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Chemical treatment of orange tree sawdust for a cationic dye enhancement removal from aqueous solutions: kinetic, equilibrium and thermodynamic studies

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ABSTRACT

In order to assess the potential use of low-cost materials for dye removal from aqueous solutions, the adsorption of cationic dye methylene blue (MB) onto orange tree sawdust was studied under static mode using raw sawdust (ROS) and chemically modified sawdust (MOS). The effect of several parameters such as contact time, initial dye concentrations, initial pH, adsorbent dose, and temperature were also investigated. Results showed that the adsorption kinetic data of MB onto both materials were well fitted by the second-order model and the equilibrium state was reached after 180 min of contact time. For both ROS and MOS, MB removal efficiency was improved by the increase in the initial aqueous concentrations, adsorbent dose, and aqueous pH. Moreover, MB adsorption data at equilibrium were well fitted by Langmuir model suggesting a probable monolayer adsorption process. The chemical treatment of the orange tree sawdust with sodium hydroxide (1 M) significantly increased the density of sorption sites and lead to the appearance of new functional groups. Therefore, MB removal capacity increased from about 40 mg/g for ROS to 111 mg/g for MOS at an initial pH value 6.0. The thermodynamic study demonstrated that MB adsorption was endothermic for ROS and spontaneous and exothermic for MOS, respectively. Desorption experiments with HNO_3 acidic solutions proved that MB was significantly desorbed from the tested adsorbents, which offers a possible reusability. All these findings indicate that alkaline-treated orange tree sawdust could be employed as an efficient low-cost and eco-friendly adsorbent for cationic dye removal from industrial wastewaters.

Keywords: Orange tree sawdust; Chemical pretreatment; Methylene Blue; Adsorption; Thermodynamics

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1. Introduction

Dyes are among the most worldwide used chemicals [1,2]. Effluents from textile, leather, painting, food, plastics, cosmetics, and rubber industries contain dyes with relatively high concentrations. Untreated dye effluents could seriously disturb the ecological balance of aquatic environments due to eutrophication induced by the organic loads and the reduction of sunlight penetration. Furthermore, dyes can cause allergic dermatitis and skin irritation and some of them are considered as carcinogenic and/or mutagenic substances [2]. Methylene blue (MB) is a cationic dye usually used as a coloring agent in paper, cotton, wool, and silk industries. Although MB is not regarded as a highly toxic dye, it can still have various harmful effects on living organisms [3]. Direct exposure to MB causes serious injuries to human and animal eyes and in some cases could lead to mental confusion, tissue necrosis, and methemoglobinemia [4]. Once inhaled, it can cause an increase in heart rate, nausea, and vomiting [5].

Various studies have been undertaken this last decade in order to establish the most suitable techniques for dye removal from aqueous solutions in terms of efficiency and cost such as biological degradation [6], coagulation–flocculation [7], membrane separation [8], ozonation [9], and anodic oxidation [10,11]. However, each of these technologies has some disadvantages such as low dye removal efficiency, enormous production of toxic sludges, high-energy consumption, and operational costs. Among the tested treatment technologies, adsorption onto low-cost materials has been identified as an effective and attractive method for dye removal from industrial wastewaters. Several adsorbents derived from natural and renewable materials have been tested for metal and dye removal from aqueous solutions [12–25]. Recently, Bhatnagar et al. [11] and Rafutullah et al. [1] published interesting reviews regarding the application, the challenges and the perspectives of this research topic. Agricultural wastes, which are produced in large amounts and considered as low cost materials, have been tested for the assessment of dye removal efficiency and the involved mechanisms under different laboratory experimental conditions [10,12,19–23]. Sawdust, a very abundant agricultural by-product, is one of the most interesting materials used for pollutant removal from urban and industrial wastewaters. This lignocellulosic material has a complex molecular structure and incorporates various functional groups insuring binding with dye molecules through different mechanisms, such as complexation, ion exchange and hydrogen bonding [12–14]. In order to increase the efficiency of pollutant removal from wastewaters, several studies have also addressed the modification of raw lignocellulosic materials through the use of various chemical reagents such as salts [26], acids [27], bases [13] and thermal activation at relatively high temperatures [28]. However, the majority of these studies have not characterized the modified biomasses in detail and missed the investigation on the involved mechanisms.

Orange tree sawdust is an agricultural waste produced with large amounts and is generally disposed off in landfills. To our knowledge, there is no relevant scientific research work on the reuse of this raw or modified biomass for pollutant removal studies. Its treatment with sodium hydroxide (NaOH) could enhance the adsorption of cationic dyes since this chemical modification could affect the constructive structure of wood, rearrange the hemicellulose and lignin matrix fibers and lead to the appearance of negatively charged sites on the cellulose chains and new functional groups. These newly generated functional groups could present favorable linking sites for the studied cationic dyes adsorption and consequently enhances the removal of these kinds of dyes from aqueous solutions. The main goals of the present study were as follows: (i) the characterization of the raw and NaOH-modified orange tree sawdust, (ii) the investigation of MB removal efficiency from aqueous solutions by these two materials under various experimental conditions, and finally (iii) a better understanding of the possible adsorption mechanisms involved in MB removal.

2. Experimental

2.1. Raw adsorbent

Raw orange tree sawdust (ROS) was collected from a local carpentry in the city of Menzel Bouzelfa, Nabeul, northeast Tunisia. The crude sawdust was sieved and washed with tap water in order to eliminate wood fragments and impurities, then dried under sunlight. Only the sawdust fraction with a diameter lower that 2 mm was used in this study. The prepared sawdust was kept in airtight bags for subsequent use.

