World Journal of Environmental Biosciences

Available Online at: **www.environmentaljournals.org**

Volume 8, Issue 1: 16-24

ISSN 2277- 8047

Elaboration of a Composite Material (PMAA / TSOH) Based on Poly (Methacrylic Acid) (PMAA) and Chemically Modified Timber Sawdust (TSOH) for the Removal of Methylene Blue in Aqueous Solution

Rechache Mustapha[1,*], Sebba Fatima Zohra[1], Ould Kada Seghier[1], Bounacer Boumediene[1], Belkadi Soumia[1], Bradai Masika[1], Bouchentouf Salim[2]

[1] Laboratory of Macromolecular Physical Chemistry, Department of Chemistry, University of Oran1 Ahmed Ben Bella, BP 1524 EL-M'Naouer, Oran 31100, Algeria.
[2] Doctor Tahar Moulay University of Saida, 20000, Laboratory of Natural Products and Bioactive-University of Tlemcen. Algeria.

ABSTRACT

The purpose of this study was to elaborate three-dimensional structures, by developing a series of biodegradable composite materials based on chemically modified sawdust (TSOH) and poly (methacrylic acid) (PMAA), adopting the method radical polymerization of methacrylic acid (AMA) and using azobisisobutyronitrile (AIBN) as initiator and tetraethyleneglycoldimethacrylate (TEGDMA) as crosslinking agent. Moreover, the various composite materials are obtained by varying the level of TSOH as reinforcement (10%, 50%, 70%). The spectral (FT-IR), morphological (SEM) and thermal (ATG) characterizations of the composite materials (PMAA / TSOH) provide an improvement in the physicochemical properties and ease implementation of the TSOH adsorbents. Subsequently, the composite materials (PMAA / TSOH) (90/10, 50/50, 30/70) are applied to the removal of methylene blue (MB) in aqueous solution in a comparative study with the TSOH material. To evaluate the effects of different conditions, including pH, contact time and temperature, on the methylene blue (MB) removal by composites, batch experiments were conducted. These results, obtained from adsorption, proved to be exothermic with the second order velocity kinetics, which followed the Freundlich isotherm. Experimental saturation capacities were 1434.38 and 1395.56, 1000.78 mg / g for (PMAA / TSOH) (30/70), (50/50) and (90/10) respectively. Negative changes in entropy (ΔS^0) and heat of adsorption (ΔH^0); and in the Gibbs free energy (ΔG^0) indicated the possible and spontaneous adsorption of methylene blue on the composite adsorbents. These results indicate that chemical treatments make it possible to transform a low-value by-product of the wood industry into a useful adsorbent.

Keywords: *Adsorption, Methylene Blue, Poly(methacrylic acid), Timber Sawdust. composite Chemical Treatment, Dyes Removal.*

Corresponding author: Rechache Mustapha
e-mail ✉ rechachemustapha @ yahoo.fr

Received: 03 October 2018
Accepted: 20 February 2019

1. INTRODUCTION

Nowadays, environment protection and pollution problems became a major concern in research programs, the scourges are caused by human activities often through ignorance, but also by a selfish and short-term vision. Our environment is facing an increase in industrial activities that can lead to major ecological disasters such as pollution of drinking water reserves, overexploitation of natural resources and massive use of fossil energy. Indeed, these activities generate a wide variety of chemical pollutants that flow into the water cycle, such as organic pollutants that come from many industries that use pigments to color their products, for example paper, plastic, textile, wood effluents and mineral processing industries (Forgacs, Cserhati and Oros, 2004). The presence of these releases in water, even at low concentrations, sometimes less than 1 $mg.l^{-1}$ (Panic and Velickovic, 2014) is highly undesirable and can cause serious problems of water pollution: The production of dyes is 700,000 tons per year, of which 140,000 tons were released into the effluents (Gupta, 2009). Several techniques and processes are adopted allowing reduction of pollutant load such that flocculation, coagulation and adsorption on certain adsorbent materials are the most used processes (Forgacs, Cserhati and Oros, 2004; Panic and Velickovic, 2014; Gupta, 2009; Pirillo, Ferreira and Rueda, 2009; Mittal, Mittal, and Kurup, 2006; Aksu, 2005). Persistent efforts have recently been made to elaborate highly efficient, inexpensive and renewable adsorbents using natural materials and vegetable waste (Blackburn, 2004). The adsorbents are clay materials, siliceous materials, zeolites, agricultural waste, industrial waste, bio-sorbents, etc. (Aksu, 2005). Plant derivatives are inexpensive and abundantly available, consisting mainly of cellulose, hemicellulose and lignin (Pekkuz, Uzun and Güzel, 2008; Raji and Anirudhan, 1998; Kirk and Farrell, 1987; Ladisch et al., 1983), which is an effective adsorbent for a wide range of pollutants containing functional groups such as hydroxyl, carboxyl, phenols, methoxy, etc and which participates in the connection with pollutants (Reddy et al., 2013). The mineralization of the dye can be confirmed by the decrease in the carbon content (Hassanein and Koumanova, 2010). The adsorption process involves the presence of a solid adsorbent which binds molecules through physical attraction forces, ion-exchange and chemical bonding.

Various studies about the chemical modification of sawdust show the improvement of the sorption capacity of dyes in aqueous media (Batzias and Sidiras, 2007; Batzias and Sidiras, 2004; Rechache and Kada, 2017). In this context, composite materials are proposed which possess indispensable properties for the applications for which they are intended. Their performances (mechanical and technical) are closely related to the properties of the constituents (reinforcement and matrix) and to the characteristics of the interface formed during their assembly. In order to improve the physicochemical properties we synthesized organic composites matrix including poly (methacrylic acid) (PMAA) and chemically modified sawdust reinforcement (TSOH), by a basic treatment followed by a treatment of acetic acid. Composite materials obtained by varying the level of poly (methacrylic acid) as a matrix (90%, 50%, 30%) are applied to remove methylene blue (MB). Batch experiments were carried for kinetic studies on the removal of MB from the aqueous solution. The influence of the various sorption parameters especially; contact time, pH, isotherms and temperature are examined in order to determine the optimal conditions of dye sorption on the elaborated materials.

