*Desalination and Water Treatment*
www.deswater.com

doi: 10.5004/dwt.2023.30008

312 (2023) 187–197
November

# Synthesis and characterization of a novel hybrid film based on polyvinyl chloride/modified clays/photosensitizers: application to pollutants photodegradation

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Received 11 February 2023; Accepted 26 September 2023

## ABSTRACT

The present study aims to synthesize a hybrid thin film with sol–gel process via dip-coating and spin-coating techniques. Prepared films are used in the elimination several pollutants using the photodegradation process. Used films are prepared by mixing polyvinyl chloride (PVC)/hydrophobic-modified clays (Hc). First, we modified natural bentonite (Bt) and sodium montmorillonite (Na-Mt) with a surfactant cetyltrimethylammonium bromide. incorporation of methylene blue (MB) as photosensitizers into Hc was realised with different percentage of hydrophobic clay/photosensitizers at ambient temperature and optimum pH for 3 h. Secondly, the PVC/modified clay thin films were elaborated with sol–gel technology, using two techniques for deposition: Dip-coating in dimethylformamide and spin-coating in tetrahydrofuran. We modified some parameters such as weight ratio polymer/modified clay, number of dipper, rotational velocity, viscosity of polymer solution, rotation time and ramping –up rate for optimum conditions. Prepared films are characterized by X-ray diffraction, scanning electron microscopy-X-ray fluorescence and Fourier-transform infrared spectroscopy, the obtained results show the good insertion of MB into different support. The deposition on PVC increase the distance basal of materials. The efficiency of our prepared films was evaluated through the degradation of some dyes such as tartrazine (TR) and methyl orange (MO), using photoreactor upon irradiation with visible light and air injection. The obtained results show a significant efficiency of the films in the degradation of MO and TR. The TR degradation yields obtained vary from 72% to 76% for films containing 5% MB, and a yield close to 99% for the degradation of MO.

*Keywords:* Photodegradation process; Sol–gel films; Spin-coating technique; Dip-coating; Photosensitizer; Organoclays; Polymer-clay hybrids

## 1. Introduction

Industrial development has grown exponentially in several areas such as pharmaceuticals, textiles, paints and varnishes, etc.

The majority of these infrastructures use large quantities of water, which subsequently leads to a large contamination of these waters by organic contaminants harmful to human health and the environment.

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In order to avoid the dispersion of these contaminants into the environment, it is imperative that wastewater be treated by physical or chemical means.

Among the physical processes, clays have attracted the interest of researchers and have proven their incomparable effectiveness in the decontamination of wastewater with its good adsorption capacities [1–4]. The most effective species used in water purification is natural bentonite and sodium montmorillonite, but their fine size less than 2 μm restrains its applications in the treatment of industrials effluents, because it necessary required an others treatment for separate the clays from water such as flocculation or high speed centrifuging. However, porous granular clay [5], porous beads [6] and immobilisation of clays on different supporting materials such as polymers [7–9] are considered a solution to remedy this difficulty.

Polymeric supporting are relatively easy to synthesise, use and flexibility. Nevertheless, polymers must have required certain performance as excellent stability and miscibility with clays. In some cases, clays need to be altered in order to make miscible with polymers. For example, the immiscibility of clays with hydrophobic polymers, namely polystyrene, polyvinyl chloride (PVC), polyethylene, polypropylene, etc., can be corrected by treating clays with surfactant. Research on polymer clay composites and nanocomposites has been motived by Toyota in the early 1990s when discovered nylon-6-clays hybrids [10]. Since that time, innovative research in this field has exploded. One of the most applications of polymers clay hybrids is the removal of organic pollutants from water [11–14]. The majority of these works used the adsorption capacity of clays for the removal of contaminants.

Another process for treatment of wastewater is the photosensitization by generation of singlet oxygen. This process involves a photosensitizers using visible light in the presence of $O_2$. The photosensitizers is supported on the clay, the observed phenomena will be adsorption–photodegradation of pollutants [15,16]. The clays are used as immobilising material due to their large surface area and chemical stability [17].

The objective of the study is (1) to elaborate new PVC/modified clays/photosensitizer hybrid thin film with sol–gel technology, (2) and application in photodegradation of some dyes.

Tartrazine (TR) and methyl orange (MO) were chosen for the present research as a model pollutant dye. Tartrazine called by other names included E102 (EFSA), FD&C Yellow 5 (FDA-U.S. Food and Drug Administration, FDA) or C.I. 19140 (Color Index International). it is certified as a colorant by FDA for its use in food, drugs and cosmetics. Tartrazine's chemical name is trisodium-5 hydroxy-1-(4-sulfonatophenyl)-4-(4-sulfonatophenylazo)-H-pyrazole3-carboxylate and incorporates azo bonding (–N=N–) in its form. Its chemical structure is presented in Fig. 1.

Methyl orange (MO) is an anionic dye preferred International Union of Pure and Applied Chemistry name sodium 4-{[4-(dimethylamino)phenyl]diazenyl}benzene-1-sulfonate. MO is one of the very common water-soluble azo dyes (commonly known as a pH indicator) that is extensively used in several industries including the textile, paper, printing, and food industries and mostly discharged in industrial wastewater. Its chemical structure is presented in Fig. 2.

Here, the choice of tartrazine and methyl orange as the target pollutants, because of its difficult biodegradability.

## 2. Experimental section

### 2.1. Materials

The natural clay bentonite (Bt) used in this study was sampled from mining site in Maghnia located in the west of Algeria. The principal characteristic was previously cited [18,19]. Sodium montmorillonite (Na-Mt) with a cation exchange capacity CEC = 78 meq/100 g was prepared from natural bentonite [20]. The cetyltrimethyl ammonium bromide (CTAB), the dimethylformamide, the tetrahydrofuran, the methylene blue (MB), the tartrazine and methyl orange were used without prior purification. The polyvinyl chloride (PVC) used with $M_W$ = 62,000 g/mol, $M_n$ = 35,000 g/mol from Aldrich Company (United States).

