

Synthesis and characterization of a novel support based on hydrophobic clays and a Photosensitizer. Application to photodegradation of dyes

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ARTICLE INFO

Article History :

Received : 01/01/2020

Accepted : 05/06/2020

Key Words:

Photodegradation;
Adsorption,
Photosensitizer;
Organoclays;
Dyes.

ABSTRACT/RESUME

Abstract: The aim of this present study is to synthesise a series of new hydrophobic- modified organo montmorillonites (Hc) using two photosensitizers both methylene blue (MB) and Hematoporphyrin (HP). First, we modified a series of natural bentonite (NB) and sodium montmorillonite (Na-Mt) with a surfactant cetyltrimethyl ammonium bromide (CTAB). The incorporation of methylene blue and Hematoporphyrinas photosensitizers into Hc was carried out at various hydrophobic clay/ photosensitizers (2, 5, 10, 15 and 20% of HP and 0.5, 1, 5, 10, 15, 20, 25, 30 and 35% of MB) at room temperature. A kinetic study was carried out by varying the contact time, the pH of suspension and the adsorbate/ adsorbent ratio. In the second step, we studied the efficiency of prepared support in the photodegradation of Tartrazine (TR), Methyl Orange (MO) and Rhodamine B (RB) by irradiation with visible light irradiation under oxygen atmosphere $\lambda > 450$ nm. The obtained results indicated that the increase of dyes concentration, decrease the adsorption yield photodegradation. The photosensitizers properties of MB were better than those of HP onto Mt-CTAB-MB with efficiencies of about 67.29 to 88.27% at different concentration of MO.

I. Introduction

The dyestuff industries are one of the largest sources of contamination of water and the environment. In fact, the wastewaters generated from these industries are characterized by a high content of pollutants, especially those generated by textile industries with about 15% dyes.

In recent years, a lot of research has been done to eliminate and / or reduce the concentration of waste water. Among these methods, we found biological ones which are based on combined enzymatic degradation (aerobic and anaerobic), microbial biomass uptake, algal degradation and microbial

cultures [1-6]. The physicochemical methods used are advanced oxidation, electrochemical destruction, Fenton reaction oxidation, ozonation, photochemical and ultraviolet irradiation [6-11], adsorption, coagulation and flocculation, ion exchange, membrane filtration, nanofiltration, ultrafiltration and reverse osmosis [6, 12-16]. Photodegradation is another process that has been used in the treatment of waste water. Some clays have been found to be able to eliminate some organic pollutants without or in the presence of photosensitizer at visible light [17-19]. In photodegradation, the use of the photosensitizer generates singlet oxygen which can be

successfully inserted into hydrophobic clays. In this context, several modified clays were used in the adsorption tests of several water-soluble pollutants. Modified organo clays materials (natural and purified sodium) have been widely used in the decontamination of water [20-23]. A lot of studies about the use of modified organo clay with photosensitizers which have done a good results in photodegradation of pollutants [18, 19, 24, 25]. The objective of this study is summarised in the following points: (1) synthesis of hybrid composites (modified clays/ photosensitizer), (2) Application in photodegradation of Tartrazine (TR), Rhodamine B (RB) (a cationic dye) and methylOrange (MO) (an anionic dye).

II. Experimental

II.1. Materials

The natural bentonite (Na-Bt) used in this study was sampled from mining site in Maghnia located in the west of Algeria. The principal characteristic was previously cited [26, 27].

Sodium montmorillonite (Na-Mt) having cation exchange capacity of CEC= 78 meq. 100.g⁻¹ was prepared from an Algerian natural bentonite [27]. Cetyltrimethyl ammonium bromide (CTAB) (Sigma- Aldrich; Chemical formula: (CH₃)₃N(CH₂)₁₅CH₃Br, Molecular weight: 360.00g.mol⁻¹) were used in the co-insertion of the Na-Mt and Na-Bt solid. The obtained organo clay CTA-montmorillonite is symbolized by CTA-Na-Mt, and CTA-natural bentonite by CTA-Na-Bt.

Methylene blue (MB) (Sigma- Aldrich; Chemical formula: C₁₆H₁₈ClN₃S, Molecular weight: 319.85 g.mol⁻¹, λ_{max} = 664 nm, pKa = 3.8) and Hematoporphyrin (HP) (Sigma- Aldrich; Chemical formula: C₃₄H₃₈N₄O₆, Molecular weight = 598.6887 g/mol, λ_{max} = 398 nm) were used as photosensitizers.

Methyl orange (MO) Tartrazine (TR) and rhodamine B (RhB) have been used as pollutants in various adsorption systems in aqueous media (mono, ...binary).