2.2. Chemical treatment of orange tree sawdust

The chemical modification of the raw sawdust (ROS) was performed by mixing 40 g of ROS with 400 mL of 1 M sodium hydroxide (NaOH) solution. The mixture was stirred at room temperature for 4 h at 900 rpm using a Thermolyne magnetic stirrer. Then, the material was filtered and the solid phase was washed with distilled water. The modified orange tree sawdust or modified sawdust (MOS) was then dried in an electric oven (Memmert, Germany) at 60˚C overnight.

2.3. Preparation and analysis of MB solutions

Methylene Blue or MB ($C_{16}H_{18}ClN_3S$, MW = 319.852 g/mol, purity = 98%), acquired from Panreac Scientific, Spain, was used during the adsorption batch tests (Fig. 1). A stock MB solution of 1,000 mg/L was prepared with distilled water and used throughout this study for the preparation of the desired solutions with specific physicochemical characteristics. MB color removal was evaluated by measuring absorbance decrease at 664 nm using an UV–vis spectrophotometer (Thermo-Spectronic UV1, Thermo Fischer Scientific, USA).

2.4. Characterization of adsorbents

2.4.1. Particle size distribution

The particle size distribution of the ROS and MOS was performed by shaking 100 g of the given adsorbent using a succession of five standard mechanical sieves (Retsch Prüfsieb, Germany) with diameters ranging between 60 μm and 2 mm for 20 min at 50 pulses per second. The amount of the adsorbent retained in each sieve was weighted in order to determine fraction percent distribution.

2.4.2. pH of zero-point charge

The pH of zero-point charge (pH_{ZPC}) is an essential parameter for the comprehension of mechanisms involved in MB adsorption onto the used adsorbents. This parameter was obtained according to the methodology of Wan Ngah and Hanafiah [29] by shaking with a Varimag-poly15 magnetic stirrer (Thermo Fischer Scientific, USA) at 200 rpm for 24 h, 0.2 g of ROS or MOS in 100 mL aqueous solution of NaCl (0.1 M) at different values of initial pH of 2, 4, 6, 8, 10, and 12.

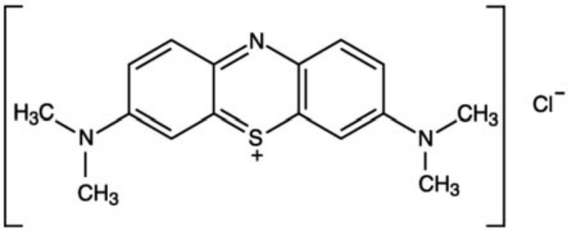

Fig. 1. Molecular structure of MB dye.

2.4.3. Proximate analysis

The proximate analysis was conducted for ROS and MOS in order to determine moisture, fixed and volatile carbon, and ash percentages. These experiments were performed using a Vulcan 3-550 programmed oven (Vulcan Co., Germany) according to the approach given by TAPPI [30].

2.4.4. Lignin, cellulose, and hemicellulose contents

The quantification of lignin, cellulose, and hemicellulose polymers contained in both adsorbents was carried out using the principle of successive degradation and the separation of different fractions based on the gravimetric method described by Sun et al. [31].

2.4.5. Fourier transform infrared spectroscopy analysis

ROS and MOS solid samples were analyzed with Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer, USA) in order to identify the main functional groups present on their surface. A mass of 0.1 g of the solid matrix was ground in 1 g of KBr (spectroscopic grade) in a mortar and pressed into 1-cm-diameter disk with 14 tons pressure. Infrared transmittance spectra of ROS or ROS were obtained using a Perkin Elmer spectroscope. The spectral resolution of the FTIR is 1 cm^{-1} measured between 4,000 and 400 cm^{-1}.

2.5. Batch sorption experiments

Batch experiments for ROS and MOS consisted in determining the MB removal kinetic at equilibrium as well as evaluating the effect of some key parameters such as solution pH, adsorbent dose, and temperature. These assays were performed at 20 ± 2˚C in 120-mL capped flasks. During these assays, a predefined amount of each adsorbent was shaken in 100 mL of MB solution during a desired time at 400 rpm using a Varimag-poly15 magnetic stirrer (Thermo Fischer Scientific, USA). The dissolved MB concentrations were determined after the centrifugation of the suspension at 3,000 rpm for 15 min using a Sigma 4–15 C apparatus (Sigma, UK).

2.5.1. Kinetic and isotherm studies

MB removal kinetic by both ROS and MOS was monitored at various times from 1 to 240 min. The initial MB concentration, the adsorbent dosage, the aqueous pH and temperature were fixed to 100 mg/L, 1 g/L, 6.0 (natural: without adjustment) and 20˚C, respectively. The equations used for the calculation of the adsorbed MB amount by unit weight of used adsorbent at a given time "q_t" (mg/g) and the related percentage dye removal (R_t (%)) are commonly presented in literature [10,13].

The equilibrium MB adsorption data were collected for initial MB aqueous concentrations varying between 10 and 50 mg/L for ROS and from 60 to 130 mg/L for MOS with constant contact time of 180 min. This time was determined on the basis of preliminary assays and judged to be sufficient to ensure an equilibrium state between MB molecules and adsorbent particles. These experiments were performed for fixed adsorbent dosages, aqueous pH and temperature of 1 g/L, 6.0 and 20°C, respectively. Several models have been used to fit the kinetic and equilibrium adsorption experiments. In the present study, we used the most common kinetic and equilibrium models namely, the pseudo-firstorder, pseudo-secondorder, intraparticle and film diffusion [13,32] and Freundlich, Langmuir, Dubinin–Radushkevich and Temkin models, respectively [5,32].

2.5.2. Effect of initial pH, adsorbent dosages, and temperature

During these experiments, the default values of the tested parameters were fixed to 100 mg/L, 6.0, 1 g/L, 180 min, and 20°C for initial aqueous MB concentration, pH, contact time and temperature, respectively. The influence of the initial aqueous pH solutions on MB removal from the synthetic solutions by the two adsorbents were investigated in a series of experiments for initial pH values of 3, 5, 7, 9, and 11. The impact of the adsorbent dosages on MB removal was assessed for ROS and MOS doses of 0.5, 1, 2, 4, 8, 12 g/L and 0.5, 0.8, 1, 2, 4 g/L, respectively. Finally, the effect of temperature on MB removal was studied at four different temperatures, 20, 30, 40, and 50°C.