### 2.2. Methodology

#### 2.2.1. Preparation of modified organoclay with photosensitizers

The organo-bentonite and organo-montmorillonite, noted CTA-Bt and CTA-Na-Mt were prepared by dispersing an amount of clay with CTAB in Milli-Q water. After purification and drying of powders, the methylene blue (MB) was inserted on the surface of the powders at different percentages (0.5%, 1%, 5%, 10%, 15%, 20%, 25%, 30% and 35% of MB). Prepared powders were noted as % MB-Bt, % MB-CTA-Bt and % MB-CTA-Na-Mt.

All the synthesis procedures were described in our subsequent work [21].

#### 2.2.2. Elaboration of the hybrid material PVC/hydrophobic modified clay with dip-coating deposition

Before any manipulation, we must perform swelling tests of hydrophobic (Hc) in organic solvents. Because PVC

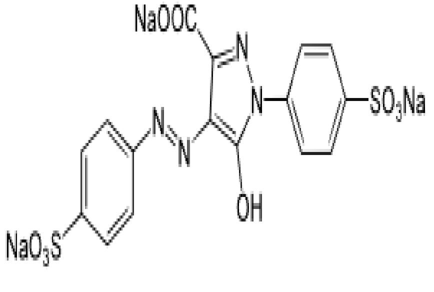


Fig. 1. Chemical structure of tartrazine.

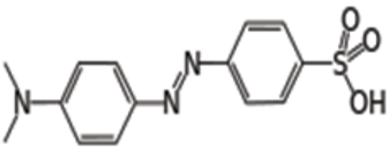


Fig. 2. Chemical structure of methyl orange.

is soluble in tetrahydrofuran (THF) and dimethylformamide (DMF), these two solvents were chosen for swelling test. Another parameter to be considered is the compatibility test between PVC and Hc.

We elaborate a thin film of PVC/Hc using sol–gel process with dip-coating technique. The assembly is made in our laboratory. The dip-coating involves the immersing a substrate (in our case a glass), and then lifting from the solution with a constant velocity. The substrates are then dried, and the solvent evaporated.

In a beaker, 4 g of PVC was dissolved in 50 mL of DMF. After dissolution of polymer, different amounts of Hc (10, 15, 20, 25, 30 and 40 mg) in DMF were incorporated into PVC solution. The substrate is a glass with dimensions (3 cm ′ 5 cm), the substrate was immersed in the PVC/Hc solution at a constant velocity for different soaking numbers (3–6). After each immersion, the film was dried using hair dryer. All the films prepared in this study were preserved for a possible application to photodegradation.

### 2.2.3. Elaboration of the hybrid material PVC/hydrophobic modified clay with spin-coating deposition

The spin-coating technique is commonly used to produce thin and uniform films on flat substrates [22]. PVC is considered to be the most widely used polymer in this technique. The spin coater used in this study is the model SUSS MicroTecRCD8.

The principle of the process consists in dissolving a known quantity of the polymer in a preferably volatile solvent such as THF. The solution is deposited on a horizontally rotating disc equipped with a glass substrate with dimension of 3 cm × 5 cm. The rotation generally goes through bearings that allow controlling the thickness of the films.

To optimize and control the thickness of the films, several parameters have been studied such as the viscosity of the PVC in the THF, the number of layers, the rotation speed, rotation times and the variation of the mass of modified clay. These parameters are:

- Viscosity of PVC/THF is: 5%, 10%, 15% and 20%.
- Number of layer: 1, 2, 3, 4, 5 and 6 layers.
- Rotation speed: 0–3,000 rpm with different bearing.
- Rotation times: 0–90 s.
- Weight ratio modified clays/PVC: 5% and 10%.

After optimisation, the program chosen in our study is illustrated in Fig. 3, with 10% of viscosity of PVC/THF.

To this solution (10% of PVC in THF), several quantities of Hc (0.5%, 1%, 5% and 10% of Hc in PVC) with different percentages of MB were added. All prepared films were preserved for a possible application to photodegradation.

### 2.2.4. Photodegradation

In order to study the efficiency of prepared thin films in the degradation of organic pollutants, we have chosen two types of dyestuff, tartrazine (TR) toxic food dyes and methyl orange (MO) (azo dye) an anionic dye. Physico-chemical properties of tartrazine and methyl orange are presented in Table 1.

The photodegradation was carried out in a glass photoreactor, equipped with air injection pump, a pH meter and a thermometer.

Degradation tests of MO were carried out on films prepared by dip-coating technique. On the other hand, the TR has been degraded using films elaborated by spin-coating technique.

In the reactor, 50 mL of a solution of dye (TR or MO) with known concentration is mixed with PVC/modified clays film in the dark to establish the adsorption–desorption equilibrium between a dye and material hybrid. The parameters such as pH, time of contact were varied during the different sets of batch experiment. pH of the solution was adjusted before addition of film using 0.1 N $HNO_3$ and 0.1 N NaOH.

The photosensitization reaction was carried in an open reactor, which was irradiated under visible radiation by a high-pressure sodium lamp through a solution filter (1 mM of potassium chromate $K_2CrO_4$ in aqueous solution of 0.22 M sodium carbonate $Na_2CO_3$) [23]. The wavelengths of radiation are >450 nm.

The conditions required in the photodegradation tests of TR are:

- 50 mL of TR with concentration: 5 and 10 mg/L.
- Thin film with surface area of 15 and 30 cm$^2$.
- 5% and 10% of Hc/PVC with different proportion of MB on organoclay: 0.5%, 1%, 5%, 10%, 15%, 20%, 25%, 30% or 35% of MB in 50 mL in batch fixed bed photoreactor.
- Temperature: $T = 298$ K.
- Optimal pH = 5.
- Irradiation times: 0–210 min.
- Under visible light, and sun light.

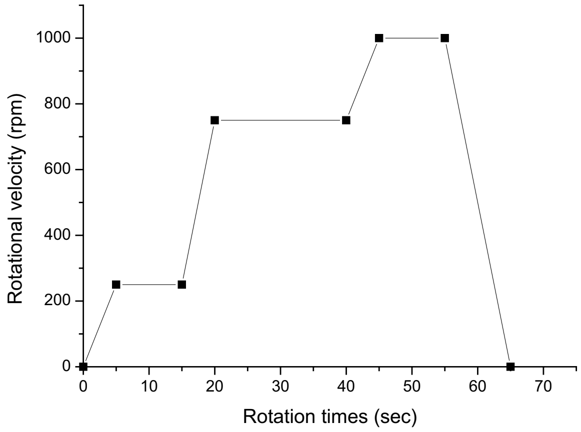


Fig. 3. Spin-coating technique rotation program.