The chemical structure of the used pollutants (TR, MO and RhB) are shown in the figure 1:

II.2. Preparation of organoclay

Organic clays (organobentonite and organomontmorillonite, noted CTA-Bt and CTA-Na-Mt) were synthesized by cation exchange reaction between CTA⁺ and Na⁺ cations at saturated level of CEC.

The procedure of the preparation of these organoclays consists of dispersing 5 g of each clay in 500 mL of MilliQ water. The two suspensions

were stirred vigorously for 24 hrs at room temperature using a magnetic stirrer. After that, the obtained suspensions were immediately treated slowly by adding a solution of 0.03M CTAB (1.09 g in 100 mL MilliQ water), and stirring for a period of 12 hours at room temperature.

The prepared solid were washed several times with distilled water, and then dried in oven at 40°C for 24 hours.

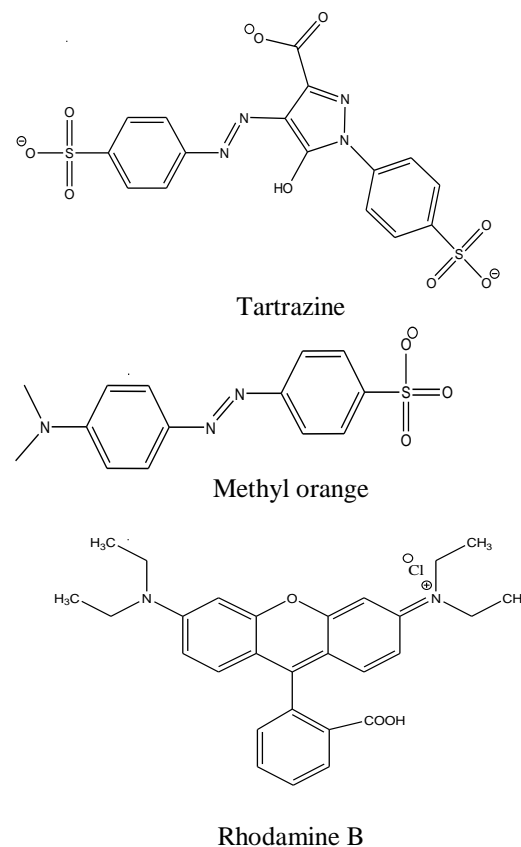


Figure 1. Chemical structure of used pollutants

II.3. Intercalation of organoclays with photosensitizer

In this work, methylene blue (MB) and hematoporphyrin (HP) were used as photosensitizers.

The solid materials MB-CTA-Na-Bt, MB-NBt and MB-CTA-Na-Mt were prepared by co-adsorption of different amounts of MB to NBt, CTA-NBt and CTA-Mt under stirring.

The kinetic adsorption studies, was taken out by mixing 0.01g of each prepared solids with 150mL of MB at various percentages (0.5, 1, 5, 10, 15, 20, 25, 30 and 35%) in MilliQ water as solvent. All obtained samples at different pH values (2 to 11) at room temperatures were stirred at rate of about 225 cps for an hour of contact times. The residual concentrations of the various solution were

measured by UV- visible spectrophotometer at appropriate wavelength ($\lambda_{\max} = 664 \text{ nm}$)

The same procedure was used with the second sensitizer HP which has prepared in 150 mL of ethanol as solvent. The different used ration HP/0,01 g CTA-Mt are (2, 5, 10, 15 and 20%).

The equilibrium concentrations were measured by spectrophotometry at the appropriate wavelength of HP ($\lambda_{\max} = 398 \text{ nm}$).

II.4. Photodegradation

In this study, we take out the photodegradation of Tartrazine (toxic alimentary azo dye), MethylOrange (anionic, azo dye) and Rhodamine B (cationic and zwitterionic form, two molecular forms). These dyes are considered very toxic and can cause harmful effects on the environment and human health.

The photodegradation was carried out in a batch fixed bed photoreactor, equipped with an air injection pump and pH meter.

Before each experiment, the various systems (pollutant/ modified organophilic hybrid clay) were first stirred at an optimum pH, in the dark for 2 hours to promote adsorption and achieve an adsorption- desorption equilibrium.

The photodegradation reaction was carried in an open reactor, under visible radiation giving by a high- pressure sodium lamp (1000 Watt) through a filter solution containing 1mM of potassium chromate K_2CrO_4 in aqueous solution of 0.22M sodium carbonate Na_2CO_3 [24].