For all the assays cited previously, pH adjustment was carried out using small volumes (lower than 1 mL) of 0.1 M HNO_3, and NaOH solutions. Moreover, each analysis point reported in this study is an average of at least three independent parallel sample solutions. The standard deviation of the results was 3%.

2.5.3. Desorption study

The MB desorption from preloaded ROS and MOS at concentrations of 30 and 55.8 mg/g, respectively, was performed using nitric acid solutions. During these experiments, 0.1 g of the dye-loaded adsorbents was shaken in 100 mL of distilled water at different initial pH values of 2, 3, 4, and 5, adjusted with nitric acid (analytical grade) at 20°C for 2 h. As for adsorption studies, the aqueous phase of the triplicate samples were separated from the solid ones by centrifugation before analysis with UV-vis spectroscopy (Thermo Fischer Scientific, USA). The mass of desorbed MB by unit of adsorbent weight at equilibrium, q_d (mg/g), and percent dye desorption (Y (%)) were determined based on the common equations given by Jain et al. [6].

3. Results and discussion

3.1. Adsorbents characterization

The particle size distribution of ROS and MOS shows that they are heterogeneous porous media since uniformity coefficient was higher than 2 (Table 1). These materials can be considered as medium to coarse solid adsorbents because their mean diameter was determined to be about 0.6 and 0.8 mm, respectively (Table 1). This granulometric distribution is due to the fact that the chemical treatment of the ROS with

Table 1
Main physicochemical characteristics of the used adsorbents

	ROS	MOS
Grains size distribution		
d_{10}[a] (mm)	0.100	0.313
d_{50}[a] (mm)	0.593	0.767
d_{60}[a] (mm)	0.771	0.917
Uniformity coefficient (UC)[b]	7.712	2.930
Charges density		
pH_{ZPC}	5.7	9.2
Proximate analyses		
Moisture	8.51	–
Volatile matter	79.69	82.07
Fixed carbon	2.43	5.79
Ash	9.37	12.14
Composition		
Lipids	4.411	2.515
Polysaccharides	2.046	1.745
Holocellulose	72.187	76.689
α-cellulose	41.008	46.344
Hemicellulose	31.179	30.345
Lignin	21.356	19.051

[a] d_x: mesh diameter that allows x% of the adsorbent to pass through.

[b] UC: uniformity coefficient: ratio of d_{60}/d_{10}).

NaOH has significantly reduced the fraction with low diameters which is probably due to the dissolution of some compounds and their disintegration such as lignin, cellulose and lipids. Moreover, the increase in the particle size after the alkaline treatment could be imputed to a possible conglomeration of the disintegrated fractions after the drying step. Similar findings were reported by Calero et al. [33] when studying the effect of chemical treatment of tree pruning wastes with sulfuric acid on lead removal efficiency. On the other hand, the alkaline treatment of ROS increased the pH_{PZC} from 5.7 to 9.2 (Table 1), indicating that for solution pH lower than these values, the adsorbent surface should be positively charged and consequently limit MB adsorption through physical adsorption [10]. Concerning the proximate analyses, moisture content was determined only for ROS because the treated sawdust was dried, and consequently, its moisture content was close to complete dryness (Table 1). The alkaline chemical treatment has increased the volatile matter content and the fixed carbon which might be due to the creation of new aromatic hydrocarbon chains [33]. Besides, the chemical treatment with NaOH increased the ash content of MOS by ~30% which could be attributed to the presence of minerals [34]. Analysis of the adsorbent composition showed that the alkaline treatment significantly increased the percentage of α-cellulose from 41 to 46.3%, which could be due to the degradation of other components of the ROS (Table 1). At the same time, a net decrease was noticed in the ROS content of lignin, lipids, and hydrosoluble polysaccharide fractions by about 10.8, 43.0, and 14.7% , respectively (Table 1). This decrease is likely due to the NaOH attack on lignin matrix leading to their fragmentation. Indeed, during the NaOH attack, the natural ROS fibers, including the constituent matrices, namely lignin and cellulose chains, swells and undergo a change in their molecular morphology. Furthermore, this operation would be accompanied with an intense surface modification, resulting in a noticeable decrease in the surface components, in this case lipids and polysaccharides [33]. These modifications were confirmed by the FTIR analyses (Fig. 2), where the absorption band at 1,738 cm^{-1} completely disappeared after the alkaline treatment. This band is typical of the carbonyl functions of carboxylic acids, esters and aldehyde groups related to lignin [13]. The peaks at 3,576 and 3,606 cm^{-1} are assigned to the stretching vibrations of hydroxyl groups of ROS and MOS, respectively. These vibrations are related to the presence of lignin and polysaccharide molecules in the samples [35]. The recorded stretching is mainly due to the interactions of NaOH molecules with hydroxyl groups on the surface of ROS resulting in a weak hydrogen linkage. The decrease in adsorbent transmittance intensity was caused by the decrease in the amount of lignin and polysaccharides after alkaline treatment. The peaks observed at 1,668 and 1,674 cm^{-1}; 1,454 and 1,446 cm^{-1}; 1,398 cm^{-1} and at 1,392 cm^{-1}; 1,160 and 1,158 cm^{-1} for ROS and MOS, respectively, are related to the vibration of C=C aliphatic groups of lignin matrix [35]; vibration of aromatic group $–CH_2$ related to cellulose matrix; bending vibration of C–O–C linkage related to holocellulose and the –C–O stretching vibration of esters [36]. The peaks ranging from 780 to 528 cm^{-1} represent an out of plane deformation vibration of –CH groups [37]. Moreover, the reaction of NaOH with wood fibers leads to the liberation of H^+ ions in the solution in order to establish an electric equilibrium between the solution and the sawdust. The –OH groups in the cellulose fibers are then changed into –ONa groups with release of H_2O molecules [37]. The resulting groups might enhance the ion-exchange process during the MB removal process and thus offer more fixation sites for dye molecules adsorption.

