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Alkaline treatment of timber sawdust: A straightforward route toward effective low-cost adsorbent for the enhanced removal of basic dyes from aqueous solutions



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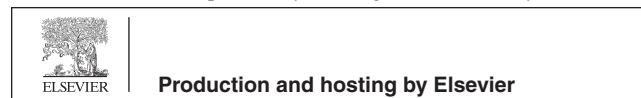
Color removal;
Lignocellulosics;
Alkaline treatment;
Sorption;
Isotherms;
Regeneration

Abstract The present study assesses the ability of two low-cost adsorbents – timber sawdust (TS–OH) and its alkaline treated analog (TS–ONa) – to remove two basic dyes, namely, Methylene Blue and Methyl Green, from aqueous solutions. The presence of new functional groups on the surface of TS–ONa resulted in a dramatic increase of surface polarity and the density of sorption sites, thereby improving the sorption efficiency of the cationic dyes. The results obtained from the sorption characteristics have revealed that the sorption process for TS–ONa was uniform and rapid. The adsorption of cationic dyes reached equilibrium within the first 10 min of contact time and the treated material acts efficiently in a wide pH range of dye solutions. The extent of adsorption was measured through equilibrium sorption isotherms and analyzed using the Langmuir model. The monolayer saturation capacities for Methylene Blue are 694.44 and 1928.31 mg g⁻¹ and for Methyl Green are 892.86 and 1821.33 mg g⁻¹ for TS–OH and TS–ONa, respectively. Therefore, the chemically treated sawdust proved two- to threefold higher adsorption capacities of these dyes than those of the untreated analog. The exothermic nature of adsorption is demonstrated by a decrease of adsorption capacity with increasing temperature, and the negative value of free energy change indicated the spontaneity of adsorption. Desorption experiments with 1 M aqueous NaCl put into evidence that cationic dyes were completely desorbed from the matrices and the reusability of the TS–ONa matrix after three repeated cycles led to just a slight attenuation in its performance. These results show that alkaline treatment of a low value by-product of the timber industry leads to a

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powerful and efficient low-cost adsorbent, which may be used for the treatment of colored wastewaters.

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1. Introduction

Dyes are an important class of pollutants that are of environmental concern because of their known toxicity and tendency to accumulate in the natural environment (Bae and Freeman, 2007; Hai et al., 2007; Husain, 2006). Effluents originating from textile, dyeing, paper and pulp, tannery and paint industries and other plants manufacturing dyes tend to contain dyes in sufficient quantities. Wastewaters containing residual color are visible to the human eye and are therefore obnoxious on esthetic grounds. The non-biodegradable nature of the residual dye may also interfere with light penetration, and thereby can potentially affect the aquatic life in the ecosystem (Rai et al., 2005; Forgacs et al., 2004; Kuo, 1992; Walsh et al., 1980).

During the past three decades, several wastewater treatment methods have been developed for the removal of dyes from industrial effluents. Comprehensive studies dealing with the treatment of dyeing effluents by these techniques have been thoroughly reviewed in the literature (Gupta and Suhas, 2009; Crini, 2006; Aksu, 2005; Forgacs et al., 2004; Pokhrel and Viraraghavan, 2004; Thompson et al., 2001; Robinson et al., 2001; Banat et al., 1996). Hence, a great deal of published papers have established and proved their feasibility with regard to wastewater treatment. Among these methods, adsorption is one of the processes which has been frequently applied in wastewater treatment and especially for dye removal.

In the past decade, researchers have endeavored to develop alternative adsorbents deriving from renewable resources or less expensive natural materials. Recently, Gupta and Suhas have published an excellent review which provides further insight into this growing and important field of research (Gupta and Suhas, 2009). The availability of agricultural wastes or byproducts in large quantities and at low price has driven a growing interest in dye wastewater treatment. Accordingly, numerous studies have been conducted to investigate the efficiencies and mechanism of removal of dyes by various types of low-cost adsorbents (Ferrero, 2007; Hamdaoui, 2006; Ozacar and Sengil, 2005; Batzias and Sidiras, 2004; Aygun et al., 2003; Bouzaida and Rammah, 2002; Ho and McKay, 1998).

Sawdust is one of the most attractive materials used for removing pollutants from water/wastewater (Shukla et al., 2002). The lignocellulosic material is a by-product of the timber industry which is available in large quantities in lumber mills and this waste often represents a disposal problem. The material consists of cellulose, lignin and hemicellulose. Cellulose is composed of a long chain of glucose molecules, linked to one another primarily with β -(1-4) glycosidic bonds. Lignin is a complex polymer composed of phenylpropane units, which are cross-linked to each other by a variety of different chemical bonds. Hemicelluloses are branched polymers composed of xylose, arabinose, galactose, mannose, and glucose. Hemicelluloses bind the bundles of cellulose fibrils to form microfibrils, which enhance the stability of the cell wall. They also cross-link with lignin, creating a complex web of bonds which provide structural strength, and also challenge microbial

degradation (Pekkuz et al., 2008; Raji and Anirudhan, 1998; Kirk and Farrell, 1987; Ladisch et al., 1983).

