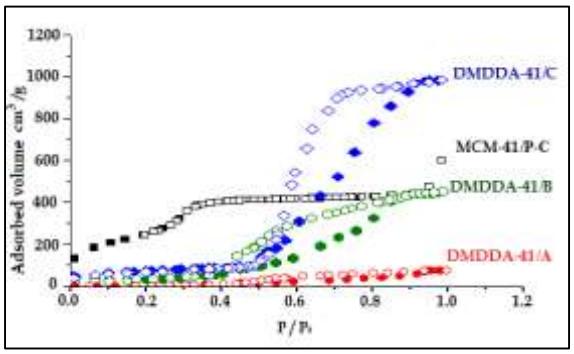

Figure 2. *Isotherm of adsorption / desorption of Si-MCM-41 materials*

For MCM-41/P-C, there is an increasing slope for low relative pressures 0 <(P/P_0)<0.3 corresponding to a single-layer filling of the surface [29, 34-35], followed by a steep slope of the curve for relative pressures between 0.3<(P/P_0)<0.8, due to capillary nitrogen condensation into mesopores. And towards (P / P0)> 0.8 there is a multilayer adsorption on the surface of the base material.

For the material DMDDA-41/A, at relative pressures (P/P_0)<0.4, a single layer filling of the surface is obtained and for (P/P_0)> 0.5 a multilayer adsorption plateau appears. The same observations as for the original material are noted for DMDDA-41/B and DMDDA-41/C. For the last two, the relative low pressure plate is almost identical ((P/P_0)<0.5), but the distinction is in the slopes of the following plate: steep slope towards the calcined material (up to 1 in (P/P_0)) unlike the deaminated material (0.5 <(P/P_0)<0.8).

In the case of these two materials, the desorption does not follow the adsorption creating an H1 type hysteresis which closes abruptly at (P/P_0)= 0.5 for DMDDA-41/C and at (P/P_0)=0.4 for DMDDA-41/B, this suggests a capillary condensation phenomenon in mesopores. The width of the hysteresis increases (DMDDA-41/C) indicating that the pore size distribution is much wider in the calcined material (Fig 3) [29, 36-38].

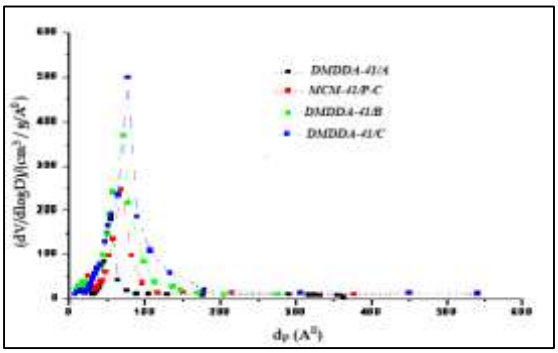

Figure 3. *Distribution of pore diameters of materials MCM-41*

The pore diameter distributions shown in Fig 3 show that the prepared materials have different pore diameters. The traces are all centered, indicating a better uniformity of pore diameter. The widening of the pore diameter distribution indicates the formation of a less homogeneous pore network.

The analysis of these data shows large differences in the parameters of the four materials. The results of pore surface area, diameter and volume decrease remarkably for amino material (the surface area and part of the pore volume are occupied by amines), unlike MCM-41/P-C. Then, the deamination increases these parameters again, while the calcination leads to higher values (see Table 1).

The FTIR spectra of the prepared MCM-41 materials are shown in Fig 4 where some vibration bands are present in the materials: they are similar to those of amorphous silica.

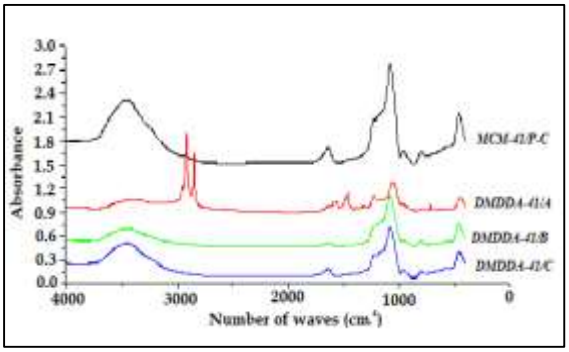

Figure 4. *IRTF Spectrum of Si-MCM-41*

The wide band between 3450 cm^{-1}, characteristic of the elongation of the bond (O-H), water and silanol groups on the surface. Another vibrating band (O-H) noted around 1650 cm^{-1} indicates the presence of water in the materials. At 1100 cm^{-1}, an asymmetric elongation junction (O-Si-O) of the tetrahedral entities SiO_4 was observed, while about 950 and 750 cm^{-1}, two bends characteristic of the asymmetric elongation of the bond (Si-O) of the same entities present. We also note the presence of