Results in Table 1 confirm that the modification applied to ROS affected mainly the lignin and hemicellulose contents. These losses were met with an increase in cellulose percentage. It was reported that alkali treatment of wood did not significantly affect the internal composition of lingo-cellulosic material but essentially changed its external morphology and enhances overall porosity and specific surface, thus allowing the appearance of steps and kinks on the external surface of the biomass [33]. Thus, we presume that NaOH attack on the ROS changed the structure of cellulose chains. According to Gwon et al. [36], NaOH treatment converted under mercerization process the polymeric chains of cellulose from the crystalline structure cellulose I, characterized with parallel chains and a low free energy to cellulose II. The obtained polymer is characterized by an even lower free energy and antiparallel chains, due to the appearance of H bonding between cellobiose units and the stable *tg*/*gt* conformation [13]. The mechanism of transformation could be assigned to the characteristics of Na^+. In fact, it was reported that cellulose, once exposed to alkali treatment, experiences a swelling phenomenon which changes its extension through space [38]. Sodium ion, as an alkali metal characterized with a relative small atom radius (1.8–1.9 Å), has the ability to go through smaller pores, at high alkali concentrations, and then broaden these pores to reach lattice plane of polymers and insure a bonding with alcohol groups after deprotonation and removal of H_2O molecules (Fig. 3) [36].

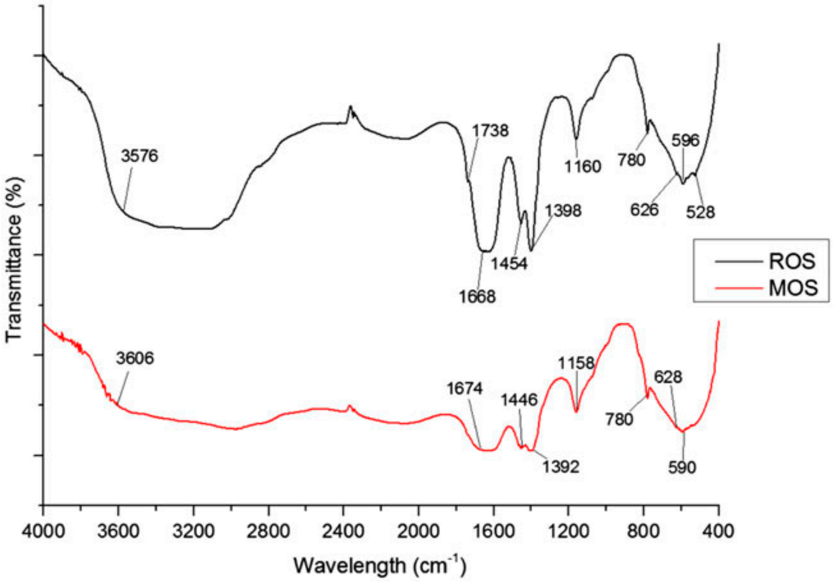

Fig. 2. FT-IR analysis of raw (ROS) and modified (MOS) orange tree sawdust.

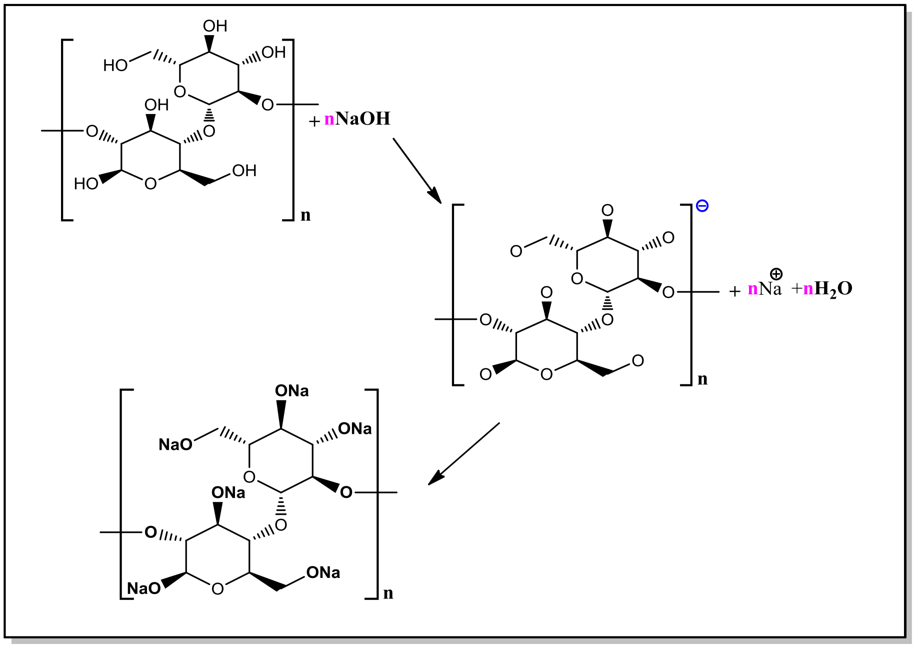

Fig. 3. Effect of NaOH attack onto cellulose chains.