In addition to its complex chemical structure, the lignocellulosic matrix of sawdust embodies a wide variety of functional groups that play a major role for binding dyes through different mechanisms. The adsorption generally takes place by complexation, ion exchange and hydrogen bonding. Consequently, the use of lignocellulosic wastes in their raw state will ultimately lead to fair adsorption capacities of contaminants due to the antagonism of different mechanisms evolving throughout the removal process. Of course, one cannot argue with the success of these low-cost adsorbents, however, different studies illustrated the efficiency of the chemical treatment of raw lignocellulosic wastes. For instance, Batzias and Sidiras examined the adsorption of Methylene Blue and basic red 22 by beech sawdust and noticed that the chemical treatment of the raw adsorbent whether with calcium chloride (Batzias and Sidiras, 2004) or by subjecting the beech sawdust to mild acid hydrolysis (Batzias and Sidiras, 2007) did improve the adsorption capacity of the treated material.

As a contribution to this matter, we postulate that alkaline treatment of timber sawdust will lead to a modified material that ensures enhanced adsorption capacities for basic dyes. As a matter of fact, the treatment of timber sawdust with aqueous NaOH will not only permit the extraction of hemicelluloses and most part of lignin but will also allow the conversion of the polyol structure into a negatively charged cellulose-based material. The newly designed material will bear a large number of negatively charged sites on its surface favoring the adsorption of cationic dyes via electrostatic attraction. In fact, the adsorption capacity is a particularly important consideration when evaluating candidates for use in low-cost sorbents. However, the regeneration capacity of these materials often poses a serious drawback, which considerably limits their practical application. Therefore, when any given sorbent is efficiently regenerated without any essential loss in the sorption capacity in repeated sorption-desorption cycles, the material could then offer a cost-effective solution to the removal process, yet a better approach to the waste disposal problem. To meet these objectives, our work was set to prepare an appropriate low-cost sorbent material by a cost-effective chemical modification, namely, by treating a low value by-product of the timber industry with aqueous NaOH. The raw timber sawdust (TS-OH) and the chemically treated sawdust (TS-ONa) were subjected to batch experiments in order to evaluate and compare their removal capacities for Methylene Blue (MB) and Methyl Green (MG) from aqueous solutions and eventually to check the performance of the TS-ONa material after regeneration to ascertain its stability and reusability.

2. Materials and methods

2.1. Materials

Timber sawdust (TS-OH) was kindly provided by a local carpenter. The material as obtained was sieved for a particle size

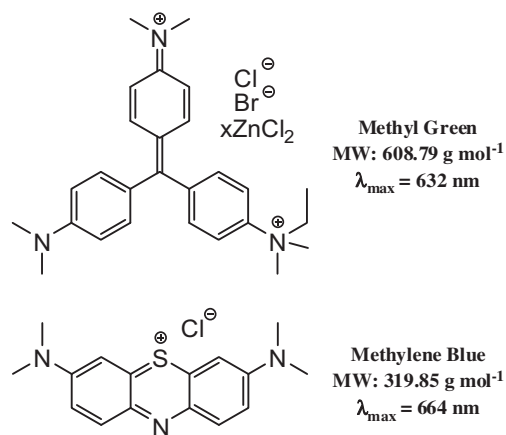


Figure 1 Molecular structures of the basic dyes.

of 250 μm . All chemicals used were of analytical reagent grade, Methylene Blue (MB) and Methyl Green (MG) were purchased from Aldrich and were used as received. The chemical structures of MB and MG are shown in Fig. 1. Stock solutions (2000 mg L⁻¹) of the dyestuffs were prepared by dissolving MB and MG in distilled water and test solutions of desired concentrations were obtained by further dilution with distilled water. Dye solutions of desired pH values were obtained by adjustment using dilute HCl (0.1 N) and NaOH (0.1 N) solutions.

The chemical modification of timber sawdust was conducted by immersing at once 50 g of TS-OH in 500 mL of 20 wt.% sodium hydroxide solution. The resulting mixture was stirred overnight at room temperature. The suspension was filtered and the solid was thoroughly washed with distilled water until neutral pH was obtained, and then washed with acetone. The material was then dried in an electric drying oven at 80 °C and passed through a 250 μm sieve to afford 28 g of TS-ONa as a yellowish powder.

2.2. Experimental procedure and analytical methods

Infrared spectra were obtained on (2.5 wt.%) samples in KBr disks from 500 to 4000 cm⁻¹ using a Nicolet Avatar 330 Fourier transform IR spectrometer. Cross polarization magic angle spinning (CPMAS) ¹³C NMR spectra of TS-OH and TS-ONa were recorded on a Bruker 300 (Digital NMR Avance) spectrometer. The concentrations of dyestuffs were measured with a HACH DR4000U UV-visible spectrophotometer at 632 and 664 nm for MG and MB, respectively. The sorbed amounts of dyestuffs were determined from the difference between the initial and final concentrations by the following mass balance equation, $q_e = (C_i - C_e)V/w$, where q_e is the amount (mg g⁻¹) of dye adsorbed, C_i and C_e are the initial and equilibrium dye concentrations (mg L⁻¹) in solution, respectively, V is the adsorbate volume (L) and w is the adsorbent weight (g).

