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Elaboration of Porous Alumina Nanofibers by Electrospinning and Molecular Layer Deposition for Organic Pollutant Removal

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Abstract

The development of heterogeneous nanomaterials with high surface to volume ratio is crucial for enhancing the adsorption of water pollutants, such as toxic organic dyes. Here, we describe the synthesis of polyacrylonitrile (PAN) nanofibers coated with porous alumina nanolayers, and their application for adsorption of the organic dye methylene blue (MB). First, we produced PAN nanofibers by electrospinning, and then coated them with an aluminum alkoxide hybrid films fabricated using molecular layer deposition. Finally, we used thermal annealing to obtain the final PAN nanofibers coated with porous alumina nanolayers. We characterized the obtained nanostructured materials by scanning electron microscopy, transmission electron microscopy, N₂ desorption/adsorption porosimetry (BET theory), and Fourier-transform infrared spectroscopy. The porous nanomaterials had a surface area of 631.79 m²/g that allowed reaching an adsorption efficiency of 88% with 10 ppm MB. The adsorption kinetics and isotherms were better described by a pseudo-first-order model and the Langmuir adsorption model, respectively, based on physical adsorption (monolayer adsorption) of the adsorbed molecules.

Key words: water treatment, adsorption, alucone, mesoporous materials, nanofibers, ALD/MLD.

Introduction

Effectual removal of organic pollutants from polluted waters is a crucial step towards a sustainable environment. Wastewater produced by the dye industry¹ is a major contributor to water pollution. Many strategies have been tested for removing such dyes from wastewaters, for instance ultrasound oxidation, biological removal, membranes-based separation, photocatalytic degradation² and adsorption^{3,4}.

Adsorption is considered as the most effective approach in wastewater treatment due to its low cost, simple design, flexibility, operation simplicity, and insensitivity to toxic pollutants.⁵ Adsorption process consists on transferring the organic dye to the surface of solid and very porous particles (i.e. adsorbents)^{6,7}, such as nano-sized materials with elevated porosity, surface area-to-volume ratio, and regeneration potential⁸⁻¹¹. Among these nanomaterials, nanofibers are excellent candidate adsorbents due to their high surface area and tunable porosity, 3D topography, flexible surface functionalities, mechanical features, and small pore diameter and consequently higher number of active sites for contaminant adsorption. Nanofibers have been widely studied for air and water filtration and for blood purification¹², particularly porous alumina nanofibers. This nanomaterial is easy to handle and presents high surface area and very good thermal stability and tensile strength, due to the sub-micrometer and tunable pore size^{13,14}. Alumina nanofibers can be manufactured using various techniques: hydrothermal growth¹⁵, solvothermal growth¹⁶, chemical vapor deposition¹⁷ and electrospinning^{18,19}.

Here we are reporting the elaboration of porous alumina nanofibers by combining electrospinning and Molecular Layer Deposition (MLD) for organic pollutant removal. Electrospinning, a low-cost method in which electrostatic forces are the driving force, is frequently chosen for nanofiber manufacturing.^{20,21} Among the used polymer for electrospinning, polyacrylonitrile (PAN) was used as a substrate for depositing thin films materials, due to its stable synthetic polymeric nature that can be easily electrospun into nanofiber. On the other hand, PAN was largely used in the literature as a substrate, since it can be completely removed upon annealing under air at high temperatures allowing to obtain nanotubes structures^{22,23}.

For the deposition of thin film on PAN nanofibers, Atomic Layer Deposition (ALD) and Molecular Layer Deposition (MLD) have been chosen in this work. ALD is a gas phase growth technique based on sequential self-limiting surface reaction of precursor's injections into the reaction chamber

separated by an inert gas as purge step. The chemical adsorption of the precursors vapor during surface reaction permits to obtain a stable covalent bonds and ensures that thin films are bonded to the substrate. That is why ALD process can be used to coat high aspect-ratio substrates and complex 3D-structures such as polymers, ceramics and metals.²⁴ The high-quality thin films obtained by ALD shows excellent conformality and thickness control²⁵. Therefore, ALD has been used for various applications, including water pollution remediation^{26–29}. MLD is a novel method directly derived from ALD³⁰. The two techniques are based on sequential and self-limiting surface reactions for the preparation of functional coatings.

Aluminum alkoxide (alucone) hybrid polymer films can be deposited on nanofibers using MLD and suitable precursors, such as trimethylaluminum (TMA) and ethylene glycol (EG). MLD-based deposition of dense organic/inorganic hybrid polymer films is followed by thermal annealing to remove the organic template and to obtain well-defined porous structures with precisely controlled thickness, in the Ångstroms range^{31,32}. MLD-based addition of thin porous films to the surface of nanomaterials can lead to new surface functionalities.^{33,34}

In this work, a new fabrication route for porous alumina nanofiber based on combining both electrospinning and Molecular Layer Deposition were presented. The synthesized polyacrylonitrile (PAN) nanofibers by electrospinning, were coated by alucone using MLD. Then the organic template was removed by calcination, allowing to obtain a porous nanofibers structure with high surface area. The high surface area is the driving force to adsorption studies on the removal of organic dyes. A comparative study between MLD and ALD was performed after annealing, showing a porous aluminum oxide (**p Al₂O₃**) and dense aluminum oxide (**d Al₂O₃**) films, respectively. The high surface area values resulting from the **p Al₂O₃** comparing to the **d Al₂O₃** showed the novelty aspect to deposit by MLD process. This was evaluated by adsorption study on the removal of methylene blue (MB) dye from aqueous solutions.

2. Experimental

2.1. Chemicals

PAN (MW = 500 000, Sigma Aldrich) and *N,N*-dimethylformamide (DMF, CAS number 68-12-2, 99.8%, Sigma Aldrich) were used to fabricate the PAN nanofibers. Alucone polymer films were grown using TMA ($\text{Al}(\text{CH}_3)_3$; 97%, Sigma Aldrich) and EG ($\text{HO}(\text{CH}_2)_2\text{OH}$; Reagent Plus >99%, Sigma Aldrich). MB (Reagent Plus >82.0%) (Sigma-Aldrich) was the reference organic dye.

2.2. Synthesis of alucone/PAN and Al_2O_3 /PAN nanofibers

2.2.1. PAN nanofibers

PAN nanofibers were produced by electrospinning. The polymer solution was prepared by dissolving PAN in DMF (2mg PAN in 18 mL DMF) by stirring at 60°C for 24 hours, and then was loaded into a plastic syringe with a stainless steel needle³⁵. Electrospinning (applied voltage: 25 kV; flow rate: 3 mL/h; needle tip-collector distance: 15 cm) was performed at $38 \pm 5^\circ\text{C}$ to evaporate the solvent and to obtain solid fibers on the collector. Nanofibers were collected on a rotating cylinder (10 cm diameter and rotating speed of 2000 rpm) covered with aluminum foil. The process lasted 7h.