2. MATERIALS AND METHODS

2.1. Reagents

All reagents were used without further purification. A methacrylic acid monomer (AMA, 99%, Sigma-Aldrich) and a tetraethylene glycol dimethacrylate (TEGDMA, 99%, Fluka) as the crosslinking agent, azobisisobutyronitrile (AIBN, 99%, Sigma-Aldrich) as the initiator, and tetrahydrofuran (THF) and acetone (99.8%, Sigma Aldrich) as the solvent were used. Acetic acid (AA, 99%, Sigma-Aldrich) and sodium hydroxide (99.8% NaOH, Merck). Methylene blue MB were purchased from Aldrich and used without modification. The chemical structure of MB is shown in Figure 1. The pH of the methylene blue solutions was adjusted by adding 0.1 mol L^{-1} of HCl or NaOH. The stock solutions (2000 mg L^{-1}) of the dyestuff were prepared by dissolving MB in distilled water and the test solutions at the desired concentrations were obtained by further dilution in distilled water.

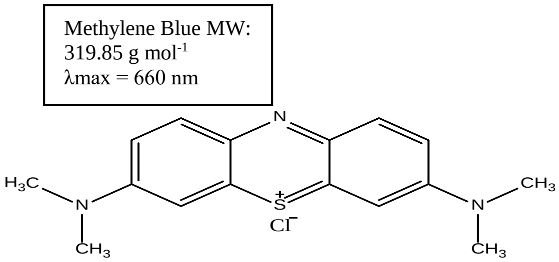

Figure 1. Molecular structure of dye.

2.2. Chemical treatments

The synthesis is done by radical polymerization, starting from methacrylic acid (AMA) and TSOH, using azobisisobutyronitrile (AIBN) and a crosslinking agent tetraethyleneglycoldimethacrylate (TEGDMA) as a radical initiator and tetra-hydro-furan (THF) as solvent. Composite materials (PMAA / TSOH) were prepared by varying the level of methacrylic acid by 30%, 50% and 90% by mass relative to TSOH. The polymerization has been initiated by thermal decomposition of azobisisobutyronitrile (AIBN), at a temperature of 60 °C, under a nitrogen atmosphere in THF during 24 hours (Bajpai, Bajpai and Sharma, 2007; Ajmal et al., 2014). The experimental conditions of the reaction are grouped in Table 1.

The TSOH material resulting from the chemical modification of the raw sawdust is obtained by an alkaline treatment of 20% by weight of NaOH followed by a treatment with acetic acid. The obtained solid after washing to neutral pH is immersed in a total volume of 500 ml containing 30% of acetic acid (150 ml) and 70% of acetone (350 ml). The mixture was stirred during 4 h at room temperature. After filtration, the material obtained was washed several times with distilled water to neutral pH, than dried in an oven for 12 hours at 80 °C (Rechache and Kada, 2017).

Table 1: Experimental conditions of radical polymerization of AMA in the presence of TSOH (solvent: THF, temperature 60 °C and initiator AIBN).

Composites	**AMA %by mass**	**TSOH %by mass**	**AIBN %by mass**	**TEGDMA %by mass**	**THF mL**	**T ^0C**	**t h**
(PMAA/ TSOH)	30	70	2	10	10	60	24
	50	50	2	10	10		
	90	10	2	10	10		

2.3. Experimental procedure and analytical methods

The infrared spectra were obtained on samples (2.5% by weight) in KBr disks from 400 to 4000 cm^{-1} using a Nicolet Avatar 330 Fourier transform IR spectrometer. The morphology of TSOH and composites was examined at high magnification using a HITACHI S-4800 SEM. The thermal analysis was carried out via a thermogravimetric analyzer (TGA, Seiko, SII TG / DTA 6300). For the analysis of an initial mass of 20 mg, samples were heated on a ceramic tray from 25 °C to 700 °C at a heating rate of 10 °C min^{-1} under a stream of nitrogen (100 ml min^{-1}) and weight loss as a function of temperature was recorded.

The dye concentrations were measured with a HACH DR4000U UV- visible spectrophotometer at 660 nm for MB. Adsorbed amounts of coloring matter were determined by considering the differences between the initial and final concentrations using the following mass balance equation:

$$qe = (Ci-Ce) V / w$$

where (qe) is the amount (mg g^{-1}) of adsorbed dye, Ci and Ce are the initial dye and equilibrium concentrations (mg L_{-1}) in solution, V is the volume of the adsorbate (L) and w is the weight of the adsorbent (g). All the experiences described below were undertaken in double or triple.

Elimination of methylene blue on composite materials and TSOH was studied in batches by shaking 10 mg of material with 10 ml of dye solution in a 100 ml capped glass bottle at 25 °C for 60 min for the composite (PMAA / TSOH 50/50) and 120 min for the composites (PMAA / TSOH 90/10, 30/70), and 30 min for the TSOH material. Each isotherm consisted of dye concentrations ranging from 200 to 2500 mgL^{-1}. The equilibrium concentrations of different combinations were measured by the spectrophotometer and referenced with the calibration curves. Kinetic measurements were performed with similar equipment and conditions. The mass of the sample was 10 mg and the volume of the dye solution was 10 ml (150 mg L^{-1}) in this series of tests. The resulting mixtures were stirred at predetermined time intervals then analyzed for dye concentration. In order to determine the impact of pH on MB removal, the dye was examined. The pH in this study ranges from 2 to 13. The mass of the sample was 10 mg and the dye concentration was 150 mg L^{-1} (10 mL) in this series of experiments. The influence of temperature on the removal process was studied at three different temperatures (25, 35 and 45 °C) with suspensions of adsorbents in MB solutions at a concentration of 150 mg L^{-1}. The suspensions were shaken during the optimal contact time, than the dye concentration was analyzed.