a band characterizing the deformation of the angle (O-Si-O) of the tetrahedral entities SiO_4, this around 450cm^{-1} [29, 35, 39, 40].

In addition to these bands, the amino material (DMDDA-41/A) records two new bands characteristic of the amino groups: the first located at 2900 cm^{-1} characterizes the vibrations (CN), while the second one is observed at 1480 cm^{-1} resulting from the deformation vibration of the bonds (NH) [36, 41, 42].

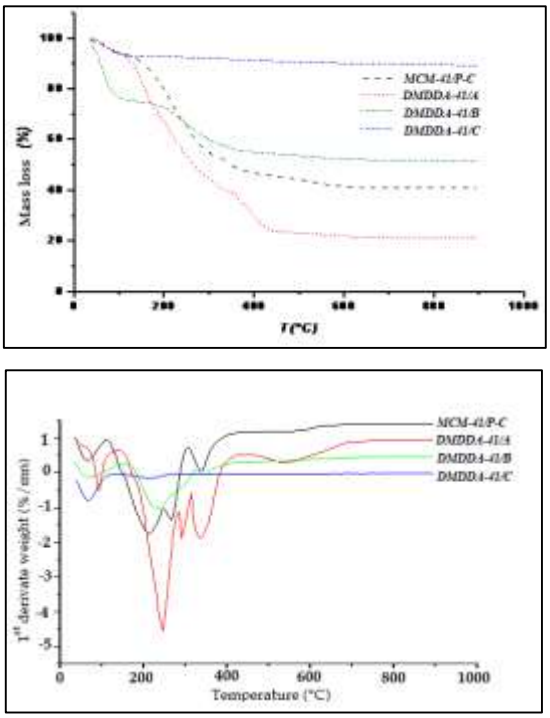

Figure 5. *Thermogravimetric Analysis A- (TGA) & Differential Thermal Analysis B-(DTA) of the different materials*

The TAG /DTA thermogravimetric analysis of all the materials is represented by two Figs 5A and 5B , from which there are three different zones of mass variation as a function of temperature [30].

The 1st zone at low temperature (25<T <160°C.) corresponds to dehydration of the water physisorbed on the surface of the material. The 2nd intermediate zone (160<T<600°C) corresponds to the decomposition and volatilization of the organic compounds (surfactants and amine) in strong interaction with the surface of the material (covalent and electrostatic bonds).

The last high temperature zone (600<T<900°C): assigned to silica dehydroxylation phenomena (condensation of the remaining silanols causing the elimination of water molecules) [3, 29, 34, 43].

Fig 6 shows the zeta potential curves ζ = f (pH) of the different MCM-41 materials in the range of pH 2 to 11. Each point ζ = f (pH) is the average of the results obtained on electrophoretic mobility measurements from 100 to 500 p at a zeta potential between 5 and 8 mV. The pH for which the zeta potential is zero (no movement of particles under the effect of the electric field) is called the isoelectric point (IPE).

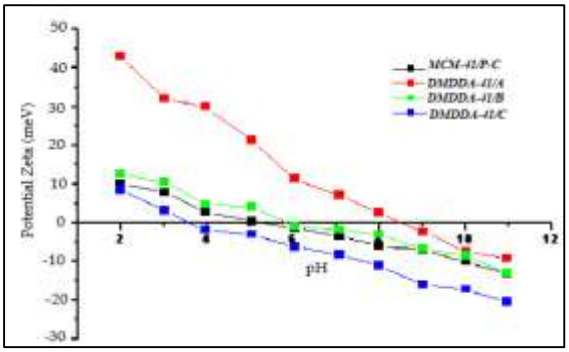

Figure 6. *Zeta potential of MCM-41 materials modified by DMDDA*

The parent material MCM-41/P has positive potentials between 2 <pH<5 and negative potentials from pH=5.5. For DMDDA-41/A, it has positive potentials between 2 <pH <8.5 and negative potentials from pH=8.5. Then, DMDDA-41/B has positive potentials between 2 <pH <6 and negative potentials from pH=6.1. And for the calcined material DMDDA-41/C, it has positive potentials between 2 <pH <3.6 and negative potentials from pH=3.6 [19, 36].