2.2.2. MLD of alucone on PAN nanofibers

MLD of aluminum alkoxide (alucone) thin films were deposited over PAN nanofibers³⁶ using a home-built ALD/MLD system. The process was obtained using TMA and EG as precursors. The EG precursor bubbler was heated at 70 °C while the TMA bubbler was maintained at room temperature. The deposition chamber was maintained at 135°C during the process and precursors line was kept at 100°C. The precursor pulses were coupled with a 10 sccm Argon (Ar) flow. MLD was carried out using an exposure mode to obtain the self-limiting surface reaction and by-products were pumped using a 100 sccm Argon (Ar) flow as gas vector during purge. Each MLD cycle (250 cycles in total) consisted of a TMA pulse for 0.1s, exposure for 30s, purge for 60s, EG pulse for 2s, exposure for 30s and purge for 120s.

2.2.2. ALD of Al_2O_3 on PAN nanofibers

Al_2O_3 thin films were deposited on PAN nanofibers by ALD using TMA and H_2O as precursors. The films were grown in a deposition chamber at 60°C. The precursor pulses were coupled with a 25

sccm Argon flow and the purge step was performed with a 100 sccm Argon flow. Each ALD cycle (50 cycles in total) consisted of a TMA pulse for 0.2s, exposure for 30s, purge for 40s, H₂O pulse for 2s, exposure for 30s, and purge for 40s.

2.2.3. Calcination in air

To convert the alucone nanofilms prepared by MLD into porous alumina (p Al₂O₃), the nanomaterial was calcined in air in a muffle oven at 600 °C with a ramp rate of 1°C/min. Then, the temperature was maintained at 600 °C for 1h before starting the cooling step.

The same process was used also for the samples prepared by ALD (i.e. PAN nanofibers coated by Al₂O₃ films to convert the Al₂O₃ into dense Al₂O₃ (d Al₂O₃)).

2.3. Characterization

The morphology and structure of the synthesized materials was examined by scanning electron microscopy (SEM) (ZEISS EVO HD-15, ZEISS, Marly le Roi, France) and high-resolution transmission electron microscopy (HR-TEM, JEOL ARM 200F, Japan) with an energy dispersive X-ray (EDX) analyzer. X-ray diffraction (XRD) was used to determine whether the deposited alumina is amorphous or crystalline after annealing (PANalytical Xpert-PRO with Cu radiation at 0.154nm). The sample porosity was measured by N₂ desorption/adsorption porosimetry with degassing under vacuum at 300 °C for 24h. The surface area was calculated with the Brunauer, Emmet and Teller (BET) method using different data points and relative pressures (P/P₀) from 0.2 to 0.8. The Fourier-transform infrared spectroscopy (FT-IR) spectra of the samples dispersed in KBr pellets were recorded with a 670 FT-IR spectrometer (Varian) (400–4000 cm⁻¹ range and resolution of 4 cm⁻¹). The thermogravimetric analysis (TGA) of the samples after calcination was performed using a TGA G500 device (TA Instruments). About 10 mg of each sample was heated in air atmosphere from room temperature to 800°C, at a heating rate of 10°C.min⁻¹. MB concentration was measured by ultraviolet-visible (UV–Vis) spectrophotometry (spectra acquired with a Jasco V-570 UV–Vis-NIR spectrophotometer (Jasco Inc., Easton, PA, USA), at $\lambda = 664$ nm, and the external calibration method.

2.4. Adsorption experiments

2.4.1. Batch equilibrium studies

MB (stock solution of 10 ppm) was used as organic pollutant reference to evaluate the adsorption performances of the prepared p Al₂O₃ and d Al₂O₃ samples. The adsorption test started with 0.01 g adsorbent and 5 mL of aqueous solution containing increasing MB concentrations (10, 15, 20, 25, and 30 ppm). The pH of the MB solution during the degradation was equal to 9. The adsorbent-dye ratio was maintained at 2 g/L for both sample types. In the next experiment, using only p Al₂O₃/PAN, the adsorbent-dye ratio concentration was maintained at 4 g/L. Flasks were placed on a magnetic stirrer (400 rpm) at room temperature in the dark, and MB concentration was checked at different time points (0, 30, 60, 120 and 180 min) to assess MB adsorption. The adsorbent was separated from the dye solution after each adsorption experiment by centrifugation at 6000 rpm for 5 min. The UV–Vis absorbance spectra of the MB solution displayed a main adsorption band at 664 nm. Isothermal and kinetic analyses were performed (see below) to describe the adsorption process.

2.4.2. Adsorption isotherms

The adsorption behavior of an adsorbate onto an adsorbent can be quantitatively described using different adsorption isotherms. Here, the Langmuir and Freundlich models, two common theoretical models, were chosen to analyze the adsorption equilibrium process³⁷.

The Langmuir isotherm linear model assumes that a monolayer adsorption process occurs on the homogeneous surface of an adsorbent, without considering the interaction between adsorbate molecules. This model is described by Equation (1):

$$C_e/q_e = C_e/q_{\max} + 1/q_{\max} K_L \quad (\text{Equation 1})$$

where q_{\max} (mg/g) and k_L (L/mg) are the Langmuir isotherm constants that describe the maximum adsorbed quantity and the free energy function of adsorption, respectively.

According to the Freundlich isotherm linear model, a multilayer adsorption process takes place on the non-homogeneous surface of an adsorbent. This model is described by Equation (2):

$$\ln q_e = \ln k_F + (1/n) \ln C_e \quad (\text{Equation 2})$$

where the Freundlich isotherm coefficients K_F ((mg/g)(L/mg)^{1/n}) and n are the adsorption capacity and adsorption intensity, respectively.

2.4.2. Adsorption kinetics

To determine the adsorption mechanism and the rate-controlling step of the adsorption process, the relationship between adsorbed quantity and sorption time were computed using pseudo first-order and pseudo second-order kinetic models. The control experiments for MB adsorption onto pAl₂O₃ were carried out in the same experimental conditions and simultaneously.

The linear equation of the pseudo first-order kinetic model is:

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (\text{Equation 3})$$

where q_t is the dye quantity (q_t , mg/g) adsorbed onto the adsorbent at time t , and k_1 (1/min) is the kinetic rate constant of the pseudo first-order adsorption.