3. RESULTS AND DISCUSSION

3.1. Characterization

Examination of the spectrum shown in figure 2 of the chemically modified sawdust TSOH reveals the absence of the absorption band at 1711 cm^{-1} which is strongly present in all the FTIR spectra of the composites. This band is characteristic of the absorption of the carbonyl groups of the ester functions. The absorption band at 2929 cm^{-1} corresponds to the stretching vibration of the sp^3 carbon atoms of the alkyl groups. In addition, the band centered at 3370 cm^{-1} is characteristic of the stretching of the OH terminal hydroxyl groups.

The appearance of the absorption bands at 1711, 1256 and 1156 cm^{-1} in the FTIR spectra of the synthesized materials is attributed to the strong C = O carbonyl bonds and the C-O bond antisymmetric stretching and stretching the C - O - C bonds, respectively. Moreover, the two absorption bands that appear at 1364 and 1451 cm^{-1} are attributed to the sp^3 C-H bond of the poly (methacrylic acid). The strong band observed at 1028 cm^{-1} could represent the C - O - C of cellulose.

The FTIR spectrum shows all the characteristic absorption bands of the poly (methacrylic acid) as well as those of the TSOH. We note that some absorption bands of the latter have been displaced, which shows that TSOH has undergone a corresponding modification to esterification. Results show that the radical polymerization of methacrylic acid with TSOH leads to the formation of a composite (PMAA / TSOH).

The thermograms illustrated by figure 3 represent the thermal degradation of the composite materials obtained by varying the level of methacrylic acid by 30%, 50% and 90% by mass relative to the TSOH. According to figure 3 we note that the thermograms of the composite materials are not identical in all the temperature range.

The degradation of the PMAA / TSOH 50/50, 90/10 composite, is trithermal. The first step occurs at about 100 °C, this degradation is attributed to the evaporation of the solvent with a total weight loss of 20% for both composites. The degradation of the second step occurs between 220 and 300 °C with a total weight loss of 8% for the 90/10 PMAA / TSOH material, and a 10% loss of 50/50 PMAA / TSOH material between 280 and 350 °C. This loss is attributed to the loss of the reinforcing material TSOH. The last step occurs between 400 °C and 450 °C with a mass loss of 60% for the PMAA / TSOH 90/10 composite, and the same loss for the PMAA / TSOH 50/50 between 400 °C and 500 °C. This loss is attributed to the degradation of the PMAA matrix: Moreover, the thermograms reveal an almost flat region without loss of weight obtained after heating at a temperature above 450 and 500 °C, for (PMAA / TSOH, 90/10) and (PMAA / TSOH, 50/50) respectively which corresponds to the weight remaining at the end of 600 °C. The comparison of these thermograms to that of TSOH makes it possible to observe that the thermal behavior of the two composite materials is different from that of the TSOH, this difference is probably related to the structural change of TSOH by this synthesis of the composites, with a difference of mass loss of 10% which corresponds to the remaining weight between the composite and the TSOH.

On the other hand, we observe an increase in the thermal stability of 60 °C concerning PMAA / TSOH 90/10 and a thermal stability of 110 °C for PMAA / TSOH 50/50. These results are confirmed by several studies concerning the thermal stability of the organic matrix composite and TSOH thermogram is quite similar to that of cellulose (Sahiner and Sengel, 2016; Xie et al., 2009).

However, the thermogram of the composite material PMAA / TSOH 30/70 shows degradation in two steps. The first step occurs at around 100 °C which is attributed to the loss of the solvent with a total weight loss of 12%. The degradation of the second step occurs between 250° C and 450 °C with a total weight loss of 60% for the composite (reinforcement and matrix). This can be explained by the characteristics of the interface formed during their assembly. Furthermore, the thermogram reveals an almost flat region without loss of weight obtained after heating, at a temperature above 450 °C which corresponds to the weight remaining at the end of 600 °C. The comparison of the two thermograms of SBOH and (PMAA / TSOH, 30/70) shows that the thermal behaviors of the two materials are slightly different, they are probably due to the structural change that occurred at the physicochemical modification of SBOH during synthesis of composite.

The surface morphology of composite materials and TSOH was also observed by scanning electron microscopy (SEM). Images at different magnifications of 80 ×, 200 × are shown in figure 4 and figure 5 respectively. The micrograph of the TSOH particles reveals small cavities and irregular surface structures. The morphology of composites exhibits irregular porous, fibrous surfaces with rough and compact aspects. These composites have a three-dimensional structure of macrocavities due to the presence of large cavities, sufficient to allow dye molecules to penetrate the structure and interact with surface groups. The good fibrous morphology given by the composite (PMAA / TSOH) (50/50) is shown in figure 4 (c) and figure 4 (g).

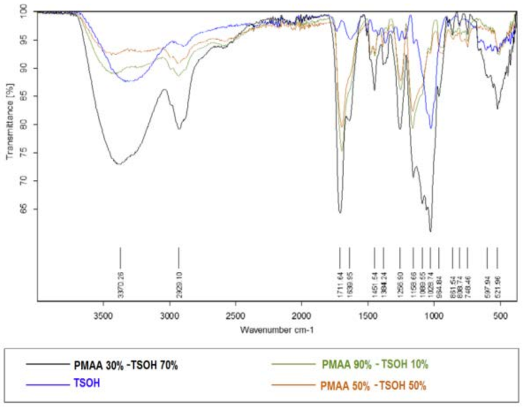

Figure 2: FT-IR spectra

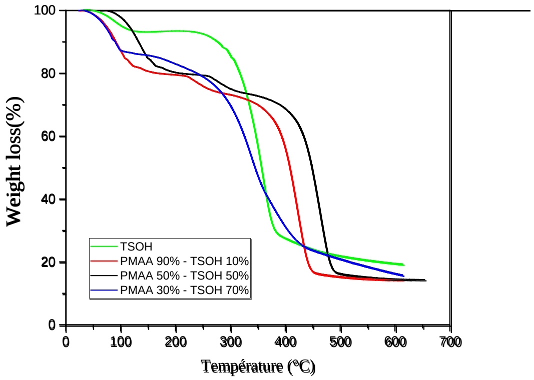

Figure 3. Thermograms of composite materials and TSOH.