3.2. Kinetic studies of MB removal

In order to determine the required adsorption equilibrium time of MB onto ROS and MOS as well as the probable involved mechanisms, a kinetic study was elaborated for contact times varying from 1 to 240 min at an initial dye concentration of 100 mg/L for both tested adsorbents. As illustrated in Fig. 4, experimental results showed that MB adsorption process is clearly time-dependent. The amount of adsorbed MB (q_t) increased rapidly for contact times lower than 40 min; at this time, it reached about 64 and 76% of the totally adsorbed amount for ROS and

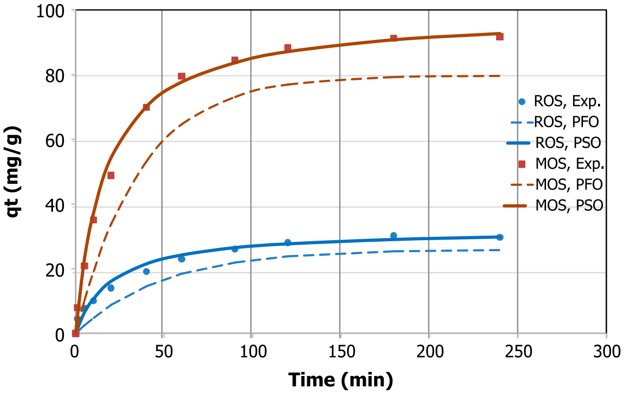

Fig. 4. MB kinetic adsorption onto MOS and ROS and their fitting by pseudo-first-order and pseudo-second-order kinetic models ($C_0 = 100$ mg/L; pH 5.5; dose = 1 g/L; temperature = 20 ± 2°C).

MOS, respectively. For exposures greater than 40 min, MB uptake was further increased but with a much slower rate. The equilibrium state characterized by an approximate constant adsorbed MB amounts was reached at 180 min. The observed stiff slope at the beginning of the experiments indicates a quick and instantaneous adsorption related to the abundance of free acidic functional groups on the surface of both adsorbents and the large number of negatively charged active sites [5]. At this step, the adsorption rate was relatively fast because the MB ions were mainly adsorbed at the exterior surfaces of the used adsorbents. When the adsorption of the exterior surfaces reached saturation, MB ions entered into the particles and were adsorbed by their interior surface. This first stage of the adsorption is due to MB diffusion through limit layer. This step was followed by the saturation of surface groups, then the diffusion of the dye through the intraparticular layer and the pores through the surface of the adsorbents for an additional adsorption [39]. It is worth mentioning that MB removal efficiency at equilibrium by MOS was about threefold higher than that observed for ROS (Fig. 4). This finding confirms the presence of more binding sites for MOS, active O-Na groups on the surface and the improvement in the physical and chemical characteristics of the used biomass after alkaline treatment (Table 1).

The parameters of the four used models: pseudo-first order, pseudo-second order, film diffusion, and intraparticle diffusion are presented in Table 2. To compare the applicability of kinetic models and their ability of fitting to experimental data, an average percentage error (APE) was calculated as follows:

$$\mathrm{APE}\ (\%) = \frac{\sum [q_{t,\mathrm{exp}} - q_{t,\mathrm{calc}}/q_{t,\mathrm{calc}}]}{N} \times 100 \qquad (1)$$

where $q_{t,\mathrm{exp}}$ and $q_{t,\mathrm{calc}}$ (mg/g) are the experimental and the calculated adsorbed amounts at a given time "t" (min), respectively, and N is the number of the experimental runs.

As it could be seen in Table 2, the determination coefficient calculated for both pseudo-first-order and pseudo-second-order models were high, matching well with the experimental data. However, for the Lagergren Pseudo-first order model, the calculated adsorbed amounts at equilibrium ($q_{\mathrm{e,calc}}$) for both ROS and MOS are less fitted to the experimental data, presuming that the adsorption kinetic is not a pseudo-first order process. Oppositely, the $q_{\mathrm{e,calc}}$ values related to pseudo-second-order kinetic model, are the closest to the experimental data with an APE lower than the one recorded for the pseudo-first-order kinetic model. Thus, results indicate that the pseudo-second-order model is the most adequate to fit the experimental results for both ROS and MOS. These findings suggest that MB adsorption onto the two used lignocellulosic materials is mainly a chimisorption process characterized by the establishment of electronic bonding between the functional groups on the surface and the molecule of MB, which involves electrostatic interactions, hydrogen-bonding formation, electron donor–acceptor or π–π dispersion interaction [14]. Similar findings have been observed by Nasrullah et al. [40]

Table 2
Kinetic parameters for MB adsorption onto ROS and MOS ($q_{\mathrm{e,exp}}$: experimental adsorbed amount)

	Pseudo-first-order					Pseudo-second-order				Film diffusion		Intraparticle diffusion	
	$q_{\mathrm{e,exp}}$ (mg/g)	K_1 (min^{-1})	$q_{\mathrm{e,I}}$ (mg/g)	R^2	APE (%)	K_2 (min^{-1})	$q_{\mathrm{e,II}}$ (mg/g)	R^2	APE (%)	D_{f} (m^2/s)	R^2	D_{ip} (m^2/s)	R^2
ROS	30.145	0.0207	26.002	0.995	35.552	0.00155	32.362	0.994	13.165	8.186 E−10	0.987	3.044 E−10	0.998
MOS	91.689	0.0276	79.999	0.993	29.339	0.00062	97.08	0.999	6;457	1.821 E−09	0.993	5.911 E−10	0.992

when investigating MB removal by *Calligonum polygonoides* biomass.

The analysis of the adsorption of MB onto the ROS and MOS with film and intraparticle diffusion models showed that the depicted two-phase plot suggests that the adsorption process proceeds by surface adsorption at earlier stages followed by intraparticle diffusion at later stages. The values of diffusion coefficients given in Table 2 indicate that intraparticle diffusion coefficients are about 2.7 and 3.1 fold lower than those of the film diffusion through the boundary layer for ROS and MOS, respectively. This finding confirms that in case of the tested adsorbents, the intraparticle diffusion process controls significantly the rate of adsorption of MB ions. Similar outcomes have been observed by Hosseini et al. [41] when investigating the MB removal by mesoporous carbon-based honeycomb monolith. It is worth mentioning that the diffusion coefficients for MOS were about two-fold higher than those corresponding to ROS (Table 2). This confirms the impact of alkaline treatments on the morphology of the modified material.