All experiments described below were undertaken with both raw sawdust (TS-OH) and modified sawdust (TS-ONa) in either duplicate or triplicate. The removal of MB and MG by both unmodified and modified sawdust was investigated in batch experiments by stirring 50 mg of material with 50 mL of dye solution in a 200 mL stoppered glass bottle at

22 °C for 120 min. Each isotherm consisted of 14 dye concentrations varying from 150 to 2000 mg L⁻¹. The equilibrium concentrations of different combinations were measured by the spectrophotometer and referenced with the calibration curves. The kinetic measurements of adsorption properties of TS-OH and TS-ONa were carried out with similar equipment and conditions. The sample mass was 50 mg, and the volume of the dye solution was 50 mL (150 mg L⁻¹) in this series of tests. The mixtures were stirred at predetermined intervals of time (10–120 min) and were drawn for dye concentration analysis. Experiments with each material and dye were performed to determine the effect of pH on dye adsorption. The pH range studied for both adsorbents and dyes was from 2 to 10. The sample mass was 50 mg, and dye concentration was 150 mg L⁻¹ (50 mL) in this series of tests. The influence of temperature on the removal process was studied at three different temperatures (22, 35 and 45 °C) with TS-OH and TS-ONa suspensions in MB and MG solutions at two different concentrations (500 and 1000 mg L⁻¹). The suspensions were stirred during 2 h and then the dye concentration was analyzed.

To assess the feasibility for the consecutive reuse of TS-OH and TS-ONa, sorption-desorption studies of MB and MG on these matrices were carried out at room temperature using 50 mg of material and 50 mL of dye solution at a concentration of 50 mg L⁻¹. Initially, the adsorbent materials were subjected to dye removal following the general procedure described above. After 2 h of contact time, the suspension was centrifuged and the dye concentration was then determined by a spectrophotometer. The recovered materials were washed with distilled water, air dried, and then suspended in 50 mL of aqueous NaCl solution (1 M). The obtained suspensions were stirred for 2 h, then centrifuged and the regenerated materials were washed with distilled water until AgNO₃ tested negative. Then, the regenerated materials were suspended in dye solutions under the same conditions as above. The sorption-desorption cycles were repeated three times.

3. Results and discussion

3.1. Characterization

The huge weight loss (22 g over the 50 g of TS-OH set to react) following the alkaline treatment gives a broad idea of the chemical composition of the raw material. Although, the chemical composition of wood sawdust is distinct according to the nature of the wood, the main macromolecular constituents, however, are cellulose (44–48%), hemicelluloses (20–30%), lignin (20–27%), and minor low molecular weight components such as mineral and extractable substances. Alkaline treatment with 20 wt.% NaOH allows at the same time all extractable and mineral substances, pectin, and hemicelluloses to be completely removed and moreover makes solubilization of a large part of lignin possible. Therefore, all these fractions are actually eliminated and only the cellulosic part remains, which has undergone the mercerization reaction. These facts are corroborated by FTIR and ¹³C NMR spectroscopies. Fig. 2 shows the FTIR spectra of raw timber sawdust (TS-OH) and modified timber sawdust (TS-ONa). A glance at the TS-ONa spectrum reveals the disappearance of the absorption band at 1732 cm⁻¹ occurring in the spectrum of the precursor TS-OH. This band is typical of the carbonyl functions of carboxylic acid, aldehyde

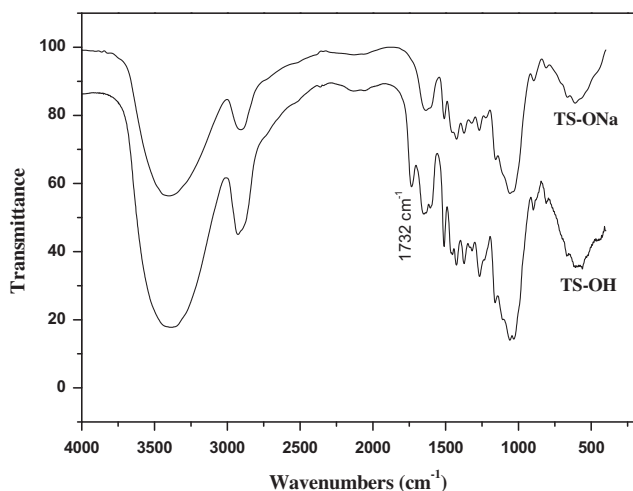


Figure 2 FT-IR spectra of raw sawdust (TS-OH) and alkaline treated sawdust (TS-ONa).

and esters groups peculiar to lignin. The shape of TS-ONa spectrum is quite similar to that of cellulose. Additional evidence that lends support to this fact lies in the ^{13}C NMR spectrum of TS-ONa (Fig. 3) where signals arising at 187, 145, and 20–30 ppm in the TS-OH spectrum and corresponding to the carbon atoms of carbonyl $\text{C}=\text{O}$, aromatic, and alkyl groups, respectively, of lignin quite disappear or become considerably attenuated in intensity.