For kinetic and isotherm studies, 50 mL of a dye solution (TR, MO or RB) at known concentration (5 and 10 mg/L of TR, 10, 25 and 50 mg/L of MO and 4, 10, 25 and 50 of RhB) are mixed with 10 mg of modified clays, firstly in the dark, in order to establish the adsorption-desorption equilibrium between the dyes and the used hybrid materials. Different parameters were varied such as effects of pH, contact time. The pH of the suspension was adjusted by adding a few drops of 0.1N HNO_3 and 0.1N NaOH .

The photodegradation conditions of TR are as follows:

- Concentration of suspension of modified organic clay: 10mg contains 0.5, 1, 5, 10, 15, 20, 25, 30 or 35% of MB in 50 mL in batch fixed bed photoreactor.
- Temperature: $T = 298\text{K}$
- Optimal pH = 5
- 50 mL of TR with concentration: 5 and 10 mg.L^{-1} .
- Irradiation times: 0 to 210 min.
- Under visible light

The photodegradation conditions of MO are as follows:

- Concentration of suspension of the modified organic clay: 10mg contains 5% MB in 50mL, under stirring.
- Temperature: $T = 298\text{K}$
- Optimal pH = 3
- 50 mL of MO with concentration: 10, 25 and 50 mg.L^{-1}
- Irradiation times: 0 to 210 min.
- Under visible light

The photodegradation conditions of RhB are as follows:

- Concentration of suspension of the modified organic clay: 10 mg of CTA-Na-Mt contains 2, 5, 10, 15 or 20% of HP in 50 mL, under stirring.
- Temperature: $T = 298\text{K}$
- Optimal pH = 3
- 50 mL of RhB with concentration: 4, 10, 25 and 50 mg.L^{-1}
- Irradiation times: 0 to 210 min.
- Under visible light.

The adsorption performances of TR, MO and RhB into all modified clays were estimated and calculated using the following equation (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^{-1}) is the initial concentration of pollutants, C (mg.L^{-1}) 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.

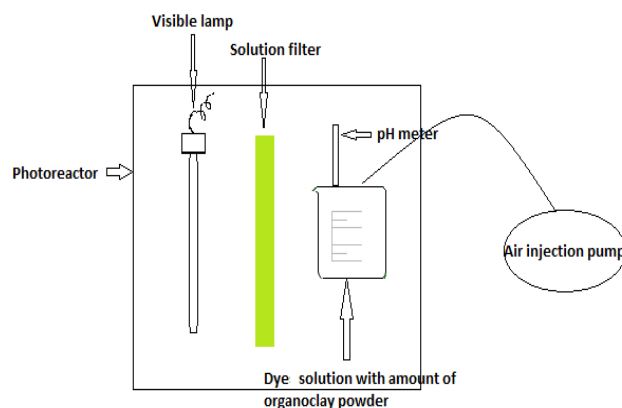


Figure 2. Schematic diagram of batch fixed bed photoreactor

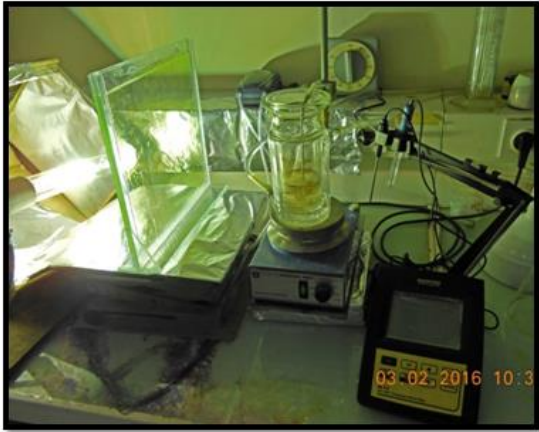


Figure 2 bis: Experimental assembly used in the photodegradation of the used dyes.

II.5. Characterization

The characterization of different powders was carried out by ATR- Fourier transformer Infrared, Nitrogen absorption desorption (BET) and scanning electron microscopy (SEM).

ATR- FTIR spectra of different powder were acquired using a THERMOSCIENTIFIC (FTIR Nicolet IS10) equipped with DTGS KBR detector an ATR Platinum mono- reflexion accessory. The OMNIC software was employed for spectra acquisition. The powder sample were deposited in the ATR, and the ATR-FTIR spectra were obtained in the rang between 4000 and 400 cm^{-1} , with a resolution of 4 cm^{-1} and scan number 32.

Specific surface area and porosity measurement of photosensitized clay are made using ASAP 2020, with nitrogen gas adsorption. All samples are heating to 200°C.

SEM measurements were performed using Thermo-Fisher Quanta 250 SEM (20kV Acceleration voltage).