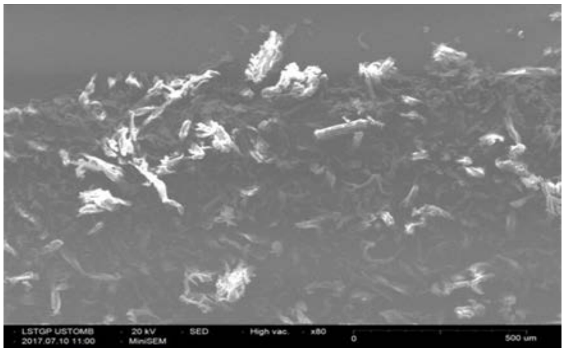

Figure (a) TSOH

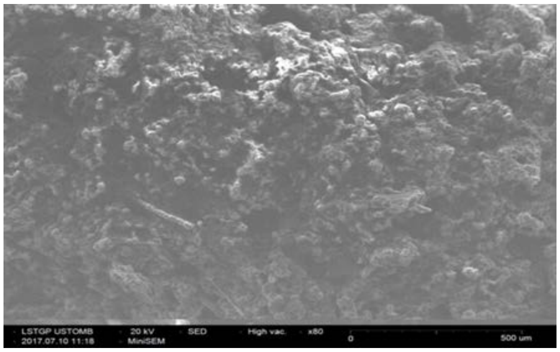

Figure (b) (PMAA90%-TSOH10%)

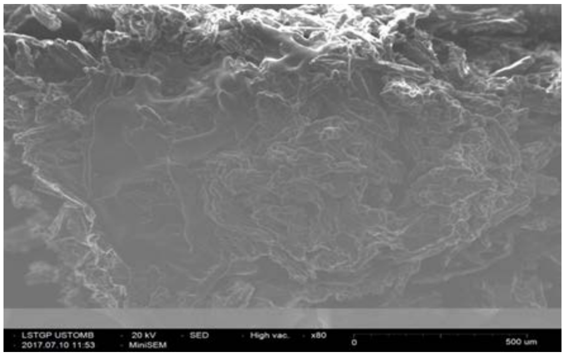

Figure (c) (PMAA50%-TSOH50%)

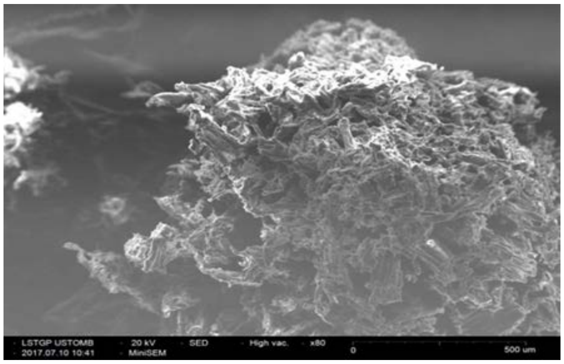

Figure (d) (PMAA30%-TSOH70%)

Figure 4: SEM photos of 80 × magnifications.

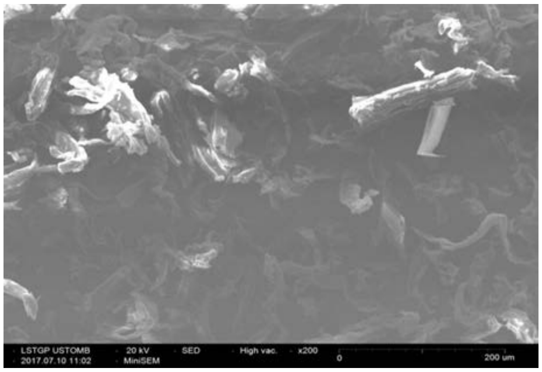

Figure (e) (TSOH)

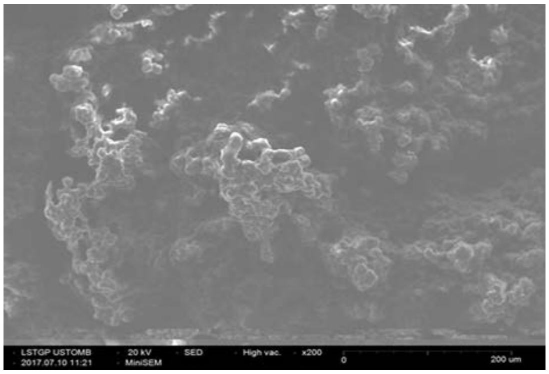

Figure (f) (PMAA90%-TSOH10%)

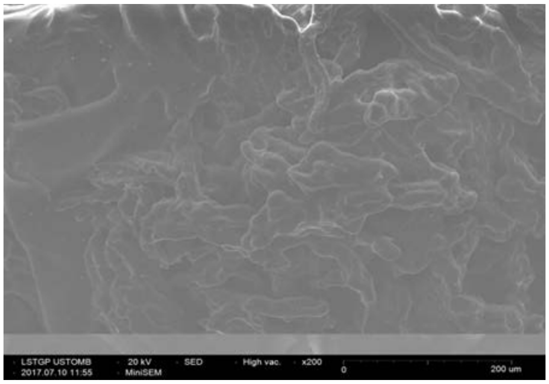

Figure (g) (PMAA50%-TSOH50%)

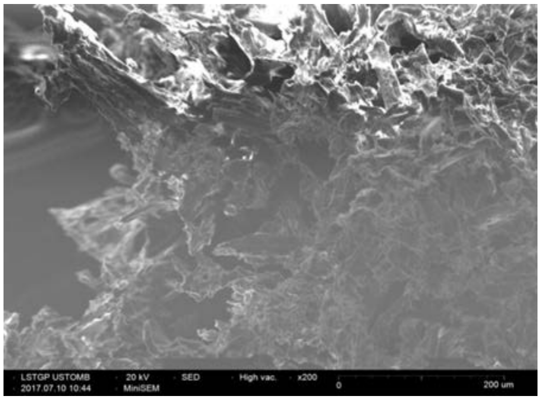

Figure (h) (PMAA30%-TSOH70%)

Figure 5: SEM photos of 200 × magnifications.