3.2. Sorption kinetics

For an initial dye concentration of 150 mg L^{-1} , the results revealed that MB and MG removal processes as a function of contact time reaches equilibrium in the first 10 min for TS-ONa whereas for TS-OH, the process seems to occur in two

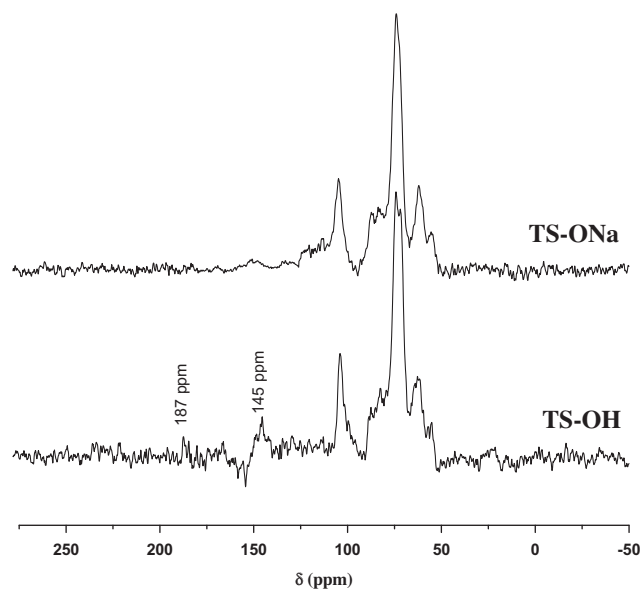


Figure 3 MAS ^{13}C NMR spectra of TS-OH and TS-ONa adsorbents.

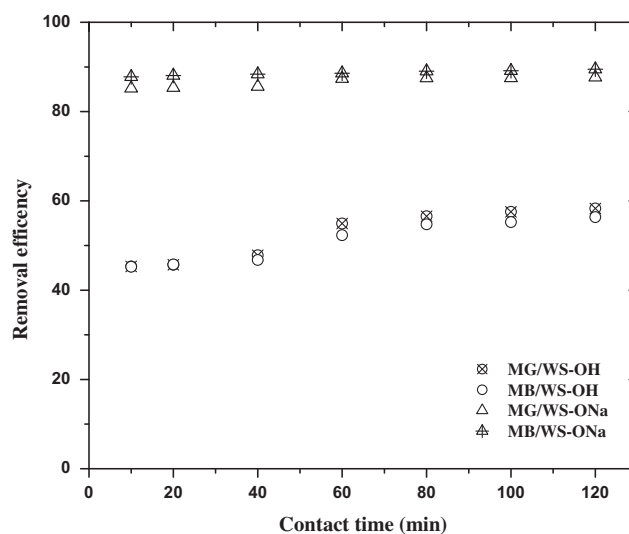


Figure 4 Effect of contact time on MB and MG removal by TS-OH and TS-ONa. Dye concentration: 150 mg L^{-1} ; adsorbent dose: 1 g L^{-1} ; temperature = 22°C .

steps (Fig. 4). The rate of the dyes' sorption onto TS-ONa is remarkably high so that maximum dye is sequestered from the solution. Typically, up to 85% of the adsorption takes place within the first 10 min of contact time. This fast adsorption indicates the presence of abundant readily accessible adsorption sites and also suggests that the removal process is very likely driven by strong ionic interactions between the negatively charged -ONa groups anchored at the surface of the material and cationic dyes in solution. Similar sorption results were obtained when cellulose-based materials have been subjected to alkaline treatment prior to the sorption experiments of heavy metals (Aziz et al., 2009; Belhafaoui et al., 2009). However, the adsorption of MB and MG onto TS-OH is less efficient as only 57–58% of the ultimate dye removal was achieved within 2 h of contact time. Besides, the first step involves a quite rapid dye uptake within the first 60 min of contact time, and then subsequent removal of the dyes continues moderately for another 60 min period until equilibrium is reached. The first rapid and quantitatively predominant step is certainly due to the presence of available sorption sites incorporated by the polyol structure of TS-OH lignocellulosic adsorbent, which is partially negatively charged (Shi et al., 1999). Then, the sorption becomes insignificant and less efficient afterward, with a gradual occupancy of these sites. In the light of these results, the subsequent sorption experiments were conducted over a period of 120 min of contact time.

Contrary to the removal process of cationic dyes by TS-ONa which takes place within a short time, the sorption rate law of MB and MG removal by TS-OH was however investigated. The kinetic data obtained from batch experiments have been analyzed using the pseudo-second order equation (Ho and McKay, 1999). The equation that describes the pseudo-second order can be written as Eqs. (1) and (2).

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (\text{differential form}), \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (\text{integral form}), \quad (2)$$

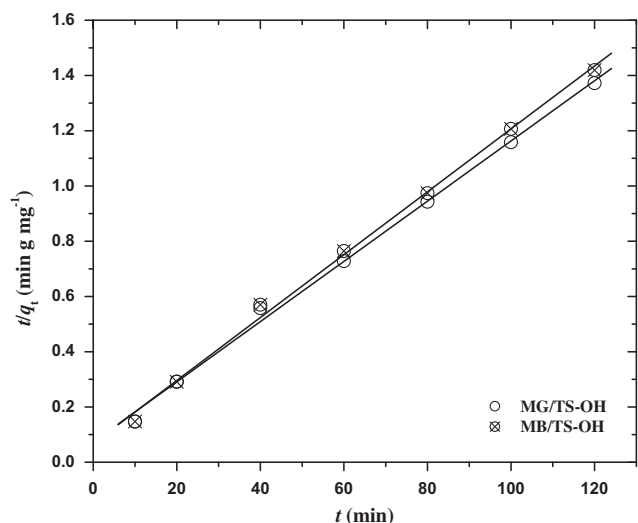


Figure 5 Pseudo-second order plot for MB and MG removal by TS-OH.

where k_2 is the rate constant of sorption ($\text{g mg}^{-1} \text{min}^{-1}$), q_e and q_t (mg g^{-1}) are the amounts of dye sorbed at equilibrium and at time t , respectively.