All the data from the characterization of the different prepared materials are grouped in Table 1.

Table 1. *Characterization Data of Si- MCM-41 Materials*

Materials	X-Ray diffraction			BET (at 77°K)			TGA/DTA (Mass loss %)			Zetametery
	2θ (°)	d_{100} (nm)	a_0 (nm)	S_{BET} (m^2/g)	d_P (nm)	V_p (cm^3/g)	1 st Zone	2 nd Zone	3 rd Zone	PIE (isoelectric point)
DMDDA-41/C	2.02	4.48	5.17	1246	10.6	1.86	7.02	2.76	0.87	3.6
DMDDA-41/B	2.10	4.21	4.86	387	5.84	1.07	15.67	45.97	1.63	5.8
DMDDA-41/A	1.97	4.39	5.07	74	-	0.28	3.51	70.67	3.59	8.7
MCM-41/P-C	2.28	3.87	4.47	1147	3.22	0.85	8.23	48.41	1.43	5.6

III.2. Adsorption study

Different adsorption tests were performed on three (03) active ingredients selected as pollutants for the different mesoporous materials MCM-41, calcined MCM-41, functionalized MCM-41 (DMDDA), deaminated MCM-41 and functionalized calcined MCM-41(DMDDA). Under magnetic stiring, each material is added to 20 ml of drug solution at a diluted concentration, then after filtration through a filter of 0.45 µm, the filtrates are analyzed by UV-Visible spectrophotometry to measure absorbance at λ_{max}= 236, 262 and 276 nm for Prednisolone, Cefalexin and Diclofenac respectively.

It should be noted that the functionalized and then deaminated form DMDDA-41/A has the greatest binding capacity with respect to Prednisolone and Cefalexin, followed by DMDDA-41/A (amino form) then MCM-41/P (parent form) and finally the two calcined forms of MCM-41.

In the case of Diclofenac, the amino form DMDDA-41/A has the highest adsorption affinity, followed by the deaminated material, then the parent and lastly the calcined forms. These variations are due to the physico-chemical properties of the materials in terms of specific surfaces, porosity and most importantly the surface load as a function of existing groups (the amino material DMDDA-41/A is loaded with NH_2 compared to DMDDA-41/B).

Fig 7 illustrates the kinetics study of the four pollutants selected on the DMDDA-41/B (the material that presented the maximum retention capacity). This study is necessary to predict the equilibrium time that will be taken into account for further work. According to the figure, the appearance of the curves presents two areas:

- From 0 to 50 min: zone that reveals rapid adsorption and occurs at accessible sites on the surface.
- From 50 to 120 min: the adsorbed quantities evolve more slowly, due to the diffusion inside the pores of the material, until reaching a plateau corresponding to the equilibrium at the end of 120 minutes [22, 26, 44-48].

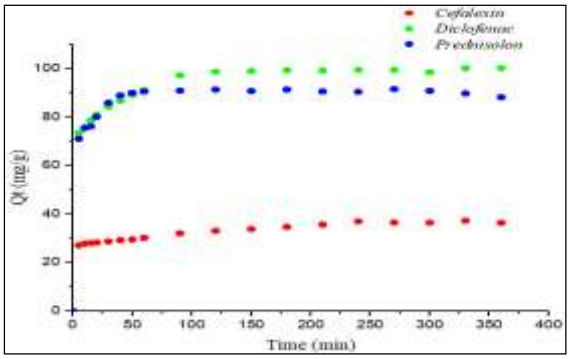

Figure 7. *Kinetics of elimination of active ingredients on DMDDA-41/B*

The same findings were noted for the amino material DMDDA-41/A. It is also noted that there are no major differences between the two materials (the nature and especially the charge of their specific surfaces allow them to have an almost typical attractive behaviour towards the chosen active ingredients).