Table 1
Relevant characteristics of tartrazine and methyl orange

| Name | Molecular (g/mol) | $\lambda_{max}$ absorption (nm) | Color |
|---|---|---|---|
| Tartrazine | 534.36 | 427 | Yellow 23 |
| Methyl orange | 327.34 | 464 | Orange |

The conditions required in the photodegradation tests of MO are:

- Thin film with surface area of 15 and 30 cm$^2$.
- 10% of modified clay/PVC with different proportion of MB on organoclay contain 5% of MB in 50 mL in batch fixed bed photoreactor.
- Temperature: $T = 298$ K.
- Optimal pH = 3.
- 50 mL of MO with concentration: 10, 25 and 50 mg/L.
- Irradiation times: 0–210 min.
- Under visible light.

The adsorption performance of TR and MO into thin film hybrid was estimated and calculated using the Eq. (1):

$$R\% = \frac{C_0 - C}{C_0} \times 100 = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

where $C_0$ (mg/L) is the initial concentration of pollutants, $C$ (mg/L) is the concentration at time $t$ (min), or $A_0$ is the initial absorbance (Abs), $A$ is value of absorbance at the time $t$ of UV-Vis.

Since the objective of this work is the elaboration of a film with economic interests in the field of industrial waste treatment, we have carried out a comparative study with powders. To do this, we would have to deduce the mass of the powders on each film. For example, if the mass of a film that contains 10% of Hc is equal to 10 mg, by a simple calculation it is assumed that the mass of the powder is equal to 0.7 mg.

## 3. Results and discussion

### 3.1. Characterisation of modified clays

The characterization of powders is quoted in the following reference [21]. Nevertheless, we consider it useful to present briefly the main characteristic results of Hc.

The attenuated total reflectance-Fourier-transform infrared (ATR-FTIR) spectroscopy of different materials (Fig. 4) confirmed the good insertion of photosensitizer, by appearance of bands at 1,590 cm$^{-1}$ corresponding to aromatic C=N bending and 1,336 cm$^{-1}$ corresponding to C–N bending [21].

Examination of the X-ray diffraction spectra of 5-MB-Bt, 5-MB-CTA-Bt and 10-MB-CTA-Na-Mt (Fig. 5) confirms the correct insertion of the photosensitizer:

- Adsorption of MB on natural bentonite caused a decrease in basal distance from 14.71 Å (θ = 6° for Na-Bt) to 14.15 Å (θ = 6.1° for MB-Bt).
- 5-MB-CTA-Bt has a basal distance 18.8 Å (θ = 4.59°) greater than 5-MB-Bt.
- Modification of montmorillonite by CTAB and then MB causes an increase of the basal distance from 12.58 Å (θ = 7.02° for Na-Mt) to 20.15 Å (θ = 4.38° for 10-MB-CTA-Na-Mt).

After insertion of MB on 10-MB-Bt, the Brunauer–Emmett–Teller surface area and porosity of 10-MB-Bt corresponds to non-porous or macroporous solids, because it is type III according to the International Union of Pure and Applied Chemistry classification (Fig. 6) [21]. The non-porous structure of the clay surface will certainly disfavour the adsorption phenomenon, and leaves a strong possibility for degradation by photosensitisation. This hypothesis will be verified by the tests we will carry out.

### 3.2. Characterisation of thin hybrid film PVC/modified clay hybrid

The films were produced using the sol–gel process with two deposition techniques: dip-coating and spin-coating. Two parameters have to be checked during the synthesis of these films: we should to find a solvent that would be able to completely dissolve the polymer and swell the Hc. The second point is to find the polymer that will be compatible with the hydrophobic clay. After several laboratory tests, we opted for PVC as the polymer and the two solvents DMF and THF.

THF is very volatile, so it will be used in the spin-coating technique. On the other hand, DMF is a very heavy solvent, so we will use it in the dip-coating technique.

An important release phenomenon has been observed by bringing the Hc in contact with the DMF, the film formed by dip-coating takes the blue colour of the MB. It remains to be verified whether this release phenomenon affects the efficiency of thin films on the photodegradation of pollutants.

The ATR-FTIR spectroscopy of film is shown in Fig. 7. The MB molecules are confirmed the presence of bands located at 1,590 cm$^{-1}$ C=N links. The bands at 2,970 and 2,915 cm$^{-1}$ assigned to CH$_2$ belong to PVC chains.

It should be noted that, the deposition of the 5-MB-CTA-Bt and 10-MB-CTA-Na-Mt on the PVC caused a remarkable increase of the basal distance (26.59 and 22.40 Å, respectively). Whereas with the 5-MB-Bt the distance remains practically unchanged (14.71 Å). The different graphs are shown in Fig. 8A–C.

The polymer/modified clay were examined for their morphology by scanning electron microscopy using Quanta 650 with low vacuum mode. The morphology becomes rough with addition of different modified clay as shown in Fig. 9.

The rough morphology was resulted by agglomeration of modified clay in the polymer matrix, which was caused by undistributed of clay fillers in the polymer matrix resulting by the absence by the dispersing agent. Sarkar et al. [24] stated that the clay tends to be exfoliated as individual silicate layers separated in the polymer matrix by average distances that depend only on the clay loading.

### 3.3. Tests of photodegradation on different support

For economic reasons, and because there was not a large difference in the results obtained between 5% and 10% of PVC/THF, we are going to prepare PVC solutions with a viscosity of 5%.

Before each experiment, the dye and the films hybrids were put in contact in the absence of irradiation for 2 h at 25°C to reach an adsorption–desorption equilibrium at optimum pH.