3.2. The effect of the contact time

Considering effect of contact time on the sorption rate of MB dye (figure 6) we note that the appearance of the curves is identical. For an initial concentration equal to 150 mg / l of dye, the appearance of elimination kinetics is characterized by a very fast rise from the first minutes. The rate of dye removal with time increases proportionally up to an equilibrium level which is reached after 60 minutes for the composite (PMAA / TSOH) (50/50) and 120 minutes for the two other composites (PMAA / TSOH) (30/70) and (90/10), with a maximum removal rate of 76.21%, 80.02% and 73.27% respectively. However, for the TSOH material, the equilibrium level reached after one minute of stirring with a maximum removal rate of 97.46%. These results prove the existence of a strong affinity between the dye and the surface of the adsorbents obtained. Similar results were obtained with alkaline treatment of cellulose-based materials for the removal of heavy metals. Previous studies concluded that during the initial period, the removal of the pollutant by the material was rapid, followed by a slowdown. At the beginning of the adsorption, the rate was fast because all the adsorption sites were vacant. However, as these sites were covered, the adsorption rate decreased to the equilibrium level (Belhalfaoui et al., 2009; Raji and Anirudhan, 1998). Adsorption of dye is proportional to percentages of TSOH in the composite. The remarkable difference in the rate of removal between TSOH and the composite can be explained by the compact morphology of these composites observed by SEM analysis. This allows us to conclude that the materials can constitute good adsorbents to effectively remove the dye. Our study is done with contact times of 60 and 120 minutes for composite and 30 minutes for TSOH.

Adsorption kinetics is an important controlling aspect of pollutant removal process. The kinetic models frequently used to predict the mechanism that describes the sorption phenomenon are the pseudo-first order model and the pseudo-second order model. The pseudo-first order model could be expressed in its linear form by equation (1):

$$Log\ (q_e - q_t) = Log q_e - k1t \qquad (1)$$

The pseudo-second order model could be expressed in its linear form by equation (2):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (2)$$

With q_e and q_t (mg g^{-1}) are the amounts of dye absorbed at equilibrium and at time t (min), respectively, k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the pseudo-first-order and pseudo-second-order rate constants for the sorption process, respectively. The results of the kinetic parameters of the pseudo second and first order are summarized in Table 2.

The analysis of data form table 2 allows us to note that elimination of methylene blue dye by the composites and by TSOH is better described by the pseudo-second-order model with excellent correlation coefficients (R^2> 0.99) and an optimum contact time of 60, 120 minutes concerning the composites and 30 minutes for TSOH, at an initial concentration Ci of 150 mg / l and an adsorbent / solution ratio of 1 g / l. The maximum capacities of dye elimination per unit mass of material are 147.0.5 and 121.95 and 116.279, 111.111 mg / g, for TSOH, (PMAA / TSOH) (30/70), (50/50), and 90/10) respectively.

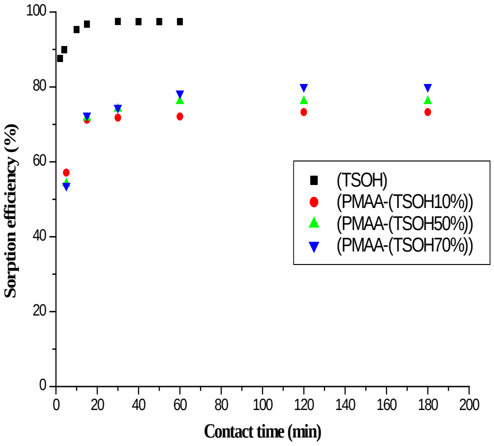

Figure 6: Effect of contact time on the sorption rate of MB dye

Table 2. Kinetics constants for BM dye sorption onto composites and TSOH.

composites	Qe (exp) (mg g^{-1})	Pseudo-first order model			Pseudo-second order model		
		Qe (cal) (mg g^{-1})	K_1 (min^{-1})	R^2	Qe (cal) (mg g^{-1})	K_2 gmg^{-1}min^{-1}	R^2
TSOH	146.20	2.2573	0.041454	0.5213	147.058	0.0272003	1
PMAA30%-TSOH70%	120.04	33.82	0.044	0.909	121.95	0.0035	0.9998
PMAA50%-TSOH50%	114.31	40.18	0.091	0.902	116.279	0.0068	0.9999
PMAA90%-TSOH10%	109.91	11.70	0.037	0.572	111.111	0.0009	0.9999

3.3. The effects of pH

The influence of the initial pH on the methylene blue dye removal rate by the composite materials and the TSOH is illustrated in Figure 7. According to figure 7, we note that the appearance of the curves of influence of pH on elimination of methylene blue by the adsorbents is identical in all the pH range, on the side, successive increase of elimination rate up to maximum values about 90% above pH 6, may be due to the attraction between the negatively charged surface of the adsorbents and the positively charged basic dye. On the other hand, at pH less than 6, the phenomenon can be explained by protonation of the materials surfaces which hinders elimination of cationic dye. These results are similar to those obtained with several adsorbents studied (Shi, Xu and Sun, 1999; Hameed and El-Khaiary, 2008; Han et al., 2006; Bulut and Aydın, 2006).

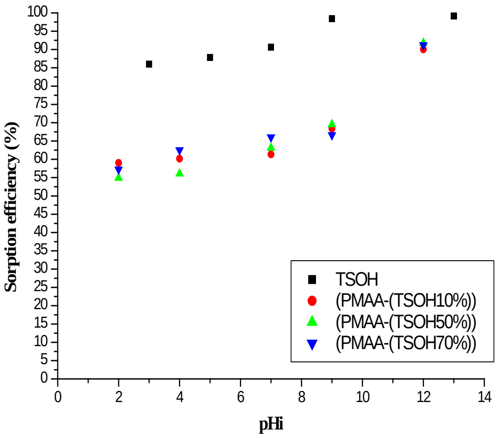

Figure 7: The effect of pH on the sorption rate of MB dye.

