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Elaboration of A Lignocellulosic Material for A Comparative Study of Adsorption of Micropollutants in Aqueous Solution

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ABSTRACT

The current examination studied the chemical treatment of raw timber sawdust $(TS–OH)_n$ by chemical agents (acid and base) used for removing two anionic dyes namely, Thiazole Yellow (TY) and Bright Yellow (BY) from aqueous solutions. To assess the effects of the different conditions including pH, contact time, and temperature on the removal of dyes, Batch experiments were conducted. This results obtained from the adsorption of the two dyes, were found to be endothermic with the second-order rate kinetics, which followed the Langmuir isotherm. The monolayer saturation capacities were 1408.4507 and 140.845 mg g-1for Thiazole Yellow and Bright Yellow; respectively. By increasing the temperature of the operation, the adsorption was positively affected. The positive changes in the entropy (ΔS^0) and heat of adsorption (ΔH^0); and the negative changes in Gibbs free energy (ΔG^0) indicated the feasible and spontaneous adsorption of (TY and BY) on the adsorbent. The results revealed that 1 M aqueous NaCl completely desorbed the anionic dyes from the matrices, and when the chemically modified $(TS–OH)_n$ was reused for three repeated cycles, there was just a slight decrease in its applicability. These findings indicated that by chemical treatments, a low value by-product of the timber industry can be modified into a useful adsorbent.

Keywords: *Chemical Treatment, Removal of Dyes, Adsorption, Thiazole Yellow, Bright Yellow, Timber Sawdust.*

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1. INTRODUCTION

Several products associated to the textile and food dyes, and dye intermediates such as benzidines, have been found to cause cancer. Additionally, the wasted dyes and colors which have been poured in the effluents disturb the transmission of light in the water bodies. 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 (Uma et al., 2009; Bae and Freeman, 2007). The treatment of dye contaminated wastewater has received significant attention in textile industries. Various approaches for the removal of dyes have been investigated, including adsorption, chemical coagulation, photo degradation, biodegradation, active sludge, etc. (Hai et al., 2007; Forgacs et al., 2004). In the last three decades, various techniques for treating wastewater have been developed in order to remove the dyes from the industrial effluents. In the literature, studies conducted on treating the dyes released into the effluents by these techniques have been comprehensively reviewed (Forgacs et al., 2004; Gupta and Suhas, 2009; Crini, 2006; Aksu, 2005; Pokhrel and Viraraghavan, 2004; Thompson et al., 2001; Robinson et al., 2001; Banat et al., 1996). Therefore, most of the published papers have proven their applicability considering the wastewater treatment. Adsorption has been one of the processes among them which has been commonly used to treat wastewater and especially removing dyes. The great amounts of the existing agricultural wastes or byproducts with the low price has caused them to be increasing taken into consideration in the field of dye wastewater treatment. Therefore, a lot of studies have examined the effectiveness and the mechanism of removing dyes through using miscellaneous kinds of cheap adsorbents (Ferrero, 2007; Hamdaoui, 2006; Ozacar and Sengil, 2005; Batzias and Sidiras, 2004; Aygun et al., 2003; Bouzaida I, Rammah, 2002; Ho and McKay, 1998).

One of the most commonly used materials for removing pollutants from water/wastewater is sawdust (Shukla et al., 2002). The lignocellulosic material is one of the by-products of the timber industry which is largely found in lumber mills indicating a disposal problem. The material consists of cellulose, lignin and hemicellulose. Glucose molecules which have been connected to each other primarily with b-(1–4) glycosidic bonds forming a long chain, constituted Cellulose. Lignin is a complex polymer which has been consisted of phenylpropane units, that have been cross-linked to each other by the various chemical bonds. Hemicelluloses are branched polymers including xylose, arabinose, galactose, mannose, and glucose. Hemicelluloses connect the groups of cellulose fibrils to make microfibrils, making the cell walls more stable. They also cross-link with lignin, and form a complex web of bonds which lead to the structural strength and also defy the microbial degradation (Pekkuz et al., 2008; Raji and Anirudhan, 1998; Kirk and Farrell, 1987; Ladisch et al., 1983).

Various studies have represented the effectiveness of the chemical treatment of raw lignocellulosic wastes as the success of these low-cost adsorbents. For example, the adsorption of

Methylene Blue and Methyl Green was tested by sawdust and it was noticed that the alkaline chemical treatment of the raw adsorbent improved its capacity (Djilali et al., 2012). And the adsorption of Methylene Blue and basic red 22 was examined by beech sawdust and it was found 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) improved the adsorption capacity of the treated material.