3.3. *Effect of initial dye concentration, adsorption isotherm*

The MB uptake increased with increasing initial dye concentration. In fact, raising initial aqueous MB concentrations from 10 to 50 mg/L and from 60 to 130 mg/L allowed for ROS and MOS to increase their adsorption capacities from 7.4 to 30.0 mg/g and from 61.6 to 102.6 mg/g respectively (Fig. 5). This trend could be explained by the fact that the higher the initial aqueous dye concentration is, the higher the concentration gradient between aqueous solution and the sawdust particles becomes, which results in more important diffusion rates. Furthermore, for high initial aqueous concentrations, the contact probability between MB contained in the aqueous phase and the adsorbent might be more privileged [32]. The Langmuir, Freundlich, Temkin and D–R adsorption constants for ROS and MOS estimated from the isotherms models at 20°C, the corresponding determination coefficients and APE are presented in Table 3. For both ROS and MOS, the highest regression determination coefficients, 0.992 and 0.995 and the lowest APE, 4.009 and 2.003 were registered for the Langmuir model. As such, the latter model was the most fitted to our experimental data (Fig. 5). This finding suggests that MB adsorption onto MOS and ROS occurs on a uniform surface with infinite number of adsorption sites and constant energy. The MB adsorption capacity, $q_{\max}$, of ROS and MOS were estimated to 39.683 and 111.111 mg/g, respectively, showing that the NaOH-modified adsorbent is about 2.8 times more efficient than the ROS. The values of the Langmuir's coefficients ($R_{\mathrm{L}} = 1/1 + K_{\mathrm{L}}C_0$) for the studied aqueous concentrations range varied between 0.409 and 0.122 for ROS and between 0.031 and 0.015 for MOS, respectively. All these values were lower than 1.0, which indicates that MB sorption process by these two adsorbents is favorable.

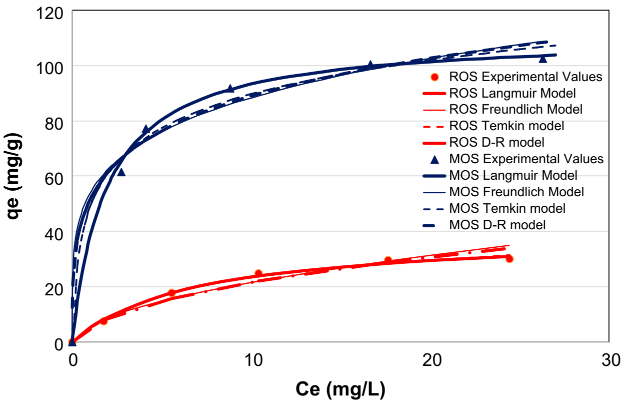

Fig. 5. MB adsorption onto MOS and ROS at equilibrium and their fitting by Langmuir, Freundlich, Temkin and D–R isotherm models ($C_{0,\mathrm{ROS}}$ = 10–50 mg/L, $C_{0,\mathrm{MOS}}$ = 60–145 mg/L, contact time = 3 h, pH 5.5, dose = 1 g/L; temperature = 20 ± 2°C).

Concerning the Freundlich model, which assumes the presence of an heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface, the calculated APE between the estimated and experimental data were about 2.7 and 2.8 times higher than the ones for Langmuir's model (Table 3 and Fig. 5). The calculated values of Freundlich exponent "*n*" were determined to 1.835 and 4.649 for ROS and MOS, respectively (Table 3). They are in the range of 1–10, which indicates a favorable adsorption of MB onto the both adsorbents.

The Temkin isotherm assumes that the heat of adsorption of all the molecules in a layer decreases linearly due to adsorbent–sorbate interactions and that adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [14]. The determination coefficients and the APE values showed that this model did not predict the experimental data very well (Table 3 and Fig. 5).

The D–R isotherm is more general than the Langmuir model because it does not assume a homogeneous surface or a constant sorption potential [42]. This model assumes the presence of a fixed volume of sorption space close to the adsorbent surface and the existence of sorption potential over these spaces. This sorption potential is considered to be temperature-independent but it varies according to the nature of

Table 3
Used isotherms parameters for MB adsorption onto ROS and MOS ($T = 20^\circ\text{C}$; $D = 1$ g/L; ROS: $10 < C_0 < 50$ mg/L; MOS: $60 < C_0 < 130$ mg/L)

	Langmuir				Freundlich			
	$q_{\max}$ (mg/g)	K_L (L/mg)	R^2	APE (%)	K_F	n	R^2	APE (%)
ROS	39.683	5.377	0.992	4.009	6.120	1.835	0.949	10.764
MOS	111.111	4.649	0.995	2.003	53.839	4.649	0.901	5.658

	Temkin				Dubinin–Radushkevich (D–R)			
	A (L/mg)	b (J/mol)	R^2	APE (%)	q_m (mg/g)	E (kJ/mol)	R^2	APE (%)
ROS	1.324	273.384	0.988	3.008	336.505	10.783	0.963	9.168
MOS	5.869	137.649	0.935	4.646	268.973	16.991	0.916	5.181

sorbent and sorbate [42]. According to D–R adsorption isotherm, the magnitude of the value of the free energy "$E = 1/\sqrt{2\beta}$" allows to conclude if the sorption process is physical ($E < 8$ kJ/mol) or chemical ($E > 8$ kJ/mol). The calculated "E" values for both ROS and MOS were higher than 8 kJ/mol, indicating that the MB removal process was mainly chemical (Table 3). Similar results have been reported by Pistari et al. [43] when investigating lead removal by chemically modified unbleached newspaper pulp. As indicated above for Temkin and Freundlich models, the D–R determination coefficients and APE proved that this model did not sufficiently match the experimental data (Table 3). Besides, the corresponding sorption capacity (q_m) was much higher than the calculated ones using the Langmuir model (Table 3), which may be attributed to the assumptions taken into consideration by this model.