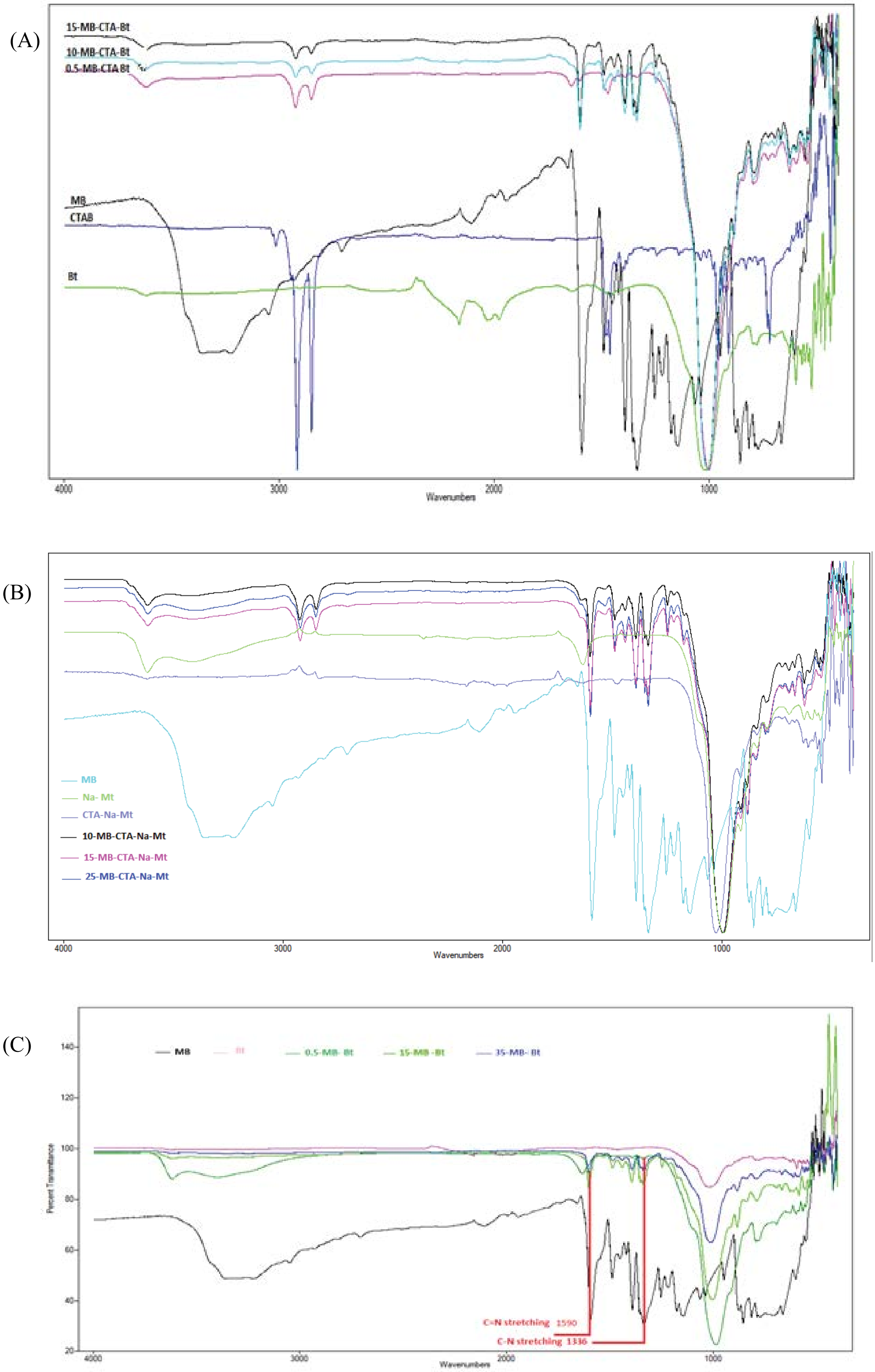


Fig. 4. ATR-FTIR spectra of: (A) MB-CTA-Bt, (B) MB-CTA-Na-Mt and (C) MB-Bt.

The photodegradation results of 5 mg/L of TR onto different thin film prepared by spin-coating technique with surface area of 15 $cm^2$ are illustrated in Fig. 10.

The photodegradation of tartrazine on the different films gives a good yield. However, the decomposition is very slow, it takes more than 90 min for the degradation to reach a yield of about 30%. This may be due to photolytic resistance of tartrazine under visible light [25]. Yield results are very similar with all three materials, with a small improvement with MB-CTA-Na-Mt. We also note that materials that contain 1% and 5% of the photosensitizers give the best degradation yields. On the other hand, with materials containing 20%, 25%, 30% and 35%, the degradation yields are low with the appearance of a phenomenon of release of the photosensitizer into the solution. The release is confirmed by the appearance of a band at 664 nm by characterizing the tartrazine solution by UV-Vis spectroscopy.

### 3.3.1. Reusability of 0.5-MB-Bt/PVC thin film

To assess the reusability of 0.5-MB-Bt/PVC film, after the first use, the thin film was washed with distilled water and dried at ambient temperature. Afterwards, a new tartrazine solution with same concentration 5 mg/L was put in contact with the film, and the same procedure was adopted. For this, we tested three uses of the film. The results presented in Fig. 11 show that 61.22% of degradation was obtains after 210 min. After the second use, 59.78% of tartrazine was degraded which corresponds to 1.45% of efficiency loss. After the third use, 49.5% of tartrazine was degraded, and correspond to 10.62% of efficiency loss.

This loss of efficiency is due to the detachment of clay particles on the polymer matrix during the second use or cleaning step [25–27].

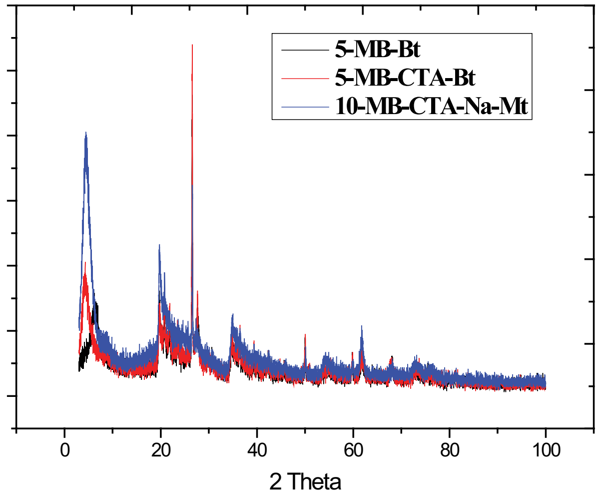


Fig. 5. X-ray diffraction patterns for different modified powders.