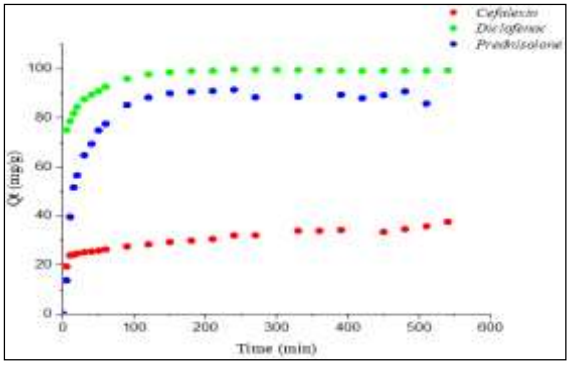

Figure 8. *Kinetics of elimination of active ingredients on DMDDA-41/A*

The adsorption process is best described by studying first- and second-order pseudo-kinetic models. For pseudo-first order process, the Lagergren rate equation is the one generally used:

$$Ln\ (Q_e - Q_t) = Ln\ Q_e - k_1 t \quad (1)$$

Where Qe is the equilibrium adsorption amount, Qt the adsorption amount at time t and k_1 is the pseudo-first order rate constant.
The pseudo-second order process can be expressed as the equation:

$$\left({}^{t}/_{Q_t}\right) = \left[\frac{1}{k_2 \times Q_e^2}\right] + \left[\frac{1}{Q_e}\right] \quad (2)$$

Where Qe is the equilibrium adsorption amount, Qt the adsorption amount at time t and k_2 is the pseudo-second order rate constant.

Figs 9A and 9B and Figs 10A and 10B represents the linearization of the two kinetic models for pharmaceutical pollutants and the parameter values of the two kinetic models applied to their removal are grouped in Table 2.

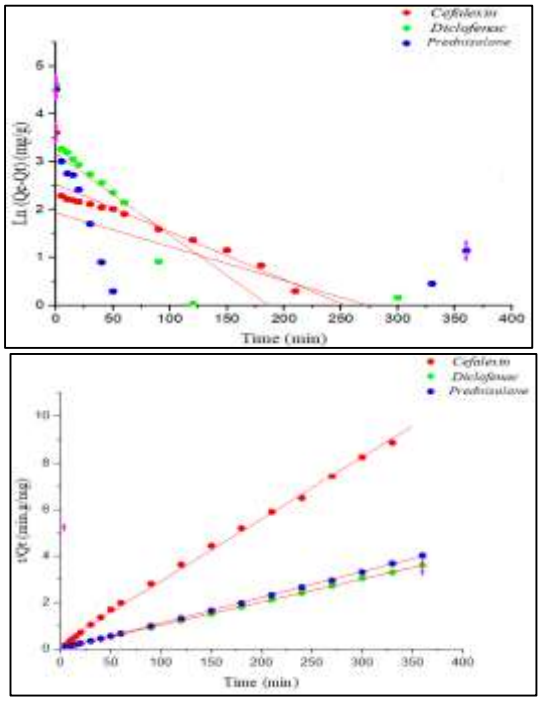

Figure 9. *Application of the pseudo-first order (A) and pseudo-second order (B) model to the elimination of active ingredients on MCM-41/DMDDA-B*