3.4. Sorption isotherms

The cationic dye MB sorption isotherms on the adsorbents have been reported in Figure 8. The shape (appearance) of the curves indicates that the adsorbed quantity increases according to initial concentration by existence of vacant sites on the surface of the adsorbents, up to the equilibrium level which shows the occupation of sites by the dye with a stability of adsorbed quantity which expects maximum values of 2162.48, 1434.38 and 1395.56, 1000.78 mg / g for TSOH, (PMAA / TSOH) (30/70), (50/50) and (90/10) respectively. This phenomenon occurs when the interactions between the adsorbed molecules and the surface of the solid are very strong. We also observe a difference in the adsorbed amount of dye by the composite materials on one hand and TSOH on the other hand, which is represented graphically by different slopes. The experimental data were analyzed using isothermal models of Langmuir and Freundlich. The linear form of the Langmuir isothermal model is given by equation (3):

$$\frac{C_e}{(x/m)} = \frac{1}{Q_0.b} + \frac{C_e}{Q_0} \qquad (3)$$

The isothermal equation of Freundlich could be written in the linear form indicated by equation (4):

$$Log\,\frac{x}{m} = \frac{1}{n}.LogC_e + Log\,K \qquad (4)$$

where x / m (qe.mg g^{-1}) is the amount of dye adsorbed per gram of sorbent, Q_0 (qmax.mg g^{-1}) is the maximum sorption capacity per gram of adsorbent, C_e (mg L^{-1}) is the equilibrium concentration of the dye in solution and b (L mg^{-1}) is the Langmuir constant related to the adsorption energy, K and n Freundlich constants in relation with temperature; K (L g^{-1}) represents the amount adsorbed for a solute unit concentration in the equilibrium solution. 1 / n: is the intensity parameter of the adsorption reaction of the isotherm, reflecting linearity degree of the isotherm. The value of n makes possible estimation of adsorption effectiveness such that for 1/n <1; n has a fixation which follows an adsorption phenomenon (Langmuir, 1916). The results of the Langmuir and Freundlich isotherm parameters are summarized in Table 3.

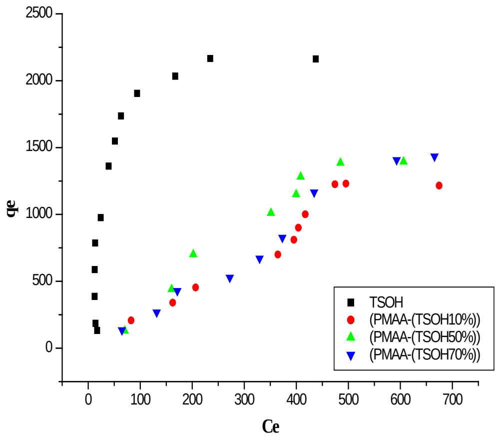

Figure 8. The sorption isotherm for MB dye.

Table 3: Langmuir and Freundlich isotherm constants and the correlation coefficients.

Composites	Freundlich constants			Langmuir constants		
	n	K_F	R^2	Qe(max) (mg g^{-1})	b (L mg^{-1})	R^2
TSOH	1.99322304	178.341455	0.8423	2500	0.02877698	0.9914
PMAA30%-TSOH70%	0.958	1.73	0.993	14285.7	0.0001	0.391
PMAA50%-TSOH50%	0.949	1.70	0.980	5000	0.0003	0.334
PMAA90%-TSOH10%	0.945	1.705	0.980	2500	0.0005	0.527

Data from table 3 allows us to note that from determination coefficients the experimental results obtained by the composites are more suitable to Freundlich model than that of Langmuir compared to TSOH. This could be explained by the homogeneous nature of the TSOH material which is composed mainly of cellulose. In addition the surface of the composite adsorbents heterogeneous confirmed by SEM. The heterogeneity favors the formation of multilayers during the interaction of the adsorbent / adsorbate pair (Shukla et al., 2002). Table 4 shows results from different studies compared to our obtained results

Table 4- Comparative studies of the elimination of methylene blue by various adsorbents

Adsorbents	Q_{max}mg g^{-1}
Commercial AC (E. Merck Inde) Basic Blue 9 (Kannan and Sundaram, 2001)	980.3
Active carbon from waste biomass (Karagöz et al., 2008)	15.798
Activated carbon prepared from rattan sawdust (Hameed, Ahmad and Latiff, 2007)	294.12
Castor seed shell (Oladoja et al., 2008)	158.73
Giant duckweed (spirodela polyrrhiza) (Waranusantigul et al., 2003)	144.9326
Activated carbon from waste news paper (Okada et al., 2003)	260
AC-Pinewood (Tseng, Wu and Juang, 2003)	556
Guava leaf powder (McKay, Porter and Prasad, 1999)	295
Sewage sludges (Otero et al., 2003)	114.94
Raw and activated date pits (Banat, Al-Asheh and Al-Makhadmeh, 2003)	80.3
Raw Timber sawdust (Djilali et al., 2016)	694.44
TSOH [our study]	2500
(PMAA/TSOH) (30/70) [our study]	1434.38
(PMAA/TSOH) (50/50) [our study]	1395.56
(PMAA/TSOH) (90/10) [our study]	1000.78

3.5. Thermodynamic parameters

Results of temperature influence on the methylene blue adsorption phenomenon by the composite materials and the TSOH is summarized in Table 5. The thermodynamic parameters (ΔG^0, ΔH ° and ΔS^0) have been calculated using the following equation:

$$\mathrm{Ln}K_d = -\frac{\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

Where T is the temperature (° K), R is gas perfect constant (8.314 J mol^{-1} K^{-1}) and K_d is the distribution coefficient (amount of dye eliminated per gram of material divided by its concentration in the liquid phase). From table 5 the Van'Hoff plot of LnK_d versus 1/T gives straight lines from which the values of ΔH^0 and ΔS^0 are calculated respectively.