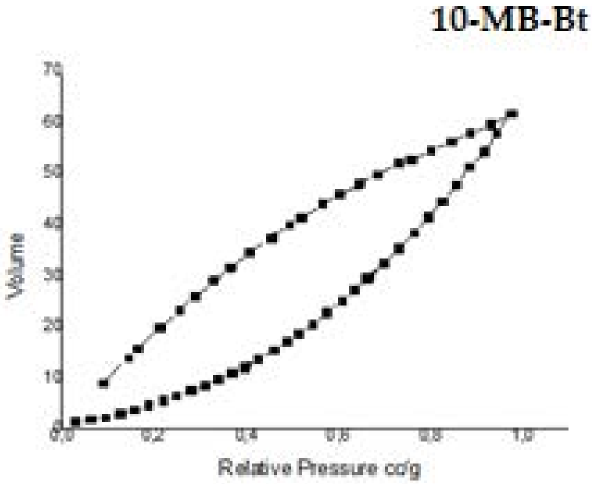


Fig. 6. Curves of nitrogen adsorption/desorption isotherms of 10-MB-Bt.

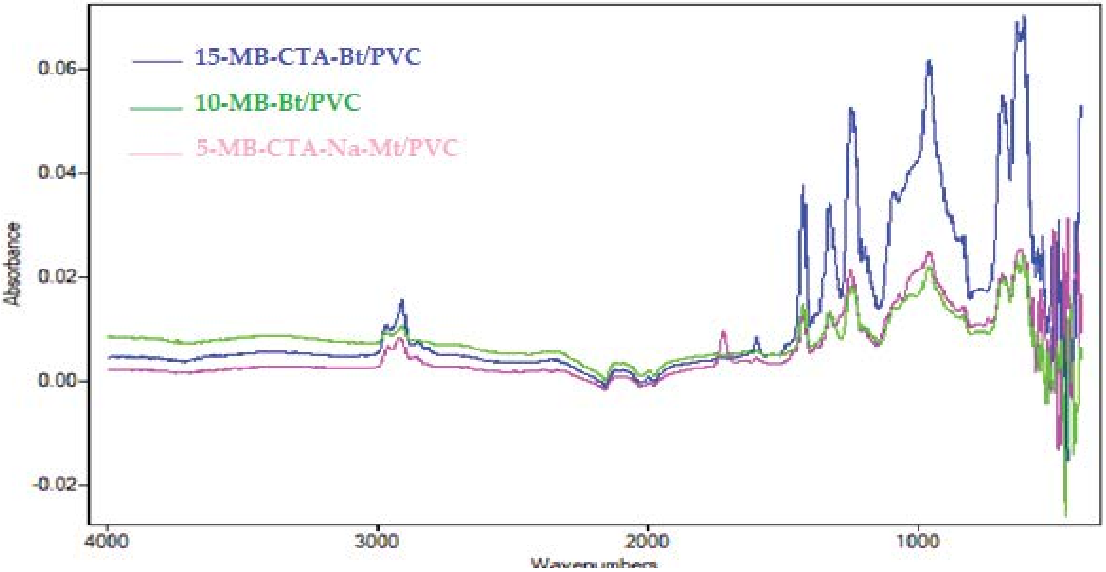


Fig. 7. ATR-FTIR spectra of thin films prepared with spin-coating technique.

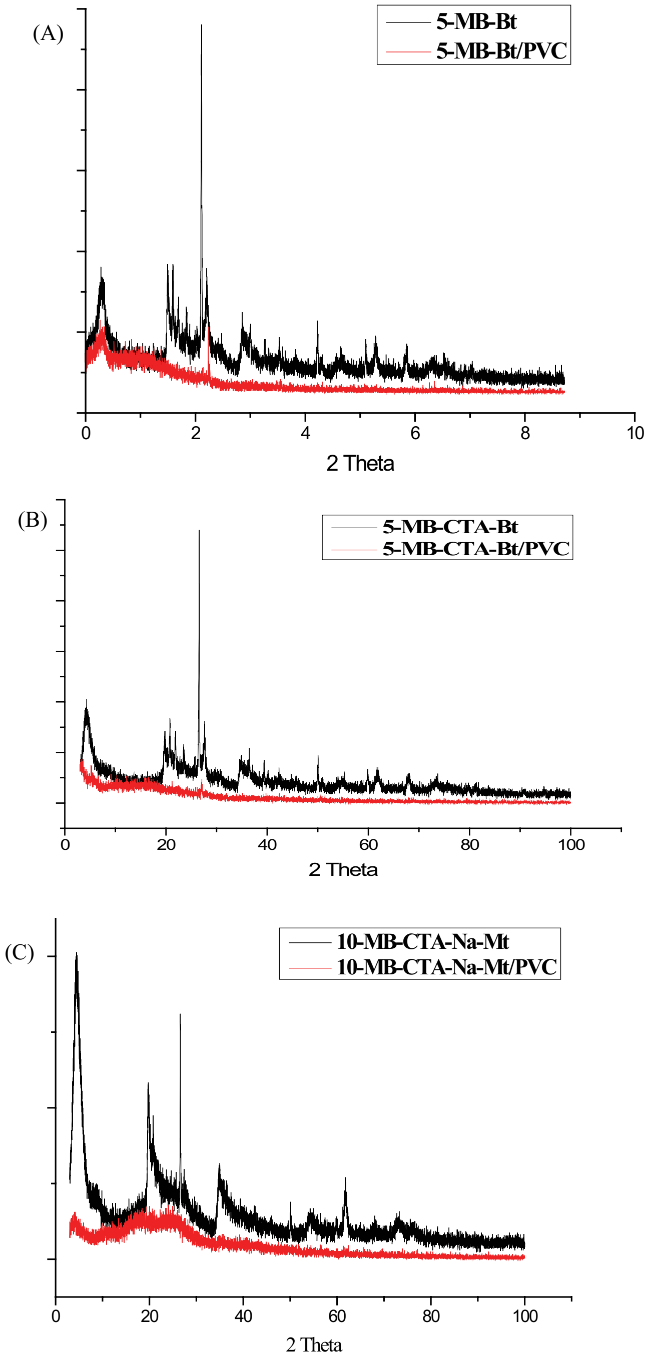


Fig. 8. X-ray diffraction patterns for different modified powders and corresponding thin films.