The linear equation of the pseudo second-order kinetic model is:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (\text{Equation 4})$$

where K_2 (g/(mg.min)) denotes the rate constant of the pseudo second-order adsorption model.

3. Results and discussion

The nanofibers coated with a porous alumina layer (MLD; alucone/PAN) and with dense alumina layers (ALD; Al₂O₃/PAN) were first structurally and morphologically characterized.

3.1. Characterization of p Al₂O₃ and d Al₂O₃ nanofibers

3.1.1 Morphological properties of p Al₂O₃ and d Al₂O₃ nanofibers

SEM investigation of the surface morphology and microstructural properties of pAl₂O₃ and dAl₂O₃ deposited on PAN nanofibers used as substrate. After ALD/MLD deposition, the samples were calcinated at 600°C for 1h to ensure the elimination of the polymeric template. Figure 1 shows that well structured nanofibers were obtained in both cases after ALD (figure 1 a-b) and MLD

(figure 1 c-d) deposition. The mean diameters of the dAl₂O₃ films (ALD) and pAl₂O₃ layers (MLD) were 550 ± 10 nm (**Figure 1a-b**) and 460 ± 7 nm (**Figure 1c-d**) respectively.

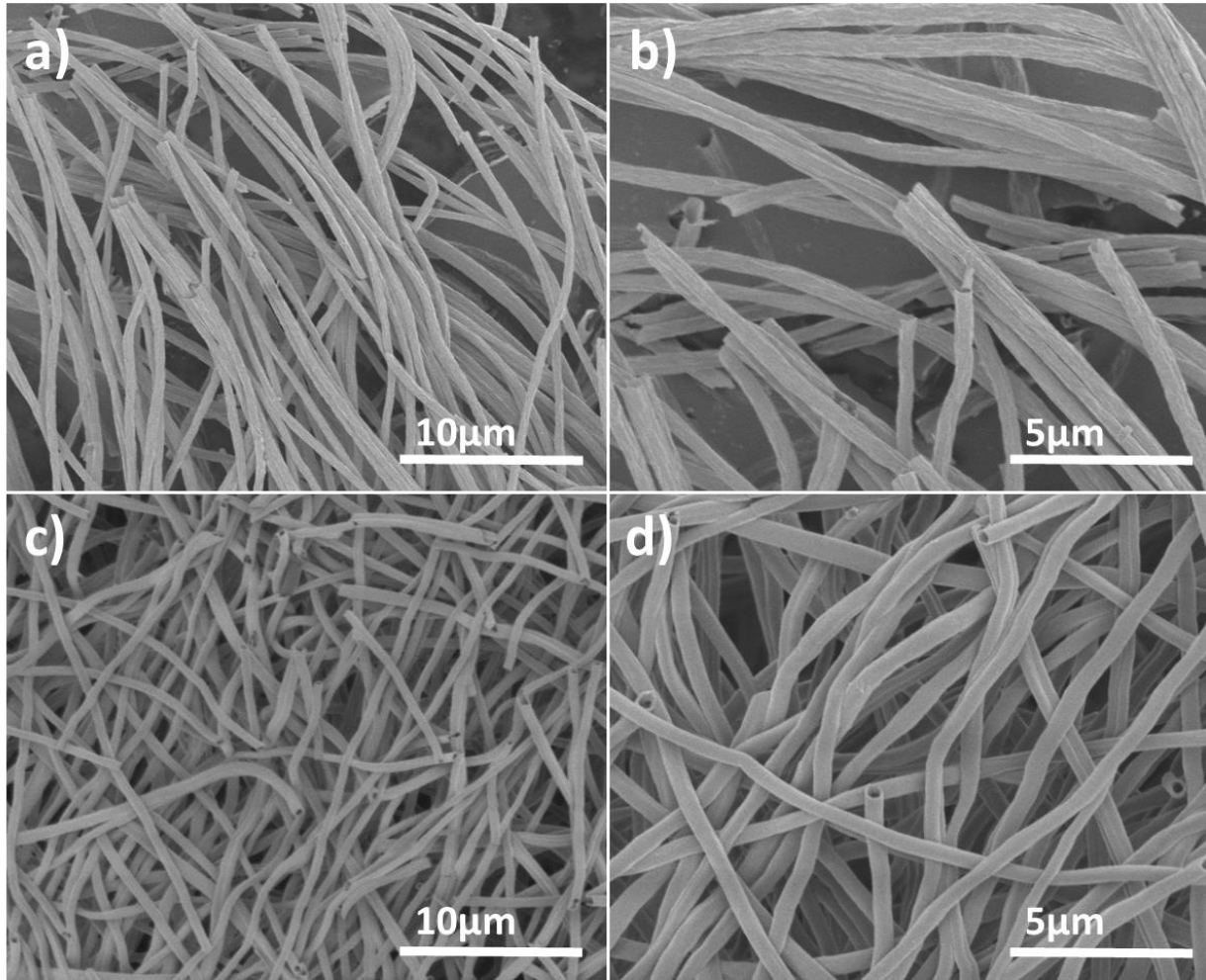


Figure 1: Scanning electron microscopy images a-b) d Al₂O₃ and c-d) p Al₂O₃.

To further understand the structure of prepared nanofibers, HRTEM was investigated. The TEM data confirmed the tubular structure of both samples that was also observed by SEM. It was found that p Al₂O₃ (Figure 2 b) and d Al₂O₃ (Figure 2 e) are both amorphous after annealing. Figure 2 a and S1 revealed the porous structure obtained after calcination of the deposited alucone layer on PAN NFs by MLD. Thus after the deposition of 50 cycles of alumina by ALD on PAN (figure 2 d-

e), dense structure was obtained after annealing under air. Contrary to ALD, MLD allows the formation of porous structure due to the TMA-EG layer. The calcination of the sample allow the elimination of the CH₂-CH₂ bond generated by ethylene glycol. Many parameters including the deposition thickness, the temperature ramp and temperature of calcination affect the porosity^{34,38}. This structure allow a higher surface area than the dense alumina which will be confirmed by BET. Furthermore, Figure 2 c revealed the wall thickness of the tubular structure of p Al₂O₃ with a value of 69.8±4.2 nm compared to 27.7±4.7 nm in d Al₂O₃ (Figure 2 f).