Thus, straight lines were obtained when plotting t/q_t versus t (Fig. 5). The equilibrium sorption capacity (q_e), the rate constant (k_2), and the coefficients' (R^2) values were calculated from the linear plots. Perfect correlation is observed between experimental data and the pseudo-second order kinetic model with excellent correlation coefficients (higher than 0.998). Additionally, the calculated q_e values from the model show that the equilibrium removal capacity of MB ($0.275 \text{ mmol g}^{-1}$) is notably higher than that of MG ($0.177 \text{ mmol g}^{-1}$), which was totally in agreement with the experimental data (differences lower than 1%), emphasizing therefore the efficiency of the model. These results suggest that the adsorption process occurs dominantly via weak coulombic interactions between the dye molecules and the polyol structure of cellulose within the heterogeneous TS-OH material until most functional sites at the surface are occupied (Shi et al., 1999). Then dye molecules may diffuse into the heterogeneous matrix of the lignocellulosic material for further interactions.

3.3. Effect of pH

Fig. 6 presents the effect of solution pH on MB and MG removal by TS-OH and TS-ONa materials at room temperature. First of all, it is noteworthy to point out that solution pH has practically no effect on the amount of dyes sorbed onto TS-ONa. Indeed, within the wide pH range (from pH 2 to 10) of dye solutions, sorption efficiencies of MB and MG onto TS-ONa are basically constants and reached removal percentages higher than 85% within the whole pH range. This can be explained by the fact that at low pH, the surface properties of the adsorbent are not altered since the active sorption sites on the surface remain actually negatively charged and hence preponderant over sorption of the cationic dyes. To summarize, TS-ONa can be consistently described as an ion exchange adsorbent that performs efficiently in a wide pH range of dye solutions.

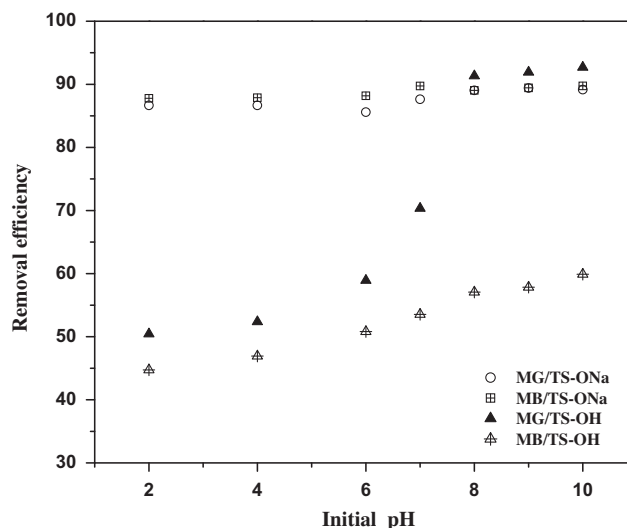


Figure 6 Effect of the initial pH solution on MB and MG removal by TS-OH and TS-ONa. Dye concentration: 150 mg L^{-1} ; adsorbent dose: 1 g L^{-1} ; contact time: 2 h; temperature = $22 \text{ }^\circ\text{C}$.

On the other hand, Fig. 6 shows a steady-state adsorption of MB and MG onto TS-OH where dye removal is clearly dependent on initial solution pH. Dye removal progressively increases with increasing solution pH. At pH 2, the sorption whether of MB or MG onto TS-OH is less efficient as only removal percentages of 44.74% and 50.43%, respectively are achieved. The low sorption is indubitably inherent to proton which is preponderant at pH 2 and consequently can compete with cationic dyes for surface sites. Similar behavior has been frequently reported through different studies where the authors investigated dye sorption by numerous biomaterials (Hameeda and El-Khaiary, 2008; Han et al., 2006; Bulut and Aydın, 2006; Batzias and Sidiras, 2004; Shi et al., 1999). Beyond pH 2, MB sorption gradually increases without saturation from 44.74% to attain 59.89% removal percentage at pH 10. This is rather contrasting with previous results reported by Hameeda and El-Khaiary, that for initial pH ranging from 4 to 10, the sorption efficiency of MB onto broad bean peels shows a plateau and the dye removal remained nearly constant beyond pH 4 (Hameeda and El-Khaiary, 2008). Enhancement of sorption at higher pH can be explained by the fact that TS-OH material becomes partially negatively charged, showing concurrently greater affinity toward basic dyes via coulombic forces of attraction (Hameeda and El-Khaiary, 2008; Shi et al., 1999). As to the sorption of MG onto TS-OH, the trend is quite similar to that of MB except that MG removal becomes exceptionally high, approaching 93% at pH 8. This could be attributed to the attack of the hydroxyl ion over the ethylene bridge at the center of MG molecule. In fact, Rytwo and co-workers reported that the slow addition of OH^- to MG dication leads to the formation of a carbinol compound $[\text{MG-OH}]^+$ that behaves as a monovalent cation (Rytwo et al., 2000). The break of the conjugated double-bond system in the center of the MG molecule reduces the delocalization of π electrons, causing the disappearance of the band at 632 nm, and therefore making the solution colorless. As for our experiments, although reaching pH 10, we have not noticed the