As a contribution to this matter, the objective of the present study was to develop a low-cost adsorbent by chemical treatment of timber sawdust with aqueous NaOH which not only would permit the extraction of hemicelluloses and most parts of lignin but would also allow the conversion of the polyol structure into a negatively charged cellulose-based material, followed by a treatment of acetic acid and a treatment of sebacoyl chloride. The last obtained material TS–Sebacoyl was applied to the comparative removal of two anionic dyes thiazole yellow (TY) and bright yellow (BY).

Batch experiments were carried out for kinetic studies on the removal of TY and BY from the aqueous solution. The influence of the various important parameters such as pH, contact time, temperature on the performance of the TS–Sebacoyl material after the regeneration was checked to ascertain its stability and reusability.

2. MATERIALS AND METHODS

2.1. Reagents

All the chemicals used were of the analytical reagent grade. Thiazole Yellow (TY) and Bright Yellow (BY) were purchased from Aldrich and were used as received. The chemical structures of TY and BY have been shown in (Fig1). The pH of Thiazole Yellow (TY) and Bright Yellow (BY) solution was adjusted by adding 0.1 molL^{-1}HCl or NaOH solution. The stock solutions (2000 mg L^{-1}) of the dyestuffs were prepared by dissolving TY and BY in distilled water, and the test solutions of the desired concentrations were obtained by further dilution with distilled water.

2.2. Chemical treatments

Raw timber sawdust $(TS–OH)_n$ was provided by a local carpenter. The material as obtained was sieved for a particle size of 250 µm; 50g of (TS-OH)n was mixed with 500 mL (20 wt.%) NaOH solution and the mixture were stirred for 4 h at room temperature. The suspension was filtered and the solid was washed for several times to remove the excess NaOH with distilled water until neutral pH was obtained, and then washed with acetone. The material was then dried overnight in an electric drying oven at 80 ^{0}C and passed through a 250 µm sieve to afford 21g of TS–ONa as a yellowish powder. A dark effluent was noticed during washing the sawdust with distilled water, which indicated the removal of lignin and base soluble extractives from the sawdust (Meena et al., 2008). The 21 g of TS–ONa was immersed in 500 ml total volume, 30% acetic acid (150 ml), and 70% acetone (350 ml). The mixture was stirred for 4 h at room temperature; After the filtration, the obtained TS–OH was washed several times with distilled water until the neutral pH, and then dried in the oven for 12 h at 80 ^{0}C. The material obtained followed by immersing in 500 ml of toluene, and the mixture was stirred for 48 h at room temperature. Then, 150 ml of pyridine was added, and the stirring was continued for 12 h. Subsequently, 27 ml of sebacoyl chloride and 27 ml of toluene were poured into the material, and the mixture was stirred for 12 h at room temperature. Finally, after the filtration, the obtained material was washed with distilled water and acetone several times, and then dried in the oven. The last obtained material was designated as TS–Sebacoyl.

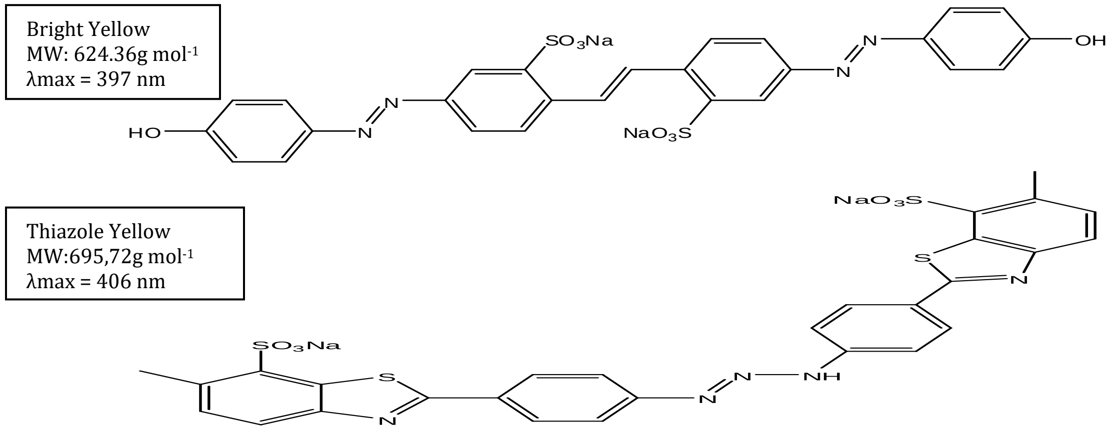

Figure 1. Molecular structures of dyes.

2.3. Experimental procedure and analytical methods

Infrared spectra were obtained on (2.5 wt.%) samples in KBrdisks from 400 to 4000 cm^{-1} using a Nicolet Avatar 330 Fourier transform IR spectrometer.