III- Results and discussion

III.1. Characterization of modified clays

III.1.1. ATR- FTIR analysis

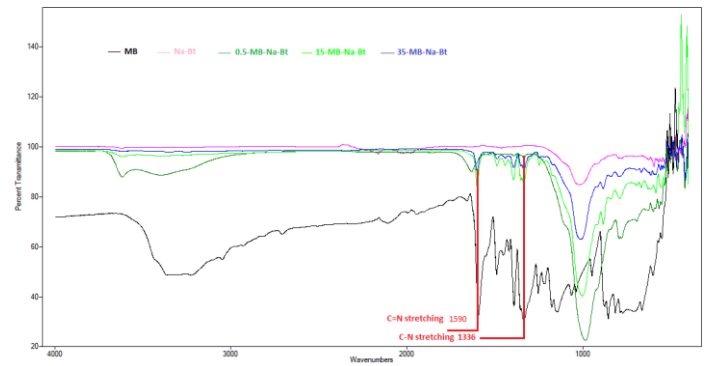
To elucidate the structure of different photosensitized organoclay chains and to prove the good insertion of MB into different organoclay, we have used the FTIR-ATR spectroscopy.—The spectrums of MB-Na-Bt, MB-CTA-Na-Bt and MB-CTA-Na-Mt at different percent of MB were shown on Figure 3.

The main characteristic bands of natural bentonite between 3400 cm^{-1} and 3800 cm^{-1} corresponding to OH bonds and 1050 cm^{-1} attribute to Si-O-Si bonds appears in all spectra (Figure 3 A and 3 B). The superposition of the different spectra show that the most intense absorption band appeared at 1590 cm^{-1} and 1336 cm^{-1} are appropriate to the MB spectrum (Figure 3 A, B and C). These latter, are associated to C=N and C-N vibration bands. The appearance of

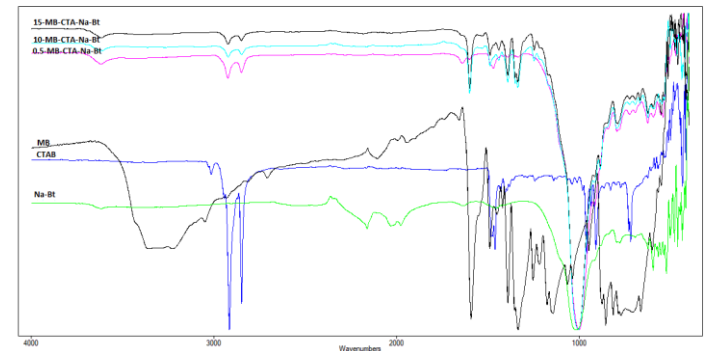
both bands on modified clays spectrum confirms the good retention of photosensitizers in the layer silicates.

The main characteristic bands of Na-Mt (Figure 3 C) are at 980 cm^{-1} corresponding to Si-O bond and 3400 cm^{-1} corresponding to OH bond

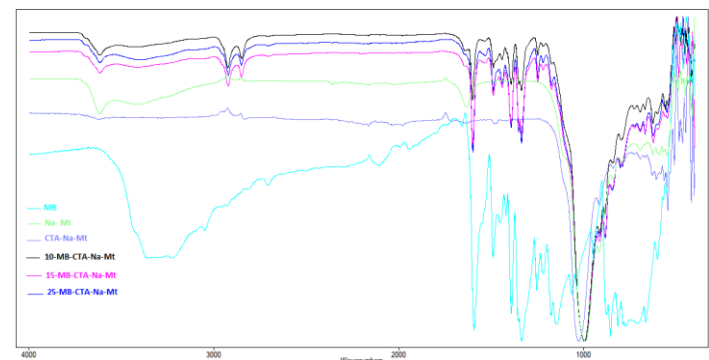
The band between 1360 cm^{-1} and 1400 cm^{-1} (Figure B and C) are assigned to CH_3 -R link of surfactant CTAB. Another band at 2900 cm^{-1} attribute to CH_3 -N of CTAB.



(A)



(B)



(C)

Figure 3. ATR- FTIR spectra of: MB-Na-Bt (A), MB-CTA-Na-Bt (B) and MB-CTA-Na-Mt (C)

III.1.2. BET analysis

The Brunauer- Emmett- Teller (BET) surface area and porosity were measured for the three modified clays: 10% of MB co- adsorbed onto Na-Bt (10-MB-Na-Bt), 10% of MB co-adsorbed onto CTA-Na-Mt (10-MB-CTA-Na-Mt) and 1% of MB co-adsorbed onto CTA-Na-Bt (1-MB-CTA-Na-Bt) at a temperature of 77.4K°. The results were summarized in table 1. All three powders have close values in terms of specific surface area. As the chosen model, the nitrogen adsorption/desorption curve of 10-MB-Na-Bt corresponds to non-porous or macroporous solids, because it is type III according to the IUPAC classification (Figure 4).