disappearance of the adsorption band at 632 nm. However, the dye solutions do in fact become colorless whether at pH 1 or 12. Since the introduction of a strong base could alter the ionic character and aggregation state of the dyes, our experiments were carried out without adjusting the solution pH. However, a change in the solution pH was methodically noticed after contact with the adsorbents, and when equilibrium was reached, the pH drop was limited to 0.4–0.6 units for raw TS–OH and from 0.8 to 1.0 units for the TS–ONa material, which suggests the ion-exchange character of the latter adsorbent.

3.4. Sorption isotherms

The adsorption isotherms of cationic dyes MB and MG for both TS–OH and TS–ONa adsorbents are shown in Fig. 7. The adsorption isotherm of the dyes for TS–ONa is characterized by a regular shape with a steep initial slope. The great affinity of TS–ONa adsorbent for the cationic dyes is suggested by the quantitative uptake at low adsorbate concentrations. The experimental data were compared by using the Langmuir isotherm equation (Langmuir, 1916) that can be written as Eqs. (3) and (4).

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (\text{non-linear form}), \quad (3)$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} b} \quad (\text{linear form}), \quad (4)$$

where q_e (mg g^{-1}) is the amount of dye adsorbed per gram of sorbent, q_{\max} (mg g^{-1}) is the maximum sorption capacity per gram of adsorbent, C_e (mg L^{-1}) is the equilibrium concentration of dye in solution, and $b\psi$ ($\text{L}\psi \text{ mg}^{-1}$) is the Langmuir constant related to the energy of adsorption.

As shown in Fig. 8, the analysis of the equilibrium experimental data of MB and MG adsorption onto TS–OH and TS–ONa by utilizing the Langmuir isotherm equation gave linear plots. The linearized forms of the Langmuir isotherm were found to be linear over a broad concentration range, with ex-

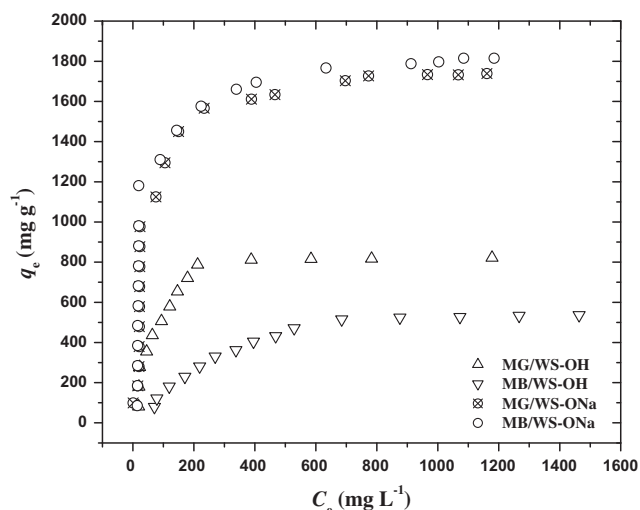


Figure 7 Adsorption isotherm for MB and MG removal by TS–OH and TS–ONa. Adsorbent dose: 1 g L^{-1} ; contact time: 2 h; temperature = $22 \text{ }^\circ\text{C}$.

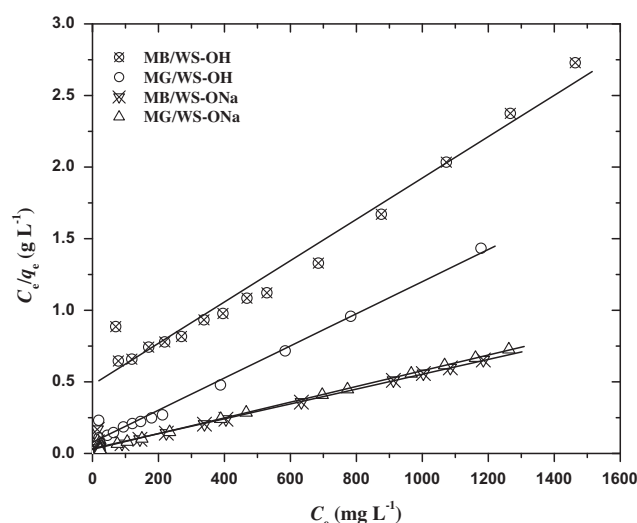


Figure 8 Langmuir plots for MB and MG removal by TS–OH and TS–ONa adsorbents.

remely high correlation coefficients (see Table 1). These results clearly indicate that the Langmuir model fits adequately the experimental data of the dyes' sorption onto TS–OH and TS–ONa to an equal degree. As shown in Table 1, the q_{\max} values of the cationic dyes on the alkaline treated material TS–ONa were dramatically changed. The maximum adsorption capacities of MG and MB on the treated sawdust were increased about two to almost three times, respectively, than those of the raw material. These huge adsorption capacities confirm the presence of abundant readily accessible adsorption sites and strongly suggest the homogeneous distribution of active –ONa groups on the surface of the treated material.