The ΔG^0 values obtained at each temperature indicates the spontaneity and the feasibility of the adsorption and confirm the affinity of the adsorbents for the cationic dye. The negative values of ΔH^0 show that adsorption is exothermic and suggest that the process is physical involving low forces of attraction. However variation of ΔH^0 concerning MB sorption system by TSOH is positive which means that the process is endothermic (Salam, Gabal and Obaid, 2012; Renault et al., 2008; Eskandarian, Arami and Pajootan, 2014; Bendjelloul et al., 2017).

Results show that the adsorption physical order involving electrostatic attraction forces which are closely associated to the chemical characteristics of adsorption sites on the surface of the adsorbents. We noticed for the rest of the experiments the regular decrease of the adsorption by temperature increase, which suggests the feasibility of the low temperature adsorption process. The ΔS^0 values obtained for adsorption reveal the random appearance at the solid interface / solution during the adsorption phenomenon.

Table 5. Thermodynamic parameters of MB adsorption.

Composites	ΔS^0 (J mol^{-1} k^{-1})	ΔH^0 (KJ mol^{-1})	qe (mg g^{-1})			ΔG^0 (KJ mol^{-1})		
			298 K	308K	318K	298K	308K	318K
TSOH	32.89	4.38	112.5	113.25	115.3	-1.61	-1.74	-1.85
PMAA30%-TSOH70%	-14.76	-5.98	98.17	95.54	92.90	-1.58	-1.43	-1.28
PMAA50%-TSOH50%	-2.30	-1.95	93.78	92.90	92.02	-1.26	-1.24	-1.21
PMAA90%-TSOH10%	-13.16	-4.697	86.75	84.12	82.36	-0.778	-0.646	-0.512

4. CONCLUSION

Obtained results from our study and compared to other studies allows us to conclude that the synthesized composite with indicated proportions is likely to be a good adsorbent of MB. Different implicated parameters in adsorption process were in perfect accordance with expected results which encourage use of the composite at industrial level. Also further investigations on different dye removal by our synthesized composite are necessary.

REFERENCES

1. Ajmal, M., Siddiq, M., Al-Lohedan, H., & Sahiner, N. (2014). Highly versatile p (MAc)–M (M: Cu, Co, Ni) microgel composite catalyst for individual and simultaneous catalytic reduction of nitro compounds and dyes. RSC Advances, 4(103), 59562-59570.
2. Aksu, Z. (2005). Application of biosorption for the removal of organic pollutants: a review. Process biochemistry, 40(3-4), 997-1026.
3. Bajpai, S. K., Bajpai, M., & Sharma, L. (2007). Inverse suspension polymerization of poly (methacrylic acid-co-partially neutralized acrylic acid) superabsorbent hydrogels: synthesis and water uptake behavior. Designed monomers and polymers, 10(2), 181-192.
4. Banat, F., Al-Asheh, S., & Al-Makhadmeh, L. (2003). Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters. Process Biochemistry, 39(2), 193-202.
5. Batzias, F. A., & Sidiras, D. K. (2004). Dye adsorption by calcium chloride treated beech sawdust in batch and fixed-bed systems. Journal of Hazardous Materials, 114(1-3), 167-174.
6. Batzias, F. A., & Sidiras, D. K. (2007). Dye adsorption by prehydrolysed beech sawdust in batch and fixed-bed systems. Bioresource Technology, 98(6), 1208-1217.
7. Belhalfaoui, B., Aziz, A., Elandaloussi, E. H., Ouali, M. S., & De Ménorval, L. C. (2009). Succinate-bonded cellulose: A regenerable and powerful sorbent for cadmium-removal from spiked high-hardness groundwater. Journal of hazardous materials, 169(1-3), 831-837.
8. Bendjelloul, M., Elandaloussi, E. H., de Ménorval, L. C., & Bentouami, A. (2017). Quaternized triethanolamine-sebacoyl moieties in highly branched polymer architecture as a host for the entrapment of acid dyes in aqueous solutions. Journal of Water Reuse and Desalination, 7(1), 53-65.
9. Blackburn, R. S. (2004). Natural polysaccharides and their interactions with dye molecules: applications in effluent treatment. Environmental science & technology, 38(18), 4905-4909.
10. Bulut, Y., & Aydın, H. (2006). A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. Desalination, 194(1-3), 259-267.
11. Djilali, Y., Elandaloussi, E. H., Aziz, A., & De Menorval, L. C. (2016). Alkaline treatment of timber sawdust: A straightforward route toward effective low-cost adsorbent for the enhanced removal of basic dyes from aqueous solutions. Journal of Saudi Chemical Society, 20, S241-S249.
12. Eskandarian, Ladan, Mokhtar Arami, and Elmira Pajootan. "Evaluation of adsorption characteristics of multiwalled carbon nanotubes modified by a poly (propylene imine) dendrimer in single and multiple dye solutions: Isotherms, kinetics, and thermodynamics." Journal of Chemical & Engineering Data 59, no. 2 (2014): 444-454.
13. Forgacs, E., Cserhati, T., & Oros, G. (2004). Removal of synthetic dyes from wastewaters: a review. Environment international, 30(7), 953-971.
14. Gupta, V. K. (2009). Application of low-cost adsorbents for dye removal–a review. Journal of environmental management, 90(8), 2313-2342.
15. Hameed, B. H., & El-Khaiary, M. I. (2008). Sorption kinetics and isotherm studies of a cationic dye using agricultural waste: broad bean peels. Journal of Hazardous Materials, 154(1-3), 639-648.
16. Hameed, B. H., Ahmad, A. L., & Latiff, K. N. A. (2007). Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. Dyes and pigments, 75(1), 143-149.
17. Han, R., Wang, Y., Han, P., Shi, J., Yang, J., & Lu, Y. (2006). Removal of methylene blue from aqueous solution by chaff in batch mode. Journal of Hazardous Materials, 137(1), 550-557.
18. Hassanein, T. F., & Koumanova, B. (2010). Evaluation of ad-sorption potential of the agricultural waste wheat straw for Basic Yellow 21. Journal of the university of Chemical Technology and Metallurgy, 45(4), 407-414.
19. Kannan, N., & Sundaram, M. M. (2001). Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study. Dyes and pigments, 51(1), 25-40.
20. Karagöz, S., Tay, T., Ucar, S., & Erdem, M. (2008). Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption. Bioresource technology, 99(14), 6214-6222.
21. Kirk, T. K., & Farrell, R. L. (1987). Enzymatic" combustion": the microbial degradation of lignin. Annual Reviews in Microbiology, 41(1), 465-501.
22. Ladisch, M. R., Lin, K. W., Voloch, M., & Tsao, G. T. (1983). Process considerations in the enzymatic hydrolysis of biomass. Enzyme and Microbial technology, 5(2), 82-102.
23. Langmuir, I. (1916). The constitution and fundamental properties of solids and liquids. Part I. Solids. Journal of the American chemical society, 38(11), 2221-2295.
24. McKay, G., Porter, J. F., & Prasad, G. R. (1999). The removal of dye colours from aqueous solutions by adsorption on low-cost materials. Water, Air, and Soil Pollution, 114(3-4), 423-438.
25. Mittal, A., Mittal, J., & Kurup, L. (2006). Batch and bulk removal of hazardous dye, indigo carmine from wastewater through adsorption. Journal of Hazardous Materials, 137(1), 591-602.
26. Okada, K., Yamamoto, N., Kameshima, Y., & Yasumori, A. (2003). Adsorption properties of