### 3.3.2. Effect of initial concentration of tartrazine

We study the effect of initial concentration of tartrazine on degradation yields with 5-MB-Bt after 210 min. We have chosen two concentrations 5 and 10 mg/L. The results are illustrated in Table 2. It was found that there is a relationship between the percentage of photodegradation and the initial concentration of the dye. The concentration decrease from 88.88% to 76.58% with increasing concentration of the dyes from 5 to 10 mg/L. The rate of photodegradation is related to the availability of active sites present on the surface of the material. The high concentration of pollutants reduces the adsorption of visible light by photosensitizers, leading to lower photodegradation efficiencies. The same phenomena is observed in catalysis reaction [25,28].

### 3.3.3. Effect of area surface of thin film

In this party, we used 5 mg/L of tartrazine on 5-MB-Bt/PVC with two area surfaces 15 and 30 $cm^2$ after 5 h of radiation exposure. The increase of the film surface leads to a clear increase of the degradation yield from 81.88% to 88.98%.

The results are illustrated in Table 3.

### 3.3.4. Comparative study between the film and the corresponding powder

In our work cited in reference [21], we have study the photodegradation of tartrazine on several powder of Hc. The quantities of the powdered materials correspond perfectly to those present on the polymer. The results of this comparative study are illustrated in Fig. 12. The histogram shows the results of the photodegradation of 5 mg/L of tartrazine on powders and films with 5% MB for an exposure time of 210 min.

Even if powders are very efficient in photodegradation, their use in continuous systems remains limited because of the problem of powder entrainment. The immobilization of the powder on film form is recommended.

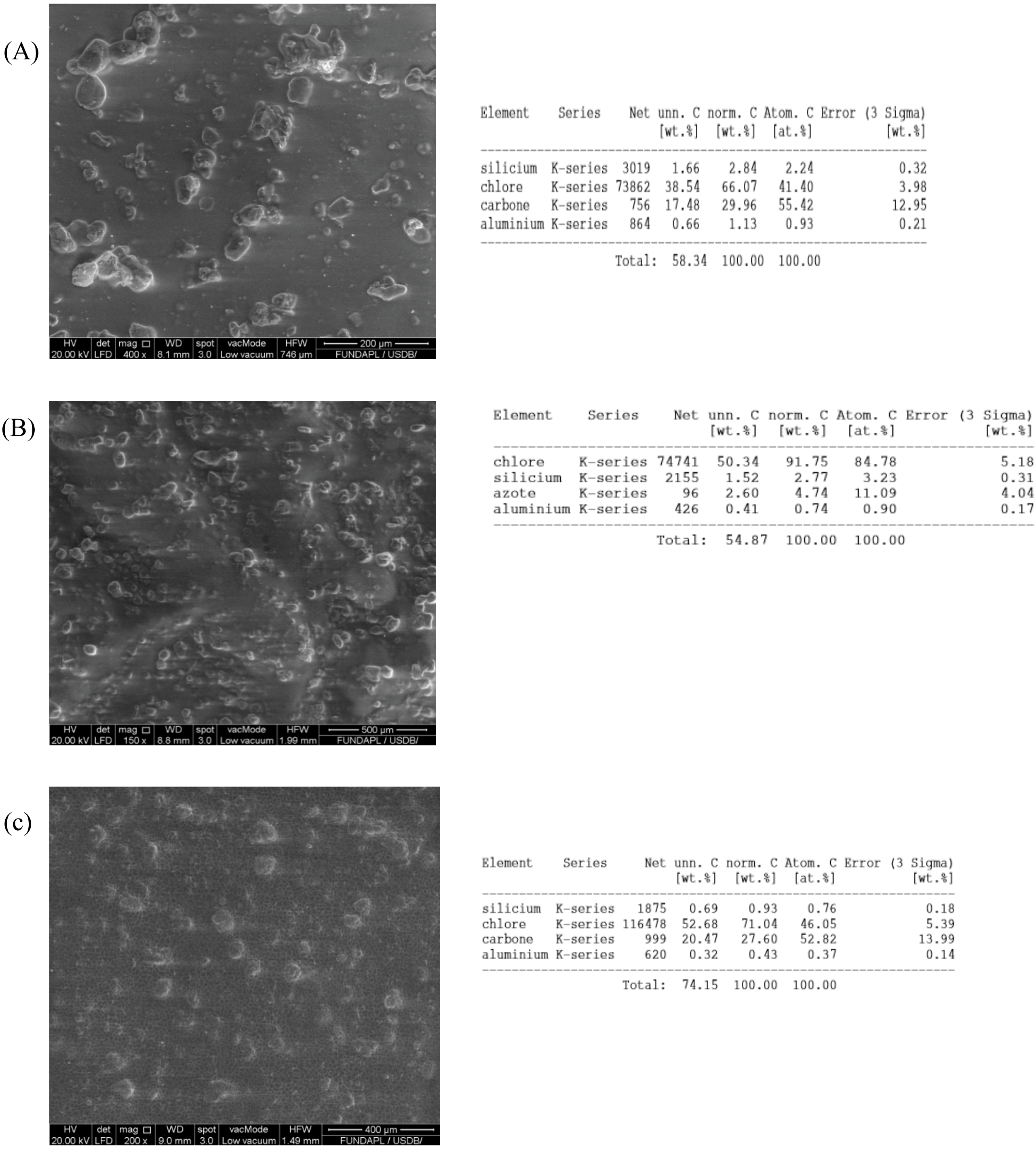
### 3.3.5. Photodegradation of methyl orange onto film elaborated with dip-coating technique

Due to the MB release phenomenon in the DMF solution observed during film preparation (which is not the case for films prepared in THF), it was impossible to predict the amount of MB adsorbed on Hc.

To test the efficiency of these films in the photodegradation of MO, we mixed 10 mg of Hc containing 10% MB with the solution of PVC in THF. Obviously, this percentage cannot be taken into account, which leads us to note the Hc per MB-Bt and MB-CTA-Na-Mt.

As shown in Figs. 13 and 14, the degradation at different concentrations of MO is very rapid. After 5 min, a photodegradation efficiency of 96% is achieved on a 6-layer 5-MB-Bt/PVC film with an initial concentration of 10 mg/L of MO. This rate increases to 99.61% after 180 min. The multiplication of the number of layers improves the efficiency of the film in photodegradation, for example, a film with 3 layers degrades 90% of the MO whereas one can reach 99.61% degradation with a 6-layer film.