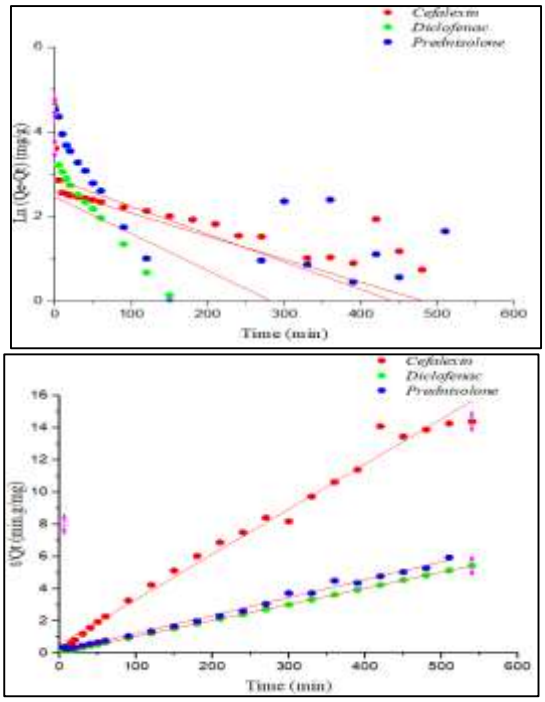

Figure 10. *Application of the pseudo-first order (A) and pseudo-second order (B) model to the elimination of active ingredients on MCM-41/DMDDA-A*

According to the kinetic constant values, the kinetics of pharmaceutical pollutants follow the pseudo second order model ($R^2 \approx 0.99$), rather than the pseudo first one.

Batch solutions of the selected active ingredients were prepared separately and then tested, each with the deaminated material DMDDA-41/B and then the amino material DMDDA-41/A. These tests are performed to determine the amount of adsorption achieved according to the modifications made and to describe the adsorption process in heterogeneous systems. The results obtained can be adjusted by different isothermal equations, including those worked with: the Langmuir model, Freundlich and Sips [32].
Langmuir assumes that adsorption is done in a monolayer on the surface of the solid, Freundlich's considers that there are different types of adsorption sites distributed when at Sips, it is an isotherm that allows to simulate both the Langmuir model and Freundlich's behaviours. Mathematical expressions of the equations are as fellows [21]:

$$Q_e = \frac{Q_{max} \times K \times C_e}{1 + K \times C_e} \quad (3)$$

$$Q_e = K\ C_e^{1/n} \quad (4)$$

$$Q_e = \frac{Q_{max} \times (K \times C_e)^n}{1 + (K \times C_e)^n} \quad (5)$$

Where Ce is the equilibrium concentration of solute in solution (mg/L); Qe is the amount of solute adsorbed per unit mass adsorbent (mg/g); Q_{max} is monolayer adsorption capacity, (mg/g); b is the

constant related the free energy of adsorption; K is the constant indicative of the relative capacity of the adsorbent, (L/g); 1/n is a constant indicative of the intensity of the adsorption.

The isotherms for adsorption of pharmaceutical pollutants by the materials DMDDA-41/A and DMDDA-41/B are shown in Figs 11 and 12.

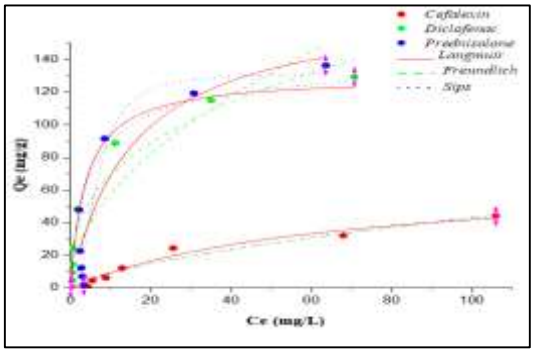

Figure 11. *Adsorption isotherms of Cefalexin, Diclofenac and Prednisolone on MCM-41/DMDDA-A*

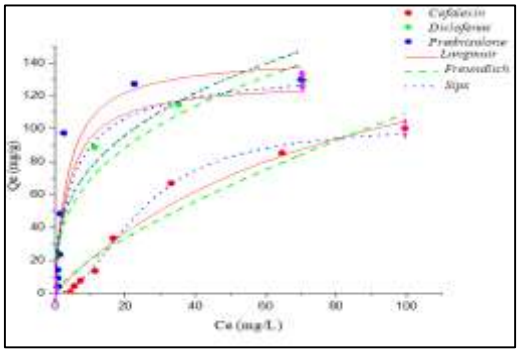

Figure 12. *Adsorption isotherms of Cefalexin, Diclofenac and Prednisolone on MCM-41/DMDDA-B*

Using the classification of adsorption isotherms, those obtained are of type L "Langmuir". This type is characterized by a decreasing slope as the equilibrium concentration increases, due to the decrease in the number of adsorption sites, following the gradual covering of the surface of the various materials. In this type of adsorption, there is no interaction between the adsorbed molecules: this is a physisorption [22, 44 -52].