In order to analyze the MOS efficiency for MB removal as compared to other adsorbents, a comparison based onto the Langmuir's adsorption capacity "$q_{\max}$" was performed (Table 4). It appears that MOS presents a relatively higher adsorption capacity compared to other chemically and/or chemically modified adsorbents such as oxalic acid-modified rice hull [47] and EDTA dianhydride-modified sugarcane bagasse [50]. It has, however, comparable MB removal efficiency with citric acid-modified peanut husk. Thus, MOS could be considered as a promising and attractive material for cationic dyes removal from aqueous solutions.

3.4. pH effect

The effect of initial aqueous pH on MB removal by ROS and MOS was performed according to the experimental conditions given in Section 2.5.3. The experimental results (Fig. 6) showed relatively low MB removal by the ROS and MOS at pH 2. This behavior is related to sorption competition between protons and the positively charged MB molecules for surface-binding sites. Similar findings have been reported by several authors [10,12,51]. From pH 5.5 to 9, MB removal efficiency was globally constant with an

Table 4
Comparison of MB adsorption onto ROS and MOS with other mineral and organic adsorbents

Material	C_0 (mg/L)	Adsorption capacity (mg/L)	Refs.
Raw posidoniaoceanica fibers	10–50	5.56	[44]
Pine sawdust	20–50	12.95	[45]
NaOH modified banana peel	5–100	19.70	[46]
Oxalic acid modified rice hull	50–100	29.15	[47]
Rice hull ash	500	50.50	[48]
Citric acid modified peanut husk	50–500	111.38	[49]
EDTA dianhydride modified sugarcane bagasse	50–300	202.43	[50]
Raw orange sawdust	10–50	39.68	This study
NaOH modified orange sawdust	60–145	111.11	This study

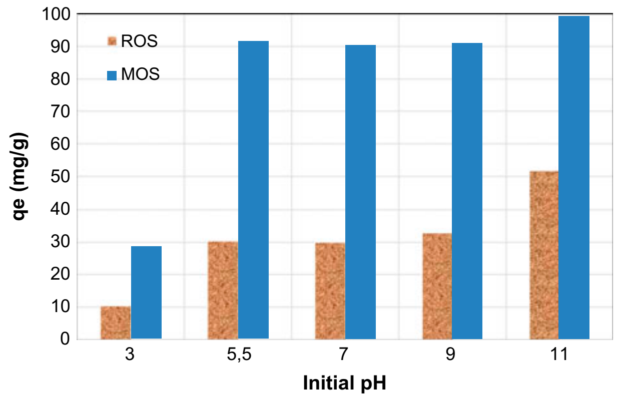

Fig. 6. Effect of initial aqueous pH on MB adsorption onto ROS and MOS ($C_0 = 100$ mg/L, dose = 1 g/L, contact time = 3 h; temperature = 20 ± 2˚C).

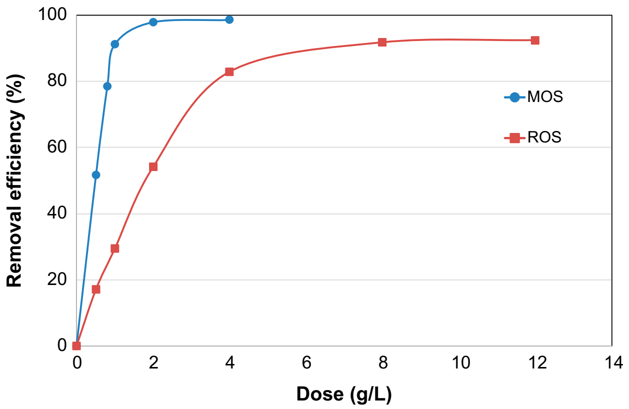

Fig. 7. Effect of adsorbent dosage on MB adsorption onto ROS and MOS ($C_0 = 100$ mg/L, pH 5.5, contact time = 3 h; temperature = 20 ± 2˚C).

average "q_e" at this plateau equal to 31.1 and 91.1 mg/g for ROS and MOS, respectively. This outcome indicates that at this pH range, the charges of the sorption sites have no significant effect onto MB sorption and confirmed that its removal was mainly a chemical process. However, at pH 11, which is significantly higher than the pH_{PZC} of the two tested adsorbents (see Table 1), the MB-adsorbed amounts reached about 51.8 and 99.4 mg/g for ROS and MOS, respectively, which are 9.2 and 66.5% higher than the average registered value at the plateau, respectively. At this initial pH, the equilibrium pH values were determined to 10.2 and 9.6 for ROS and MOS, respectively. For these pH values, the surface sites of the used adsorbents and especially ROS should be highly negatively charged which should contribute to the attraction of the positively charged MB molecules. Similar trends have been observed by Afroze et al. [52] when studying MB removal by *Eucalyptus sheathiana* bark biomass.

3.5. Effect of dose

The effect of ROS and MOS doses on MB removal from aqueous solutions confirmed that MOS can be considered as a promising and efficient material (Fig. 7). Consequently, only 1 g/L of this material was sufficient to ensure an average removal yield of more than 91%. A plateau with a relatively constant removal efficiency of more than 98% was observed beyond a dose of 2 g/L. For ROS, this plateau, with an average efficiency of 92% was observed for doses higher than 8 g/L. This behavior has been observed also for the adsorption of MB onto *E. sheathiana* bark biomass [52], onto coconut leaf [53] and onto sulfuric acid-treated Indian rosewood sawdust [54]. Therefore, there is a confirmation that ROS and MOS doses induce an increase in the total available surface area of the adsorbents particles.