activated carbon from waste newspaper prepared by chemical and physical activation. Journal of colloid and interface science, 262(1), 194-199.

27. Oladoja, N. A., Aboluwoye, C. O., Oladimeji, Y. B., Ashogbon, A. O., & Otemuyiwa, I. O. (2008). Studies on castor seed shell as a sorbent in basic dye contaminated wastewater remediation. Desalination, 227(1-3), 190-203.
28. Otero, M., Rozada, F., Calvo, L. F., Garcıa, A. I., & Moran, A. (2003). Kinetic and equilibrium modelling of the methylene blue removal from solution by adsorbent materials produced from sewage sludges. Biochemical Engineering Journal, 15(1), 59-68.
29. Panic, V. V., & Velickovic, S. J. (2014). Removal of model cationic dye by adsorption onto poly (methacrylic acid)/zeolite hydrogel composites: kinetics, equilibrium study and image analysis. Separation and Purification Technology, 122, 384-394.
30. Pekkuz, H., Uzun, I., & Güzel, F. (2008). Kinetics and thermodynamics of the adsorption of some dyestuffs from aqueous solution by poplar sawdust. Bioresource technology, 99(6), 2009-2017.
31. Pirillo, S., Ferreira, M. L., & Rueda, E. H. (2009). The effect of pH in the adsorption of Alizarin and Eriochrome Blue Black R onto iron oxides. Journal of hazardous materials, 168(1), 168-178.
32. Raji, C., & Anirudhan, T. S. (1998). Batch Cr (VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics. Water Research, 32(12), 3772-3780.
33. Raji, C., & Anirudhan, T. S. (1998). Batch Cr (VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics. Water Research, 32(12), 3772-3780.
34. Rechache, M., & Kada, S. O. (2017, November). Elaboration of a Lignocellulosic Material for a Comparative Study of Adsorption of Micropollutants in Aqueous Solution. In Euro-Mediterranean Conference for Environmental Integration (pp. 241-242). Springer, Cham.
35. Reddy, P. M. K., Raju, B. R., Karuppiah, J., Reddy, E. L., & Subrahmanyam, C. (2013). Degradation and mineralization of methylene blue by dielectric barrier discharge non-thermal plasma reactor. Chemical Engineering Journal, 217, 41-47.
36. Renault, F., Morin-Crini, N., Gimbert, F., Badot, P. M., & Crini, G. (2008). Cationized starch-based material as a new ion-exchanger adsorbent for the removal of CI Acid Blue 25 from aqueous solutions. Bioresource technology, 99(16), 7573-7586.
37. Sahiner, N., & Sengel, S. B. (2016). Tannic acid decorated poly (methacrylic acid) micro and nanoparticles with controllable tannic acid release and antioxidant properties. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 508, 30-38.
38. Salam, M. A., Gabal, M. A., & Obaid, A. Y. (2012). Preparation and characterization of magnetic multi-walled carbon nanotubes/ferrite nanocomposite and its application for the removal of aniline from aqueous solution. Synthetic Metals, 161(23-24), 2651-2658.
39. Shi, W., Xu, X., & Sun, G. (1999). Chemically modified sunflower stalks as adsorbents for color removal from textile wastewater. Journal of applied polymer science, 71(11), 1841-1850.
40. Shukla, A., Zhang, Y. H., Dubey, P., Margrave, J. L., & Shukla, S. S. (2002). The role of sawdust in the removal of unwanted materials from water. Journal of Hazardous Materials, 95(1-2), 137-152.
41. Tseng, R. L., Wu, F. C., & Juang, R. S. (2003). Liquid-phase adsorption of dyes and phenols using pinewood-based activated carbons. Carbon, 41(3), 487-495.
42. Waranusantigul, P., Pokethitiyook, P., Kruatrachue, M., & Upatham, E. S. (2003). Kinetics of basic dye (methylene blue) biosorption by giant duckweed (Spirodela polyrrhiza). Environmental pollution, 125(3), 385-392.
43. Xie, H., Jarvi, P., Karesoja, M., King, A., Kilpelainen, I., & Argyropoulos, D. S. (2009). Highly compatible wood thermoplastic composites from lignocellulosic material modified in ionic liquids: Preparation and thermal properties. Journal of Applied Polymer Science, 111(5), 2468-2476.