The highest b values found for MG dye on TS–OH and to a lesser extent on TS–ONa materials indicate that both adsorbents show a clear preference on binding divalent cation MG over monovalent MB (Table 1). Despite the fact that MG molecule has a greater size than that of MB, it is nonetheless sorbed onto TS–OH with quite similar effectiveness ($1.467 \text{ mmol g}^{-1}$ for MG vs. $2.171 \text{ mmol g}^{-1}$ for MB). This is likely due to the great predisposition of the MG dye to weak coulombic interactions at the surface of the lignocellulosic material by means of its extra positive charge. Another explanation could be that the additional charge of MG may also play a significant role when other cooperative mechanisms occur throughout the adsorption process, especially complexation. The extra charge could then take part in the process when in proximity to carboxylic and other carbonyl groups present in the lignin part of raw TS–OH material. However, the trend is considerably prominent for adsorption of the dyes onto TS–ONa as to

Table 1 Langmuir isotherm constants for the adsorption of MG and MB on TS–ONa and TS–OH.

| Adsorbent | Dye | q_{\max} (mg g^{-1}) | $b\psi$ ($\text{L}\psi \text{ mg}^{-1}$) | R^2 |
|-----------|-----|-----------------------------------|--|-------|
| TS–OH | MB | 694.44 | 0.0030 | 0.986 |
| | MG | 892.86 | 0.0144 | 0.994 |
| TS–ONa | MB | 1928.31 | 0.0151 | 0.989 |
| | MG | 1821.33 | 0.0193 | 0.998 |

the q_{\max} values found (2.992 mmol g⁻¹ for MG vs. 6.029 mmol g⁻¹ for MB), TS-ONa shows a definite pronounced affinity for the MB dye than for the MG one. The maximum adsorption capacity of MB is twice superior to that of MG. This could be explained by the homogeneous nature of the material which is mainly composed of cellulose as confirmed by FTIR and ¹³C NMR spectroscopies. Furthermore, the surface of the TS-ONa adsorbent is tidily negatively charged which makes it a powerful reactant toward cationic species. This suggests that no cooperative adsorption mechanisms occur besides the predominant ion-exchange which takes place very rapidly. This implies that once the sorption sites are fully occupied there will be no more space for further contaminants to lie on the surface of the material. Eventually, the additional charge of MG becomes ineffectual and therefore, thanks to its smaller size, MB is easily loaded on the surface of TS-ONa adsorbent than MG.

The most appropriate sorption mechanism occurring during the removal of cationic dyes onto TS-ONa is certainly the ion exchange mechanism. This is corroborated by an adsorption process that takes place very rapidly so that equilibrium is established as early as 10 min of contact time. This implies that sorption active sites present on the surface of the adsorbent, in this case the negatively charged -ONa groups, are readily accessible to dye molecules during the adsorption process. Furthermore, the abundance of these incorporated functional groups onto the TS-ONa matrix is well-established since the alkaline treatment of TS-OH leads to a cellulose-based material containing only hydroxyl groups that have undergone a total acid-base exchange reaction. Finally, the adsorbed amounts of MB and MG dyes onto TS-ONa, which are of the order of 6.029 and 2.992 mmol g⁻¹, respectively, are far below the exchange capacity of the TS-ONa sorbent (13.15 mmol g⁻¹, assuming that TS-ONa is simply composed of cellulose). As previously mentioned, the presence of empty sorption sites is related to the steric hindrance of the dyes which govern the anchorage of dye molecules on the surface of the adsorbent. Nevertheless, when comparing the adsorption capacities of the two dyes onto TS-ONa, we note that less-sized MB is better removed than MG.

3.5. Thermodynamic parameters

The adsorption of the two cationic dyes at two concentrations onto TS-OH and TS-ONa adsorbents was studied at three temperatures to determine the thermodynamic parameters, and the results are summarized in Table 2. Expect for MG

dye at a concentration of 500 mg L⁻¹ where the temperature has nearly no effect on the equilibrium capacity, in all other experiments however, the adsorption capacity decreased as the temperature rises. This regular decrease of adsorbed dye at higher temperature suggests the exothermic nature of the adsorption process. For both dyes, the decrease in the adsorbed amounts of dyes is more pronounced with TS-OH than for TS-ONa. This could be explained by the fact that when temperature increases the physical bonding between the dye molecules and the active sites of the adsorbent will weaken. Another explanation is the possibility of the occurrence of a desorption step proper to the reversibility of the established interactions between adsorbent and dye molecules (Renault et al., 2008; Crini and Badot, 2008; Baouab et al., 2000).

The thermodynamic parameters (ΔG° , ΔH° and ΔS°) were calculated by using the following equation:

$$\ln K_d = -\frac{\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (5)$$

where T is the temperature (K), R is the ideal gas constant (8.314 J mol⁻¹ K⁻¹) and K_d is the distribution coefficient (amount of removed dye per gram of material divided by its concentration in the liquid phase).