Photodegradation tests were performed by examining the effects of irradiation time (0–180 min) with different concentrations of MO on MB-Bt/PVC films with 6 layers. The corresponding results presented (Fig. 14) clearly show that at concentration of 10 mg/L of MO, the efficiency of dye degradation increases rapidly to 96.04% after 5 min, while the maximum photodegradation is obtained after 180 min with 99.61% photodegradation.



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Element    Series     Net unn. C norm. C Atom. C Error (3 Sigma)
                          [wt.%]  [wt.%]  [at.%]          [wt.%]
-----------------------------------------------------------------
silicium  K-series  3019   1.66    2.84    2.24             0.32
chlore    K-series 73862  38.54   66.07   41.40             3.98
carbone   K-series   756  17.48   29.96   55.42            12.95
aluminium K-series   864   0.66    1.13    0.93             0.21
-----------------------------------------------------------------
                 Total:  58.34  100.00  100.00
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Element    Series     Net unn. C norm. C Atom. C Error (3 Sigma)
                          [wt.%]  [wt.%]  [at.%]          [wt.%]
-----------------------------------------------------------------
chlore    K-series 74741  50.34   91.75   84.78             5.18
silicium  K-series  2155   1.52    2.77    3.23             0.31
azote     K-series    96   2.60    4.74   11.09             4.04
aluminium K-series   426   0.41    0.74    0.90             0.17
-----------------------------------------------------------------
                 Total:  54.87  100.00  100.00
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Element    Series      Net unn. C norm. C Atom. C Error (3 Sigma)
                           [wt.%]  [wt.%]  [at.%]          [wt.%]
------------------------------------------------------------------
silicium  K-series   1875   0.69    0.93    0.76             0.18
chlore    K-series 116478  52.68   71.04   46.05             5.39
carbone   K-series    999  20.47   27.60   52.82            13.99
aluminium K-series    620   0.32    0.43    0.37             0.14
------------------------------------------------------------------
                  Total:  74.15  100.00  100.00
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Fig. 9. Scanning electron microscopy images of the sample (A) 5-MB-Bt/PVC, (B) 5- MB-CTA-Bt/PVC and (C) 10-MB-CTA-Na-Mt/PVC.

With a concentration of 25 mg/L of MO, the photodegradation increases to reach 69.84% after 5 min and 89.36% after 180 min then it stabilizes.

Finally, at a concentration of 50 mg/L of MO, the photodegradation increase to reach a photodegradation maximum of 79.6% for 180 min.

The same phenomena were observed with MB-CTA-Na-Mt with values close to those obtained with MB-Na-Bt (Fig. 15). Thin films prepared with 6 layers prove their efficiency in the photodegradation of MO, a rate of 99.73% was obtained with 10 mg/L of MO. However, this rate decreases when the concentration of the pollutant increases, that is, 81.44% with 25 mg/L of and 79.44% with a solution of 50 mg/L of MO. This phenomenon has been reported in several studies on photocatalysis [29–31]. High concentrations of pollutants lead to saturation of the surface of the

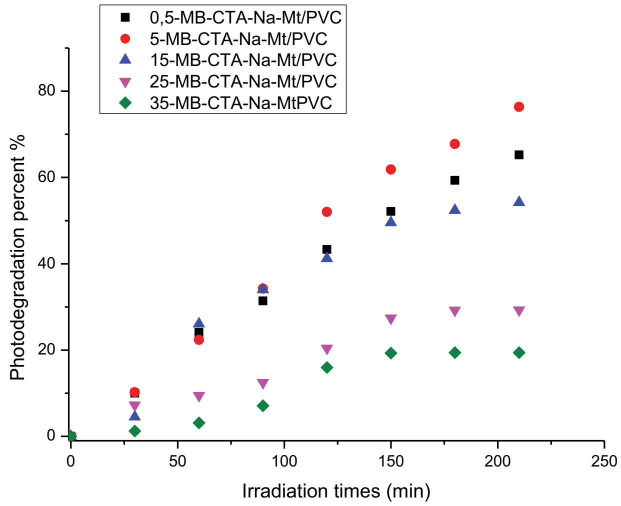

Fig. 10. Shows the results of photodegradation of 5 mg/L of tartrazine on 10% of different thin film elaborated by spin-coating deposition.

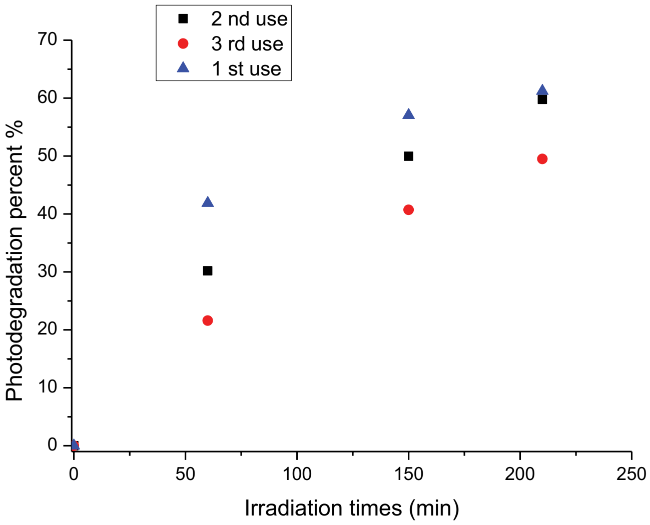

Fig. 11. Photodegradation of tartrazine ($C_0 = 5$ mg/L) with 0.5-MB-Bt in three consecutive uses under 210 min of visible exposure.