The representation of the adsorption isotherms is markedly better by the Sips model in the fixation of the three pharmaceutical polluants by DMDDA-41/B (**R^2> 0.97**) and by the Langmuir model in the fixation of the same polluants by DMDDA-41/A (**R^2> 0.95**).

The study of the linearizations of the Langmuir, Freundlich and Sips models (Langmuir-Freundlich), defined above, gives the various parameters of the three models that we have gathered in Table 3.

Table 2. *Parameters of the two kinetic models applied to the removal of the three organic pollutants*

Materials	Drug	Pseudo 1st ordre			Pseudo 2nd ordre		
		k_1 (min^{-1})	Qe (mg/g)	R^2	k_2 (g.min^{-1}.mg^{-1})	Qe (mg/g)	R^2
DMDDA-41/A	Céfalexine	0.002	13,704	0,218	0,001	35,701	0,987
	Diclofénac	0.003	11,64	0,680	0,002	114,942	0,999
	Prednisolone	0.002	17,884	0,230	0,112	8,992	0,994
DMDDA-41/B	Céfalexine	0.004	12,591	0,904	0,002	37,537	0,998
	Diclofénac	0.007	23,757	0,805	0,002	101,214	0,999
	prednisolone	0.003	6,908	0,269	0,021	90,252	0,999

Table 3. *Parameters of the adsorption isotherms applied to the removal of the three organic pollutants*

Materials	*Drug*	*Langmuir*			*Freundlich*			*Sips*			
		Q_{max} *(mg/g)*	K_L *(L/g)*	R^2	K_F *(L/g)*	*1/n*	R^2	Q_{max} *(mg/g)*	K_S *(L/g)*	*n*	R^2
DMDDA-41/A	**Céfalexine**	68,065	0,015	0,965	2,073	0,015	0,937	43,312	0,008	1,430	0,956
	Diclofénac	127,771	0,262	0,979	30,153	0,360	0,928	140,190	0,246	0,849	0,978
	Prednisolone	176,024	0,062	0,817	17,454	0,516	0,750	131,823	0,014	2,240	0,833
DMDDA-41/B	**Céfalexine**	193,539	0,011	0,958	3,731	0,733	0,917	102,639	0,001	2,062	0,992
	Diclofénac	129,771	0,262	0,979	30,153	0,360	0,928	140,190	0,246	0,849	0,978
	prednisolone	144,332	0,272	0,853	34,691	0,340	0,673	128,679	0,104	3,797	0,982

IV . Conclusion

The characterizations show that the parent material obtained is stable and the modification of this material by the addition of amines has not altered its basic structure: the porous diameter and the specific surface area of the materials (amine and deaminated) are greater than those of the parent material, infrared spectroscopy confirms the incorporation of the NH_2 amine groups and thermal analysis proves the resistance of the prepared materials. .

The deaminated material has a high binding capacity of Diclofenac (Qe=140.190mg/g), Prednisolone (Qe= 144.332 mg/g), and Cefalexin (Qe = 193.539 mg/g). Also, the amino material presents important values in the fixation of the selected polluants.

For the three pharmaceutical pollutants, the adsorption perfectly follows the pseudo-second order model than the first order one, with $R^2 = 0.99$.

The representation of the adsorption isotherms of the two materials, DMDDA-41/A and DMDDA-41/B, is significantly better by the Langmuir model in the case of Diclofenac and Cefalexin, and by the Sips model for Prednisolone. Also, adsorption of the micropollutant is more effective at low concentrations.

Based on the results of the effects studied, the DMDDA functionalized materials give many perspectives in the study of pharmaceutical pollutants. With these results, we can:

- Demonstrate which of the different synthesized materials will have a significant absorption capacity on a wide variety of pharmaceutical pollutants and that this capacity is better in complex solutions.
- Assume that the chosen material can provide an effective solution for the treatment of wastewater treatment plant effluents.
- Contribute to the development of existing wastewater treatment techniques and their performance, in particular in the treatment of effluents containing organic pollutants of pharmaceutical or cosmetic origin.
- Exploit other opportunities to improve the biodegradability of pharmaceutical residues, including biological processes.

V .Acknowledgments

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