3.6. Thermodynamic parameters

The adsorption of MB onto ROS and MOS was studied at four temperatures, 20, 30, 40, and 50˚C, to determine the corresponding thermodynamic parameters and to a better understanding of the involved mechanisms. For ROS, adsorbed amounts increased when increasing the temperature (Table 5). It rises from 30.145 mg/g at 20˚C to 38.28 mg/g at 50˚C. This suggests the endothermic nature of the adsorption process and could be due to (i) a rise in the kinetic energy of adsorbent particles, which increases the collision frequency between adsorbent and adsorbate increases and consequently the enhancement of MB adsorption onto the surface of the adsorbent and (ii) at high temperature due to bond rupture of functional groups on adsorbent surface, there may be an increase in number of active adsorption sites, which may also lead to enhanced adsorption [55]. Similar observations have been reported by Jellali et al. [32] when investigating phosphorus removal by phosphate mine slimes. In contrast, this process could be exothermic for MOS since the adsorbed MB amounts decreased when increasing temperature (Table 5). In fact, MB removal from the aqueous solution decreases from 91.70 mg/g at 20˚C to 79.06 mg/g at 50˚C. The thermodynamic parameters associated with adsorption processes, namely standard free energy changes ΔG° (kJ/mol), enthalpy ΔH° (kJ/mol) and entropy changes ΔS° (kJ/mol/K), were investigated for a better understanding of the probable mechanisms leading to MB

Table 5
Thermodynamic parameters for MB adsorption onto ROS and MOS

	ΔS° (J/mol/K)	ΔH° (kJ/mol)	ΔG°(kJ/mol)				q_e (mg/g)			
			293 K	303 K	313 K	323 K	293 K	303 K	313 K	323 K
ROS	0.027	10.037	2.016	1.742	1.468	1.194	30.145	34.590	36.340	38.280
MOS	−0.047	−19.560	−5.677	−5.203	−4.729	−4.256	91.689	84.205	81.240	79.060

sorption onto raw and modified orange tree sawdust. These parameters were calculated according to the following equations:

$$\Delta G^\circ = -RT\ \ln(K_C) \tag{2}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{3}$$

$$K_C = \frac{q_e}{C_e} \tag{4}$$

where R is the universal gas constant (8.314 J/mol/K), T is the temperature (K), and K_C is the distribution coefficient. The thermodynamic parameters were calculated from the Van't Hoff plot of $\ln(K_C)$ as a function of $1/T$. The calculated slope and intercept from this plot were used to determine ΔH° and ΔS°, respectively (Table 5). For ROS, the ΔH° value was positive confirming that the MB adsorption process was endothermic. Besides, ΔS° was also positive which revealed the increase in randomness at the solid/solution interface during the adsorption MB process [13]. However, for MOS, the negative values of ΔH° and ΔG° values indicated that MB removal by MOS was an exothermic and spontaneous process. Similar finding has been pointed out by Areco and dos S. Afonso [42] for Cu, Pb, and Cd removal by Argentine seaweed and Deng et al. [56] for lead adsorption onto a modified attapulgite. On the other hand, at the contrary of ROS, ΔG° increases for MOS from −5.677 to −4.256KJ/mol when increasing temperature from 20 to 50˚C. This indicates that for MOS, the spontaneous nature of the adsorption is proportional to temperature [42].

3.7. Desorption study

The MB desorption experiments were performed according to the experimental procedure presented in Section 2.5.3. The results, reported in Fig. 8, showed that MB desorption percent yields for both ROS and MOS increase with increasing the acidity of the used solutions. For instance, ROS efficiency increases from 4.0 to 84.3% when decreasing the pH solution from 5.5 to 2. This regeneration yield could be significantly improved if successive cycles were applied. This finding could be attributed to the fact that in low pH values, protons highly present in the solution replaced MB molecules from the surface of the sorbents. This process is mainly conducted with an ion exchange phenomenon [52]. The fact that these adsorbents have the ability to be easily regenerated, confirms that they could be considered as an attractive and promising materials for cationic dye removal from aqueous solutions.

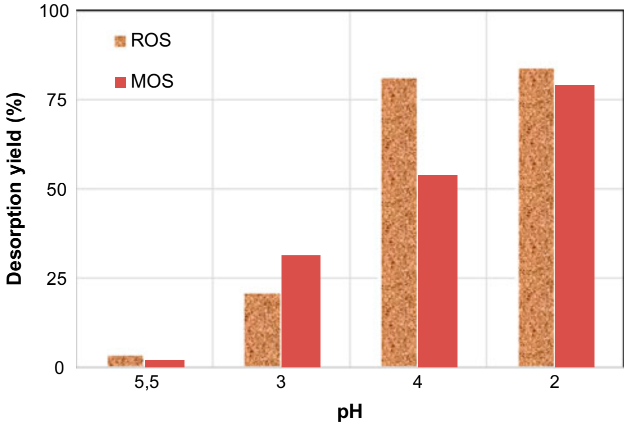

Fig. 8. Effect of initial pH on MB desorption from ROS and MOS (dose = 1 g/L; contact time = 2 h; temperature = 20 ± 2˚C).

4. Conclusions

Based on batch experimental data, chemical modification of orange tree sawdust using NaOH (1 M) increases by about threefold MB removal capacity of the ROS under various experimental conditions. Furthermore, MB removal from aqueous solutions by this modified material was relatively fast, exothermic, spontaneous and mainly of chemical nature through complexation with the surface functional groups. The relatively high MB desorption yields with either nitric acid or NaCl solutions allows us to consider this low cost material as an attractive solid matrix for the removal of basic dyes from aqueous solutions with a possible multiple reuse. Further investigations in dynamic mode using glass laboratory columns are currently undertaken in order to confirm these promising findings and to better understand the involved desorption mechanisms.

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