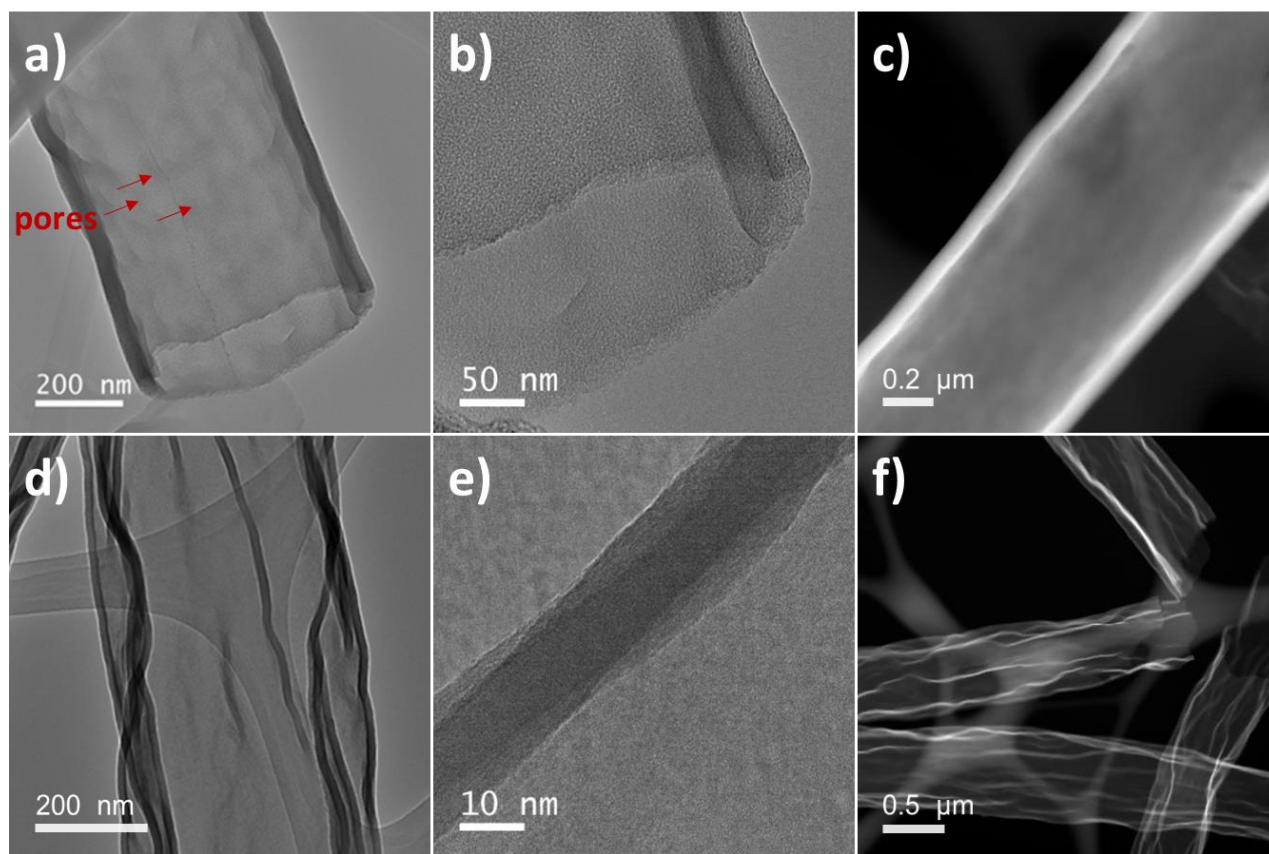


Figure 2: HRTEM image of a-c) p Al₂O₃ deposited by MLD and d-e) d Al₂O₃ deposited by ALD.

The X-Ray diffraction data confirm the amorphous structure found by HRTEM for both samples. Figure S2 shows that the calcination at 600°C did not affect the amorphous structure of the alumina nanofibers obtained by ALD and MLD

3.1.2 N₂ desorption/adsorption porosimetry (BET)

N₂ desorption/adsorption porosimetry was used to investigate the sample porosity. In this study, N₂ adsorption was considered to follow a type II isotherm model. The specific surface can be determined by exploiting the linear transformation of the BET isotherm. This analysis highlighted differences in the sorption curves of the **p Al₂O₃** and **d Al₂O₃** samples (**Figure 3**). The isotherm of the **p Al₂O₃** sample displayed a higher hysteresis loop from **d Al₂O₃** which could be explained by the presence of micropores and mesopores in the structure (**Figure 3a**). Moreover, higher BET surface area was observed for the **p Al₂O₃** sample compared to the **d Al₂O₃** sample with 631.79 m²/g for porous alumina and only 45.11 m²/g for dense alumina. The surface area of micropores for **p Al₂O₃** is calculated following t-plot model and the value obtained was 235.18 m²/g. This indicates that the mesoporous structure is dominant in the porous Alumina sample. These results are in good agreement with HRTEM analysis. The alucone was converted after calcination to a porous structure with a high surface area that will play a major role in the adsorption mechanism of dyes.

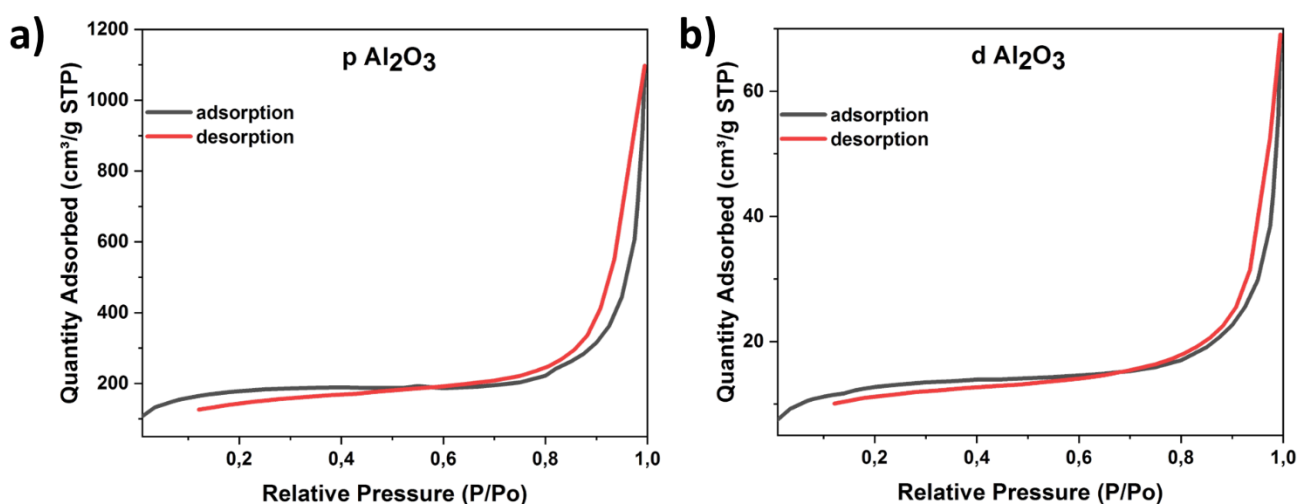


Figure 3: Nitrogen adsorption-desorption isotherms of (a) **p Al₂O₃** and (b) **d Al₂O₃** samples after calcination in air.