The vant'Hoff plot of $\ln K_d$ as a function of $1/T$ gave straight lines. The calculated slope and intercept from the plot were used to determine ΔH° and ΔS° , respectively (see Table 2). The negative value of ΔG° at each temperature implies a favorable and spontaneous adsorption process and confirms the affinity of both adsorbents for cationic dyes. The negative value of ΔH° indicates that the adsorption is exothermic and also suggests that the adsorption process is a physical adsorption enhanced by chemical interactions between cationic dyes and active sorption sites whether on TS-OH or TS-ONa adsorbents. These results show that adsorption is physical in nature involving electrostatic forces of attraction whose intensities are closely associated to the chemical characteristics of the sorption sites at the surface of the adsorbent. With the exception of the sorption onto TS-ONa of MG dye at a concentration of 500 mg L⁻¹ where the temperature has nearly no effect on the equilibrium capacity, we noticed for the rest of sorption experiments a steady decrease in ΔG° values as the temperature rises, which suggests the feasibility of the adsorption process at low temperatures. The positive value of ΔS° obtained for MG sorption (500 mg L⁻¹) onto TS-ONa adsorbent revealed the increased randomness at the solid/solution interface during the adsorption of MG onto TS-ONa adsorbent.

Table 2 Thermodynamic parameters for MG and MB removal by TS-ONa and TS-OH adsorbents.

| Adsorbent | Dye | C_i (mg L ⁻¹) | ΔS° (J mol ⁻¹ K ⁻¹) | ΔH° (kJ mol ⁻¹) | ΔG° (kJ mol ⁻¹) | | | q_e (mg g ⁻¹) | | |
|-----------|-----|-----------------------------|---|--|--|--------|--------|-----------------------------|--------|--------|
| | | | | | 295 K | 308 K | 318 K | 295 K | 308 K | 318 K |
| TS-ONa | MG | 500 | 76.33 | -2.05 | -24.80 | -25.56 | -26.33 | 478.80 | 478.13 | 477.38 |
| | | 1000 | -198.54 | -83.64 | -24.48 | -22.49 | -20.50 | 976.78 | 800.75 | 760.67 |
| | MB | 500 | -235.12 | -93.62 | -23.54 | -21.20 | -18.85 | 484.27 | 358.79 | 312.72 |
| | | 1000 | -385.02 | -138.51 | -23.77 | -19.92 | -16.07 | 981.00 | 527.27 | 415.15 |
| TS-OH | MG | 500 | -304.73 | -111.02 | -20.21 | -17.17 | -14.12 | 436.33 | 256.93 | 75.84 |
| | | 1000 | -180.66 | -72.81 | -18.98 | -17.17 | -15.36 | 787.64 | 414.79 | 267.79 |
| | MB | 500 | -125.98 | -54.24 | -16.70 | -15.44 | -14.18 | 281.06 | 134.85 | 93.18 |
| | | 1000 | -359.24 | -121.58 | -14.52 | -10.93 | -7.34 | 471.21 | 54.55 | 18.18 |

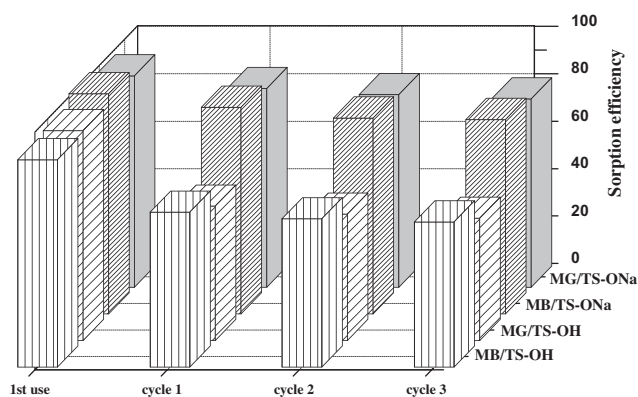


Figure 9 Percentages of MB and MG removal by TS-OH and TS-ONa adsorbents over three repeated adsorption-desorption cycles.

3.6. Regenerability

Desorption experiments put into evidence that NaCl aqueous solution provided excellent desorption performances for both adsorbents. Even though, the NaCl solution was able to desorb cationic dyes from the TS-OH material with excellent yields (~95%), nevertheless, slightly higher desorption yields were obtained from TS-ONa adsorbent over three repeated adsorption-desorption cycles. As shown in Fig. 9, whereas the repeated use of the regenerated TS-ONa material ended up in just a minor change in sorption effectiveness (6–7% loss), the first reusability of the TS-OH adsorbent, however, resulted in a dramatic decrease (ca. 32%) in its re-adsorption capacity for cationic dyes sorption. The fact that the chemically modified material can be fully regenerated and the sorbent material preserves exceptional performance for subsequent reuse clearly indicates that reusability of the TS-ONa material is quite feasible.

4. Conclusion

To summarize, we demonstrated the power of alkaline treatment of a low value by-product of the timber industry. The chemically modified TS-ONa adsorbent was evaluated for its sorption efficiency for cationic dyes and compared to the raw precursor TS-OH. Based on sorption experimental data, TS-ONa in this study was more effective in removing cationic dyes from aqueous solutions by demonstrating two- to three-fold higher adsorption capacities to these dyes than those of the untreated analog TS-OH. In addition, the chemically modified adsorbent performs efficiently in a wide pH range through a uniform and fast sorption process. The repeated use of the regenerated material ended up in just a minor change in sorption effectiveness. Finally, the high recovery of the prepared adsorbent from the regeneration process allows us to consider this low-cost material as a promising candidate for the removal of basic dyes with the possibility of repeated use.

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