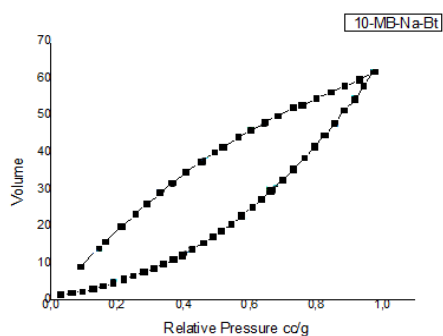


Figure 4. Curves of nitrogen adsorption / desorption isotherms of 10-MB-Na-Bt

III.1.3. SEM analysis

The morphology of different materials was studied by SEM (Figure 5). The surface of natural bentonite Na-Bt appears as flake with low porosity. The intercalation of Na-Bt by cetyltrimethylammonium bromide (CTAB) leads to increase the porosity. This phenomenon was proved by Khatib et al. [28] when they used natural and acid activated bentonite. The presence of methylene blue is clearly shown on the surface of clay with a change of the morphology of samples after adsorption reaction. The same interpretation is made for Na-Mt, CTA-Na-Mt and HP-CTA-Na-Mt.

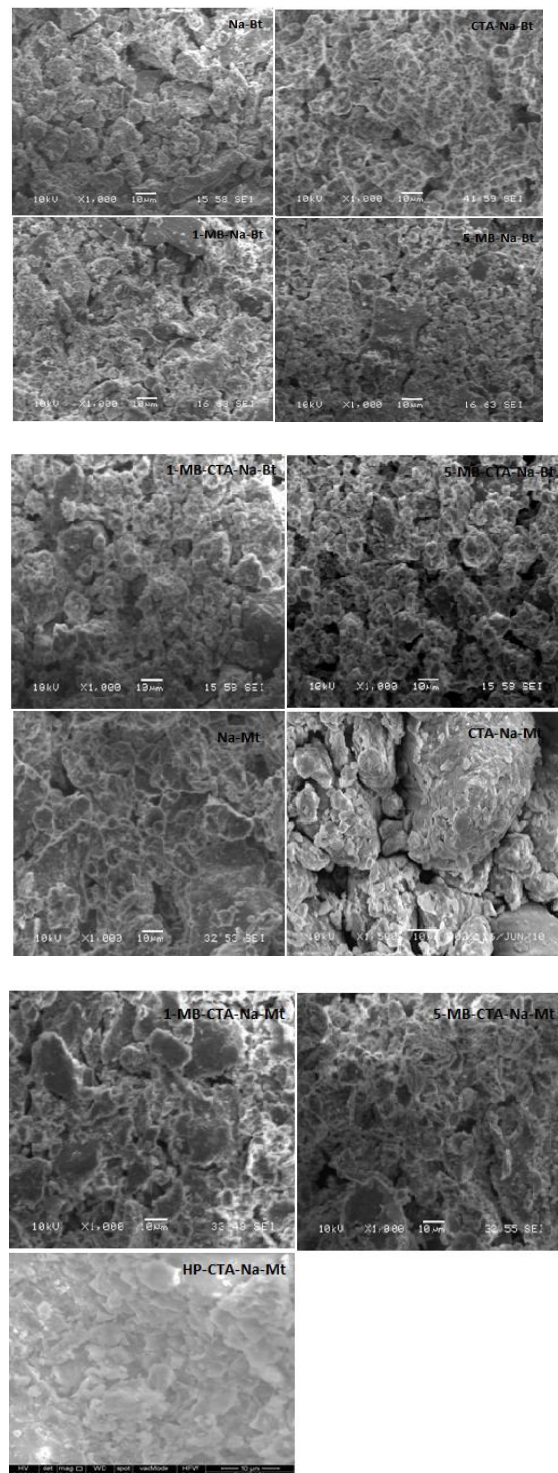


Figure 5. SEM images of the studied materials

Table 1. Different results of BET analysis

Material	Adsorption			Desorption			Total pore volume cc/g
	Surface area m ² /g	Pore volume cc/g	Pore radius A°	Surface area m ² /g	Pore volume cc/g	Pore radius A°	
10-MB-Na-Bt	61	0.11	19.08	55	0.07	15.70	9.56. 10 ⁻² for pores smaller than 390.3A° at P/P ₀ = 0.97472
10-MB-CTA-Na-Mt	44	0.08	15.54	42	0.05	15.71	6.868. 10 ⁻² for pores smaller than 410.7A° at P/P ₀ = 0.97601
1-MB-CTA-Na-Bt	50	0.10	20.42	47	0.06	15.68	7.88. 10 ⁻² for pores smaller than 473A° at P/P ₀ = 0.97925

III.2. Test of photodegradation

III.2.1. Photodegradation of tartrazine

The tartrazine photodegradation tests were carried out on different modified supports.