3.1.3 FTIR spectroscopy

The various functional groups present in the samples were identified by FTIR spectroscopy (**Figure 4**). After calcination, all carbon content was burnt in the hybrid alucone polymeric films, as previously shown³⁹. After calcination in air, the **p Al₂O₃** and **d Al₂O₃** samples showed very similar peaks in the FTIR spectra. This can be explained by alucone transformation into alumina nanofilms that have the same components as Al₂O₃ nanofilms after calcination. The peak range (800 to 950 cm⁻¹) indicated Al-O stretching vibrations, confirming the change from alucone hybrid material to alumina structure. The transmittance loss of the C-C and C-O stretching vibrations observed at 1132 and 1086 cm⁻¹, respectively, could be explained by thermal annealing. The small peak at 3300 cm⁻¹ indicated O-H stretching vibrations.⁴⁰ A stretching vibration at 1205 cm⁻¹ was previously reported and was due to methyl deformation of AlCH₃*.⁴¹ An increase in transmittance associated with CH₂ asymmetric and symmetric stretching vibrations was observed at 2956 and 2870 cm⁻¹, respectively, corresponding to the stretching vibrations of the ethylene linkages between oxygen atoms in the aluminum alkoxide polymer.³²

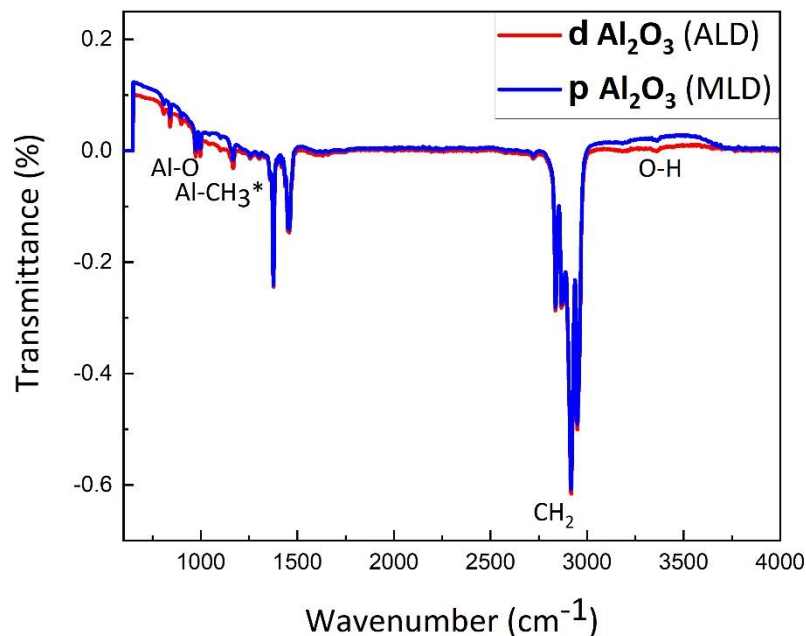


Figure 4: FTIR spectra of thin films deposited over PAN nanofibers: **d Al₂O₃** films (50 cycles of ALD) and **p Al₂O₃** films (250 cycles of MLD) after calcination

3.1.4 TGA analysis

Since trace of carbon were detected in FTIR, thermogravimetric analysis were conducted to further understand the stability of the elaborated samples. Figure 5a shows a total weight loss of almost 16% when the temperature was increased to 800°C under air. This could be attributed to the remaining CH₂ group detected in FTIR analysis due to the insufficient time of annealing or the adsorption of contaminants from air. For d Al₂O₃, a weight loss of only 3.0% (figure 5b) was observed. The weight loss of p Al₂O₃ was higher than the weight loss in d Al₂O₃ owing to the higher surface area of the porous sample that could adsorb more contaminants. The mass uptake in figure 6b of 1.2% between 600 and 800°C could be due to the oxidation of the sample at higher temperature as described elsewhere.⁴²

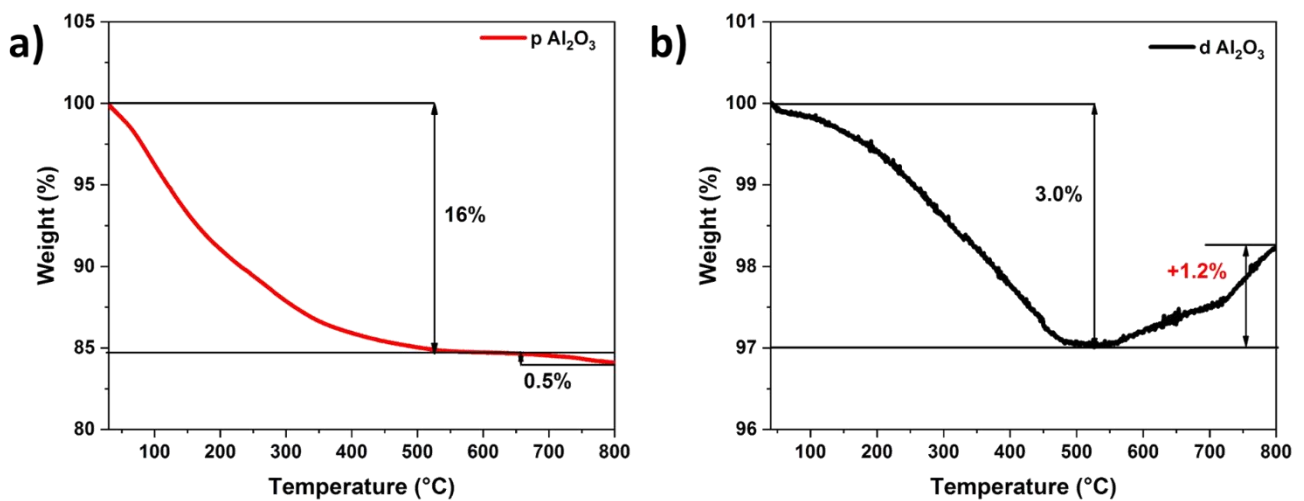


Figure 5: Thermogravimetric curve of a) p Al₂O₃ and b) d Al₂O₃

3.4 Adsorption activity

To better understand the absorption process, the adsorption of MB (i.e. organic pollutant dye) onto the prepared nanofibers (i.e. adsorbents) was monitored by UV/Vis spectrometry in view of potential applications for wastewater remediation.