Table 2
Effect of initial concentration of tartrazine on 5-MB-Bt

| Initial concentration of tartrazine (mg/L) | Photodegradation (%) |
|---|---|
| 5 | 88.88 |
| 10 | 76.58 |

Table 3
Effect of area surface of thin film

| Area surface ($cm^2$) | Photodegradation (%) |
|---|---|
| 15 | 81.88 |
| 30 | 88.98 |

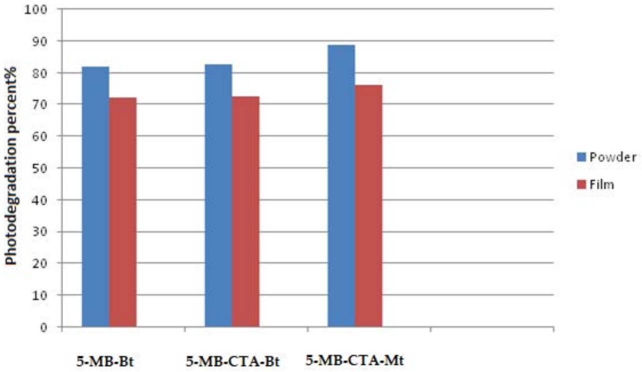

Fig. 12. Histogram which presents a comparative study between the percentage photodegradation of tartrazine on powder and thin film.

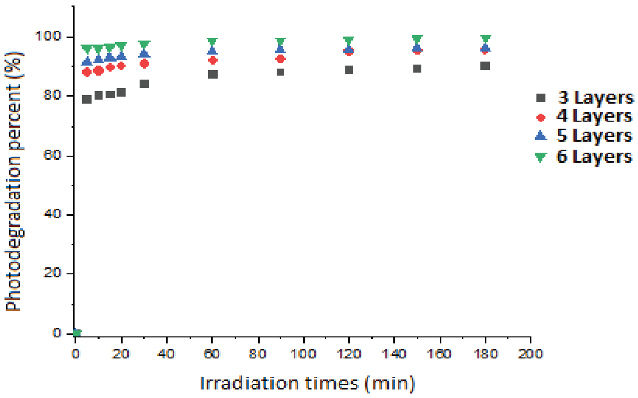

Fig. 13. Photodegradation kinetics of 10 mg/L of MO on multi-layer films at pH = 3.

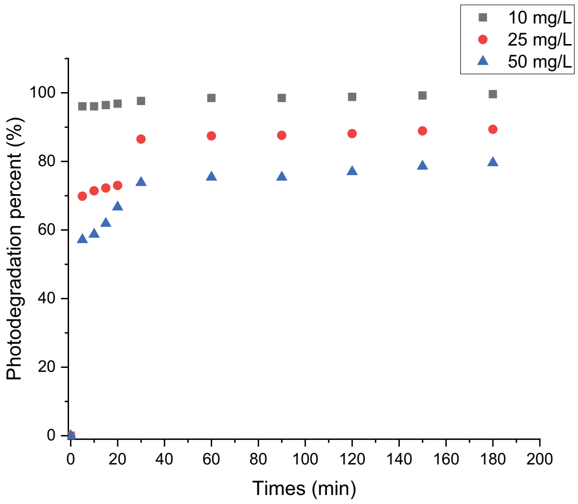

Fig. 14. Influence of irradiation time of MB-Bt/PVC with: 10, 25 and 50 mg/L of MO at pH = 3.

clays, and decreases the absorption of visible light by the photosensitizer, which naturally leads to a decrease in its activity.

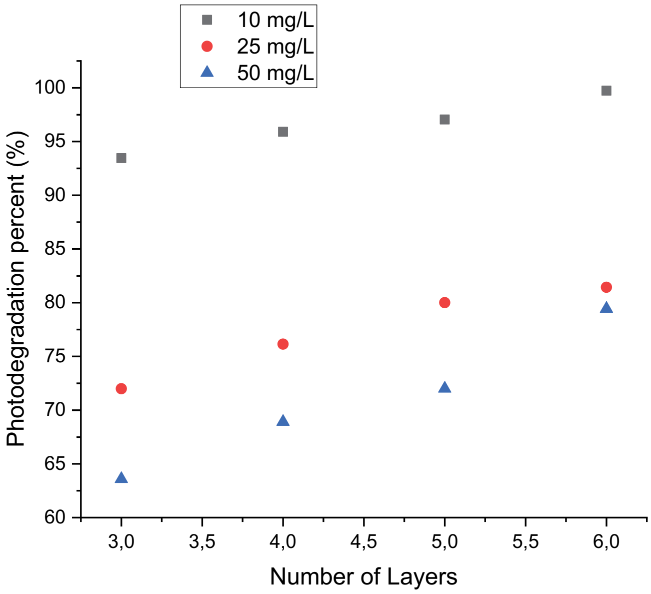

Fig. 15. Influence of irradiation time of MB-CTA-Na-Mt/PVC with: 10, 25 and 50 mg/L of MO at pH = 3.

## 4. Conclusion

New thin film material hybrids were prepared for photodegradation of pollutants with sol–gel process using two methods for deposition: spin-coating and dip-coating. Different hydrophobic clays were used as support for the photosensitizer (in our case methylene blue), then immobilised on PVC matrix. In the preparation of thin film, DMF and THF were utilised as solvent. We observed a good compatibility between PVC and clays modified by methylene blue.

During the elaboration of the films by dip-coating in DMF, we observed a significant release of the photosensitizer in the solution. The hybrid film obtained is colored by methylene blue.

In THF, the release did not occur on the powders with 0.5%, 1%, 5%, 10%, and 15% of methylene blue. On the other hand, we observed a less important leaching on the other powders with 20%, 25%, 30%, and 35% of MB.

In the application part, the photodegradation tests on the two dyes tartrazine and methyl orange were evaluated by establishing adsorption and photodegradation kinetic curves.

In general, we could access the following information and conclusions:

- The pseudo-equilibrium times obtained by the photosensitized clay powders and the hybrid films are around 2 h.
- The adsorption tests of the pollutants on the different supports present lower rates, which eliminates the hypothesis of adsorption of the pollutant on the clay instead of a photodegradation.
- The effects of the parameters used in this study in terms of pH, the initial concentration of the dye, the time of exposure to the irradiations, the type of adsorbent remain the most important and essential factors which condition the process of photodegradation.
- At low initial concentrations of the pollutants, the photodegradation is better in terms of yield.
- The degradation of methyl orange is very fast, it reaches yields of the order of 99%.
- The degradation of tartrazine is slow, the yields are about 88%.

## Acknowledgment

The films produced by the spin-coating technique were developed at the Centre de Recherche en Technologie des Semi-Conducteurs pour l'Energétique (CRTSE) CMSI Algiers, under the direction of DR Aissa KEFFOUS, whom he finds here the expression of our sincere thanks for their contributions and help.

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