The obtained results giving in the Figure 6, 7 and 8 of photodegradation of 5 mg.L⁻¹ of TR on 10 mg of modified clay showed clearly that the modified organo clay with 5% of MB gives a good result.

In the spectrophotometer analysis of the residual concentration, we have observed the appearance of a new wave length at 664 nm, this later is relative to the released of the photosensitizers from prepared solid with percent of about 20, 25, 30 and 35% of MB. This phenomenon has an effect on the effectiveness of the material in the degradation of the pollutant.

A good yield of photodegradation was observed on 5-MB-CTA-Na-Mt with 88.88%.

With all powder organo clay, the photodegradation of TR increase slowly until 60 min, this can be explained by the stability of Tartrazine under visible light.

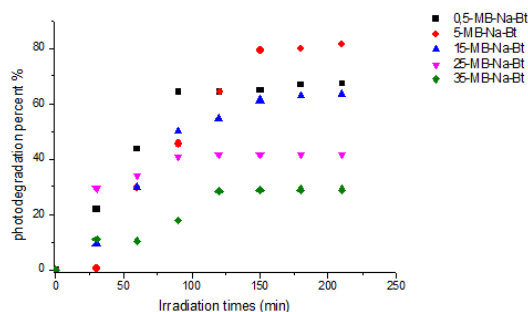


Figure 6: Photodegradation of TR on different percentage of MB-Na-Bt

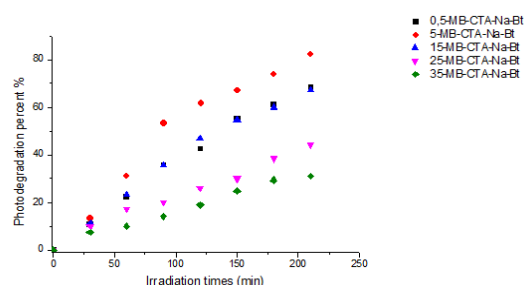


Figure 7: Photodegradation of TR at different percentage of MB-CTA-Na-Bt

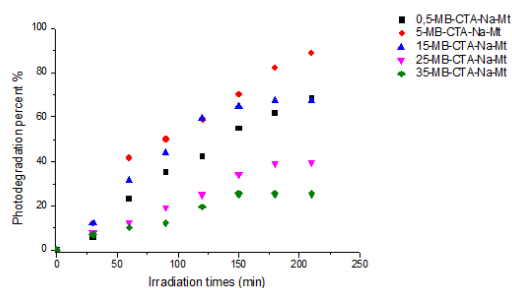


Figure 8: Photodegradation of TR on different percentage of MB-CTA-Na-Mt

III.2.1.1. Influence of concentration of TR on photodegradation

Figure 9 shows the Kinetic of photodegradation of both solution of TR (5mg.L⁻¹ and 10 mg.L⁻¹) on 5-MB-Na-Bt. At a concentration of 5mg.L⁻¹ and 10 mg.L⁻¹ of TR, the efficiency of the photodegradation increase slowly to reach respectively 79.41% and 62.49% after 150 min for both concentrations. We obtained also 81.88% and 74.59% respectively after 210 min. It should be noted here that there is a relationship between the concentration of pollutant and the photodegradation performance. Indeed, the effectiveness of the degradation decreases while the concentration of pollutant increases. This observation has been reported in several studies on

photocatalysis [29, 30, 31]. High concentrations of pollutants lead to saturation of the surface of the clays, and decreases the absorption of visible light by the photosensitizer, which naturally leads to a decrease in its activity.

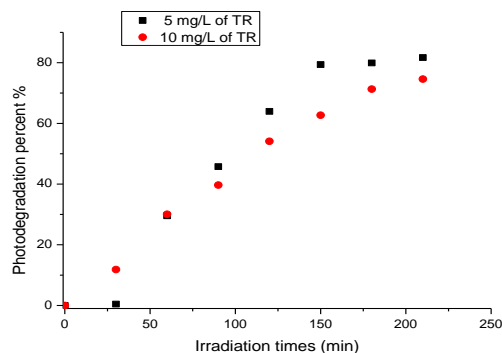


Figure 9. kinetic of photodegradation of both concentration of TR on 10 mg of 5-MB-Na-Bt

III.2.2. Photodegradation of methyl orange

MO photodegradation tests were performed by examining the effects of irradiation time (0- 180 min). The corresponding results presented (in Figure 10) clearly show that the efficiency of dye degradation increases rapidly to 75% after 5 minutes, while the maximum photodegradation is obtained after 120 minutes with 85% photodegradation.