3.4.1 MB adsorption onto $p\text{-Al}_2\text{O}_3$ and $d\text{-Al}_2\text{O}_3$ nanofibers

To measure the adsorption activity of $p\text{-Al}_2\text{O}_3$ and $d\text{-Al}_2\text{O}_3$ nanofibers after calcination in air, MB catalytic adsorption under UV light was monitored by UV/Vis spectrometry at different contact times (**Figure 6**). The UV–Vis absorbance spectra shown in **Figure 6** of the MB solution displayed a main adsorption band at 664 nm permits to calculate the adsorption of MB dye using adsorption efficiency formula (**Equation 5**). The initial MB concentration was 10 ppm and the adsorbent concentration was 2 g/L (10mg of adsorbent in 5 mL of MB).

The adsorption efficiency was calculated as follows:

$$\text{Adsorption efficiency (\%)} = (C_0 - C) / C_0 \times 100. \text{ (Equation 5)}$$

Where C_0 and C are the initial (before) and the final MB concentrations (after UV exposure).

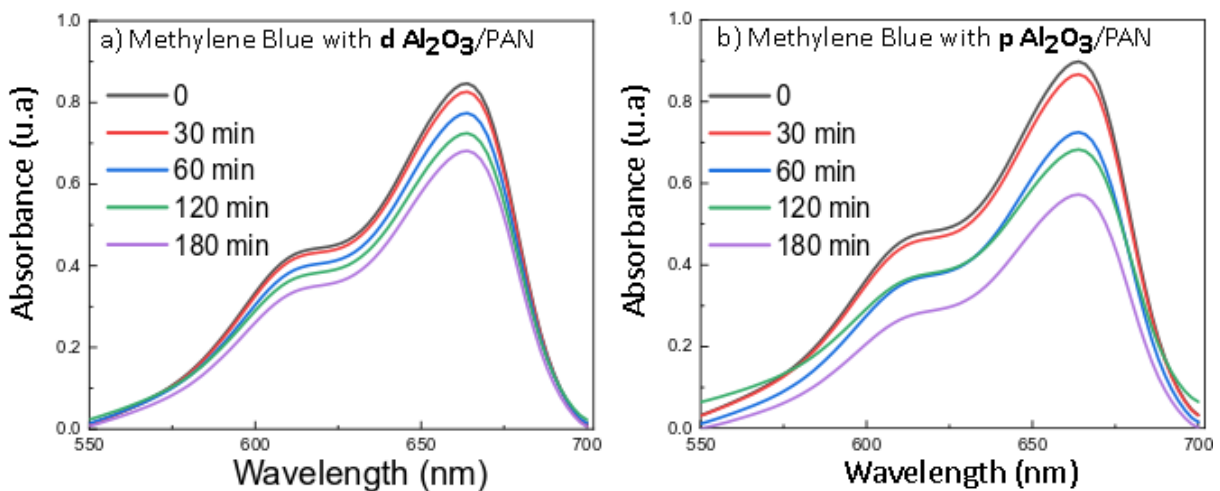


Figure 6: UV-Vis spectra of MB adsorption under UV light: a) $d\text{-Al}_2\text{O}_3$ and b) $p\text{-Al}_2\text{O}_3$.

Comparison of the adsorption efficiency of the $d\text{-Al}_2\text{O}_3$ and $p\text{-Al}_2\text{O}_3$ samples in function of the dye-adsorbent contact time (**Figure 7**) showed that after 3 hours of contact time, the maximum efficiency was 22% for the $d\text{-Al}_2\text{O}_3$ and 30% for the $p\text{-Al}_2\text{O}_3$. This indicates that the porous alumina structure prepared by MLD exhibits higher adsorption. Therefore, the next analyses concentrated only on the $p\text{-Al}_2\text{O}_3$ sample.

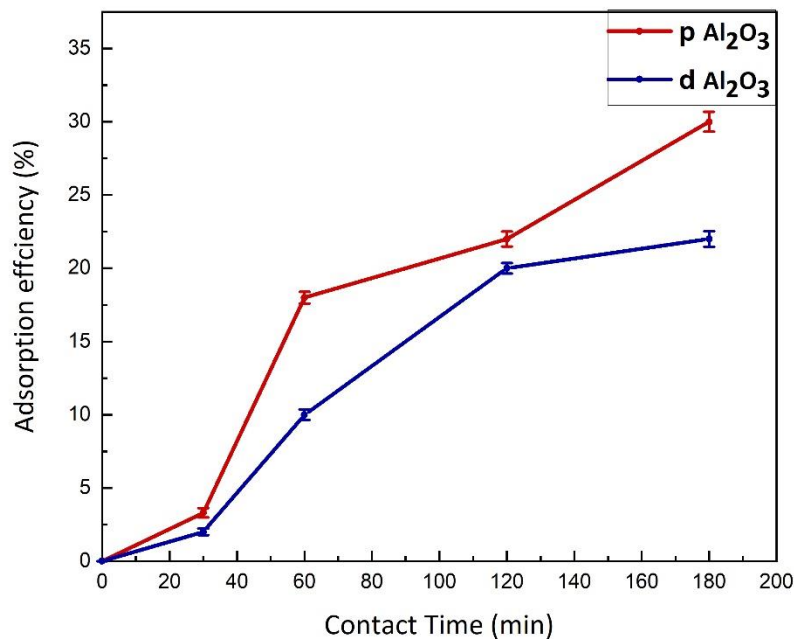


Figure 7: Adsorption efficiency of **d Al₂O₃** and **p Al₂O₃** nanofibers in function of the contact time between dye (5ppm of MB) and adsorbents.

3.4.2 Adsorption by **p Al₂O₃** nanofibers

Due to the higher adsorption capacity of **p Al₂O₃** nanofibers, only the sample coated with alucone (250 cycles of MLD) was considered for the adsorption analysis. Different concentrations of MB (10, 7, 5, 3 and 1 ppm) with 4 g/L of **p Al₂O₃** nanofibers (20mg of adsorbents in 5 mL of MB) and various contact times (0, 30, 60, 120, 150 and 180 min) were used to compute the adsorption isotherms and kinetics.

a) Adsorption isotherms:

MB adsorption onto **p Al₂O₃** nanofibers was quantitatively described using the Langmuir and Freundlich linear models, (Figure 8 a-b). **Table 1** shows the adsorption parameters for the two models, calculated using Equations (1) and (2), and the correlation coefficient R^2 of the fitting. The R^2 value was higher with the Langmuir (Figure 8a) than with the Freundlich model (Figure 8b)

(0.999 and 0.958). This indicates that MB adsorption onto porous alumina is better described by the Langmuir model (i.e. monolayer adsorption process on the adsorbent homogeneous surface, without considering the interaction between adsorbate molecules).

Table 1. Adsorption isotherm parameters for MB adsorption using the Langmuir and Freundlich linear models.

Model	Parameters	Value
Langmuir	q_{\max} (mg/g)	0.965 ± 0.002
	k_L (L/mg)	1.869 ± 0.005
	R_L	0.014 - 0.25
	R^2	0.999
Freundlich	$k_F ((\text{mg/g})(\text{L/mg})^{1/n})$	0.75
	N	2.767
	R^2	0.958

b) Adsorption kinetics

The relationship between adsorbed quantity and sorption time was described using pseudo first-order and pseudo second-order kinetic models (Figure 8 c-d), and the adsorption parameters and R^2 were calculated using Equations (3) and (4) (**Table 2**). The control experiments for adsorption of MB onto **p Al₂O₃** nanofibers were carried out in the same experimental conditions, simultaneously.

Table 2. Adsorption kinetic parameters for MB adsorption onto **p Al₂O₃** nanofibers calculated with the pseudo first-order and pseudo second-order kinetic models.

Model	Parameters	Values
Pseudo first-order	q_e (cal) (mg/g)	1.3
	$K_1(1/\text{min}) * 10^{-4}$	9.9
	R^2	0.99
Pseudo second-order	q_e (cal) (mg/g)	1.5
	$K_2(\text{g}/(\text{mg_min})) * 10^{-4}$	6.2
	R^2	0.26

Figure 8c-d and **Table 2** clearly indicated that the experimental data are better described by the pseudo first-order than the pseudo second-order kinetic model (R^2 : 0.999 and 0.26, respectively) and that the reaction is mostly explained by physisorption.

Ho and McKay found that most adsorbents in aqueous solutions show pseudo second-order kinetics, especially for long sorption times⁴³. Conversely, MB adsorption onto porous alumina nanofibers did not behave like most of the previously investigated sorption processes in water due to the difference in dye and adsorbent concentration.

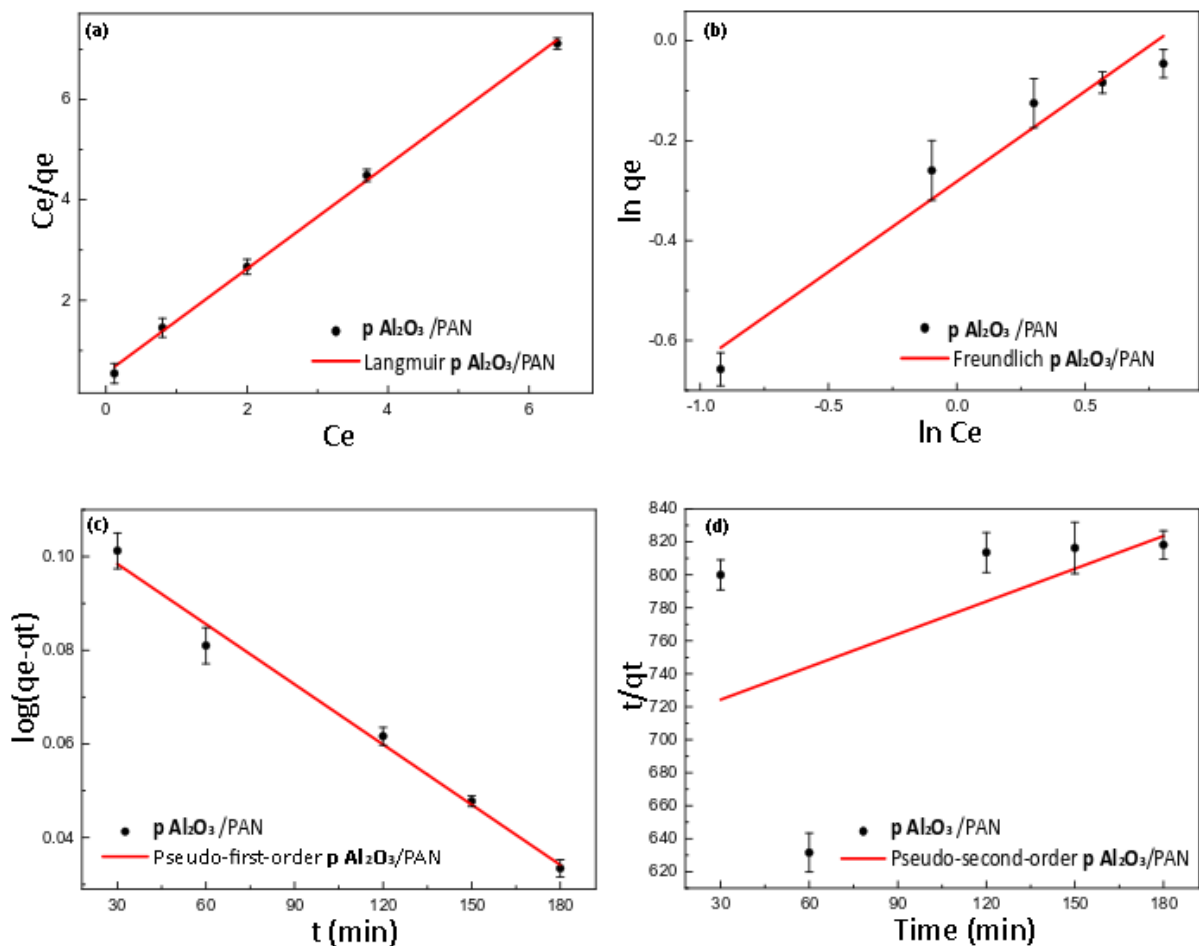


Figure 8: Isotherms calculated with the Langmuir (a), and Freundlich (b) linear models for MB adsorption onto the p Al₂O₃ nanofibers after 3 hours of contact. Kinetics calculated with the pseudo first-order (c) and pseudo second-order (d) kinetic models during 3 hours.

Compared with the results of previous studies on dye-adsorption capacities (**Table 3**), porous alumina nanofibers displayed high adsorption (88%) using a small amount of adsorbents. This is an improvement of the competitive efficiency of hybrid materials, and shows MLD suitability for the fabrication of dye adsorbents. Moreover, recyclability of the adsorbent and the mechanism of adsorption were also been discussed in the following paragraph.