All the concentration of 25 mg.L⁻¹ of MO, the photodegradation increases to reach 47% after 10 min and 85% after 120 min then it stabilizes.

Finally, at a concentration of 50 mg.L⁻¹ of MO, the photodegradation slowly increase to reach a photodegradation maximum of 64% for 120 min. It seems that in our case, MO degradation reaches a saturation limit at a high reagent concentration.

The same phenomena were observed with 5-MB-CTA-Na-Mt (Figure 11) and 5-MB-CTA-Na-Bt (Figure 12).

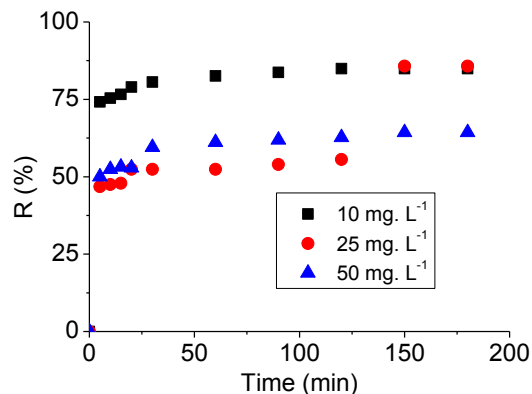


Figure 10. Influence of irradiation time of 5-MB-Na-Bt with: 10, 25 and 50 mg.L⁻¹ of MO.

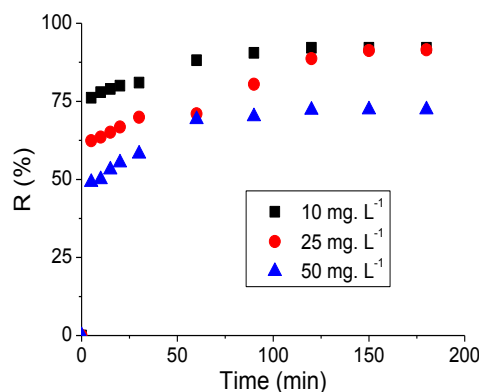


Figure 11. Influence of irradiation time of 5-MB-CTA-Na-Mt with: 10, 25 and 50 mg.L⁻¹ of MO.

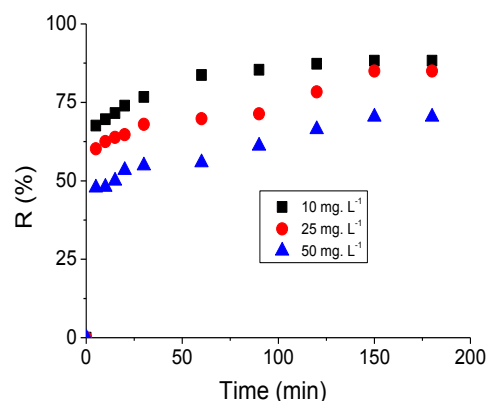


Figure 12. Influence of irradiation time of 5-MB-CTA-Na-Bt ; with: 10, 25 and 50 mg.L⁻¹ of MO.

III.2.3. Photodegradation of Rhodamine B

The photodegradation conditions of Rhodamine B are: 10 mg of modified organo clay contains 5% of MB, temperature: $T = 298 \text{ K}$, $\text{pH} = 3$ and RhB concentration: 4, 10, 25 and 50 mg.L^{-1} . we found the same remarks as in the previous tests, i.e. that if the concentration of pollutants increases the yield of phodegradation decrease (Figure 13).

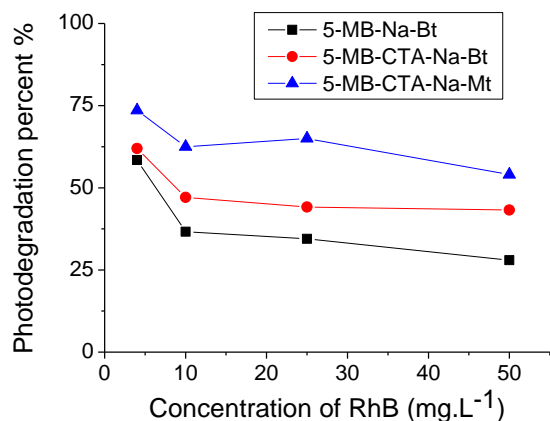


Figure 13. Photodegradation of RB on different hybrids

Table 2. Photodegradation results of Rhodamine on HP-CTA-Na-Mt

% HP	2	5	10	15	20
Yields R%	75.85	74.22	75.32	81.25	88.52

III.3. Mechanism of photodegradation

The photodegradation mechanism of TR sensitized by MB can be deduced based on above discussion and is shown schematically in figure 14. When the visible light irradiates on the surface of modified organoclays, the radiation will be absorbed by the photosensitizers. This latter can transformed adsorbed O_2 molecules on the surface of organoclay to singlet oxygen $^1\text{O}_2$ more reactive than triple oxygen $^3\text{O}_2$ [19].

IV. Conclusion

Methylene blue/organoclay and Hematoporphyrin/organoclay material hybrids were synthesized, characterized and applied in photodegradation of dyes. Insertion of photosensitizers were performed at different percents into Algerian natural bentonite and montmorillonite. The new hybrid materials were methodically characterized with ATR- FTIR, BET and MEB. The photodegradation of three dyes Tartrazine (TR), Methyl orange (MO) and Rhodamine B (RB) was found to be sensitive to several parameters, such as pH of solution, contact time and concentration of dyes.

III.2.4. Photodegradation of Rhodamine B on HP-CTA-Na-Mt

In this section, we investigated the efficacy of another photosensitizer, hematoporphyrin, in the photodegradation of rhodamine B. for this, we adsorbed HP on CTA-Na-Mt with different percentages of HP.

Table 2 illustrate the results of photodegradation of 50mL of Rhodamine B (RhB) 10 mg.L^{-1} on 10 mg HP-CTA-Na-Mt powders with different percents of HP.

The results showed that dyes should be removed from aqueous solution in the presence of visible radiation. We obtained a good yield of photodegradation of pollutants onto 5% of MB onto organo clay and 20% of HP onto CTA-Na-Mt with a good photodegradation efficiency.

Acknowledgement

Our sincere thanks to professor Omar BOURAS, director of the laboratory of water, environment and sustainable development, department of process engineering, faculty of engineering, university of blida 1 for the help and assistance.

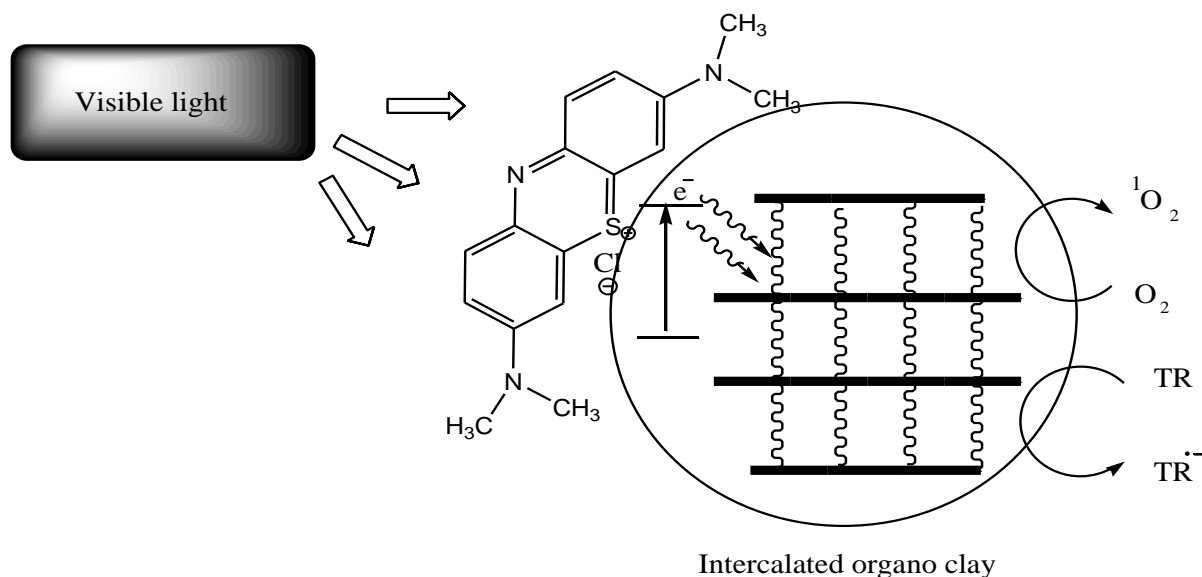


Figure 14. Schematic illustration of the proposed mechanism of degradation of TR sensitized by MB on intercalated organo clay

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Please cite this Article as:

Zeffouni Z., Cheknane B., Zermane F. , Hanani, S. Synthesis and characterization of a novel support based on hydrophobic clays and a Photosensitizer. Application to photodegradation of dyes *Algerian J. Env. Sc. Technology*, 6:3 (2020) 1502-1511.