Table 3. Comparison of the dye adsorption performances of different adsorbents

Adsorbent	Dye	pH range	% removal	Reference
Modified-Alumina	Crystal violet	2.6–10.8	80	44
Activated clay	Methylene blue	2–9	95	45
Kaolin	Crystal violet	2–7	95	46
Activated rice husk	Acid yellow 36	2–9	45	47
Fly ash	Methylene blue	2–8	45	48
Pine leaves	Methylene blue	2–11	80	49
Fe ₂ O ₃	Acid red 27	1.5–10.5	98	50
Pine cone	Congo red	3.55–10.95	60.5	51
Pine cone	Methylene blue	3.47–7.28	94.82	52
Tobacco Stem Ash	Methylene blue	2.08–7.93	81	53
Alucone	Methylene blue	3–9	88	this work

c) Recyclability and mechanism of adsorption

The MB is a cationic dye in pH =9^{54–56} which has the ability to attach with the Al₂O₃ negative surface⁵⁷. The presence of Al₂O₃ on the surface of nanofibers enhanced the charge distribution of porous adsorbents.

Furthermore, the p Al₂O₃ nanofibers have ability to be reused for several cycles (at least 5 cycles) without losing their efficiency as presented in Figure 9.

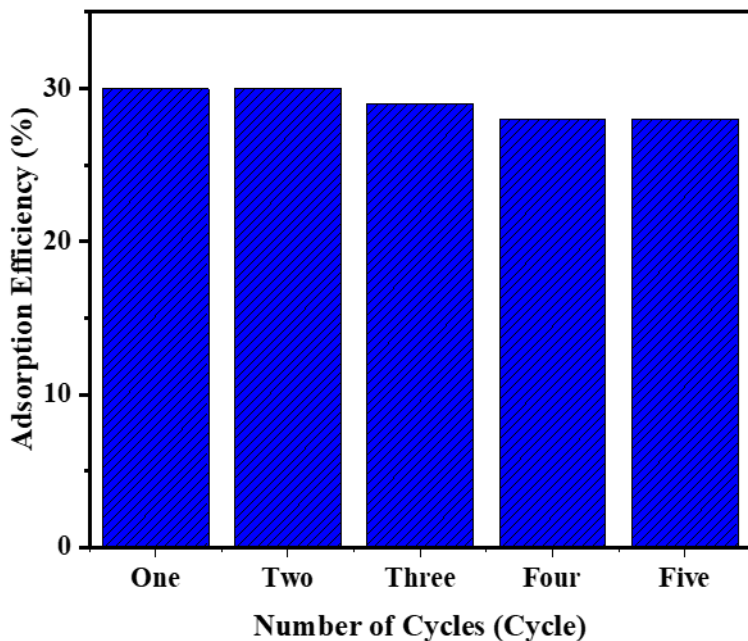


Figure 9: The adsorption efficiency of p Al₂O₃ as catalysts for removal of MB throughout five consecutive cycles of filtration and reuse.

Several probable adsorption mechanisms such as hydrogen bonding, electrostatic interaction, ion exchange, acid-base interaction, coordination, have been proposed to realize the interactions between solid adsorbent and MB dye molecules in an aqueous solution. In this present work, as a cationic organic molecule^{54,56,58}, MB was adsorbed onto the surface of prepared porous Al₂O₃ mainly through electrostatic interaction and hydrogen bonding. This can be explained by the presence of high amount of Al–OH and Al–O groups on the adsorbent surface. The adsorption capacity increases with increasing the pH of the MB solution, suggesting that more deprotonated Al–OH groups exist in the form of Al–O[–]⁵⁷, which possess stronger electrostatic interaction with cationic dye MB. In addition, the Al–OH group on the surface of the prepared p Al₂O₃ can also interact with the amine group of MB molecule via hydrogen bonding as has been reported for other mesoporous materials⁵⁹. Therefore, the adsorption mechanisms can be interpreted by electrostatic interaction and hydrogen bonding (Figure 10).

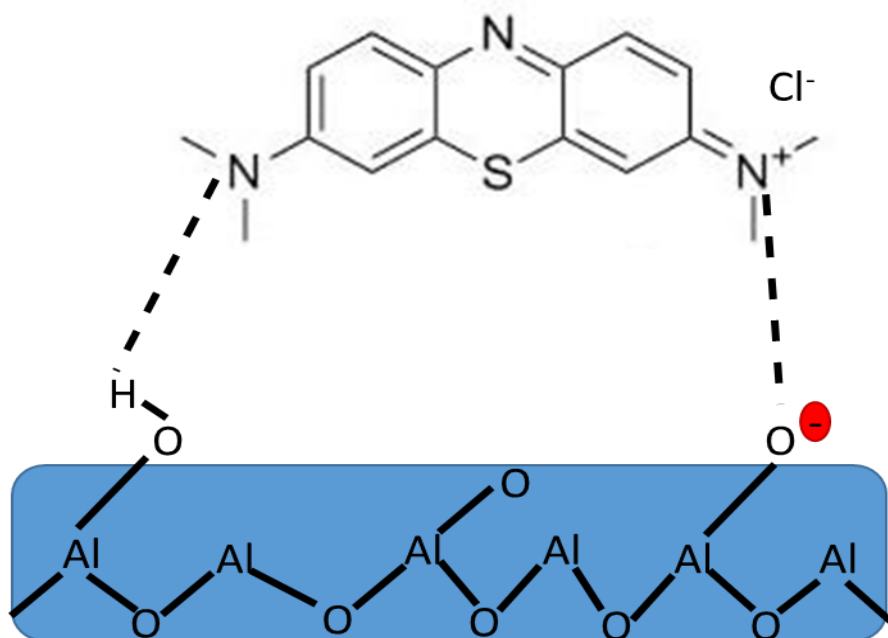


Figure 10: The adsorption efficiency of γ Al_2O_3 as catalysts for removal of MB throughout five consecutive cycles of filtration and reuse.

Conclusion

Improving the nanomaterial adsorption performance for wastewater remediation is still a challenging task. In this work, we designed and prepared highly efficient nanomaterials by coating PAN nanofibers using MLD. The calcination in air of "alucone" hybrid polymeric thin films prepared by MLD allowed the conversion of the hybrid structure into an alumina mesoporous structure. The high porosity and large surface area ($631.7 \text{ m}^2/\text{g}$) explain the high MB adsorption efficiency (88%). Moreover, the adsorption isotherms calculated with the Langmuir model showed that MB adsorption onto porous alumina nanofibers is a monolayer adsorption process (physical adsorption). The present results highlight the potential of nanomaterials coated by MLD for organic dye removal and water pollution remediation.

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