The morphology of the TS–OH and TS–Sebacoyl was examined at the high magnification using a HITACHI S-4800 SEM.

The concentrations of dyestuffs were measured with a HACH DR4000U UV–visible spectrophotometer at 406 and 397 nm for TY and BY, respectively. The adsorbed amounts of dyestuffs were determined by considering the differences between the initial and final concentrations by the following mass balance equation:

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

where (qe) is the amount (mg g^{-1}) of dye adsorbed, Ci and Ce are the initial and equilibrium dye concentrations (mg L^{-1}) in solution, respectively, V is the adsorbate's volume (L) and w is the adsorbent's weight (g). All the experiments described below were undertaken in either the duplicate or the triplicate.

The removal of TY and BYby TS–Sebacoyl was investigated in batch experiments by stirring 50mg of the material with 50 mL of dye solution in 200 mL stoppered glass bottled at 25°C for 20h and 18h for TY and BY, respectively. Each isotherm was consisted of dye concentrations varying from 100 to 2000 mg $L^{-1}$and 100to 1000 mg $L^{-1}$for TY and BY; respectively. The equilibrium concentrations of different combinations were measured by the spectrophotometer and referenced with the calibration curves. The kinetic measurements were carried out using 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 obtained mixtures were stirred at predetermined time intervals, then, were analyzed for the dye concentration. In order to find out the impact of pH on the dye removal, each dye was examined. The range of pH in this study was from 2 to 10. The sample mass was 50 mg, and the dye concentration was 150mg L^{-1} (50 mL) in this series of experiments. The influence of the temperature on the removal process was studied at three different temperatures (25, 35, and 45°C) with TS–Sebacoyl suspensions in TY and BY solutions at two different concentrations of (500 and 1000 mg L^{-1}). The suspensions were stirred during 20 h and 18 h for TY and BY; respectively, and then the dye concentration was analyzed.

2.4. Desorption and reusability

To assess the feasibility of the consecutive reuse of TS–Sebacoyl, the sorption–desorption studies of TY and BY on the matrix were carried out at room temperature using 100 mg of the material, and 100 mL of the dye solution at a concentration of 50 mg L^{-1}. Initially, the adsorbent material was subjected to dye removal following the general procedure described above. After 20 h of the contact time, the suspension was centrifuged, and the dye concentration was then determined by a spectrophotometer. Distilled water was used to wash the recovered material, then it was air dried, and after that, it was kept in 100 mL of aqueous NaCl solution (1 M). For 20 h, the obtained materials were stirred, then centrifuged, and until obtaining the result of negative AgNO3, the regenerated material was washed with distilled water. After that, under the same conditions, the regenerated material was suspended in dye solutions. The sorption–desorption cycles were repeated for three times.

3. RESULTS AND DISCUSSION

3.1. Characterization

The FTIR spectrum (Fig. 2) of the raw timber sawdust (TS–OH)n and the modified timber sawdust by the base treatment with NaOH at the peak of 1702 cm^{-1} of the precursor (TS–OH)n was disappeared because the base treatment with 20 wt.% NaOH was allowed at the same time. All the extractable and mineral substances, pectin, and hemicelluloses were completely removed making the solubilization of a large part of lignin possible (Djilali et al., 2012). This band has been typical of the carbonyl functions of carboxylic acid, aldehyde and esters groups peculiar to lignin. The shape of TS–ONa spectrum was quite similar to that of cellulose and TS–OH. The two absorption bands appeared at 2919 and 2851 cm^{-1}were mainly due to the stretching vibration of sp^3 carbons of alkyl groups. In addition, the band centered at 3367 $cm^{-1}$was characteristic of the OH stretching band of the alcohol termini groups. The appearance of the absorption bands at 1702, 1222 and 1026 $cm^{-1}$of TS–Sebacoyl assigned for C=O which featured a strong carbonyl bonds and C–O antisymmetric stretching and C–O–C bond stretching; respectively, was an indication of an efficient esterification. The two absorption bands appearing at 1361 and 1422cm^{-1} were assigned to the sp^3C–H of the sebacic acid. The strong peak observed at 1026cm^{-1} might represent the C–O–C of the cellulose.

The SEM images at different magnifications of 80×, 200× and 400× of TS–OH and TS–Sebacoyl have been shown in (Fig 3). The micrograph of TS–OH particles (Fig.3a) revealed low cavities and irregular surface structures. TS–Sebacoyl had a structure of macrocavities due to the presence of the large cavities (Fig. 3b), which were enough to allow the molecules of dye to penetrate into the structure and interact therein with the surface groups.

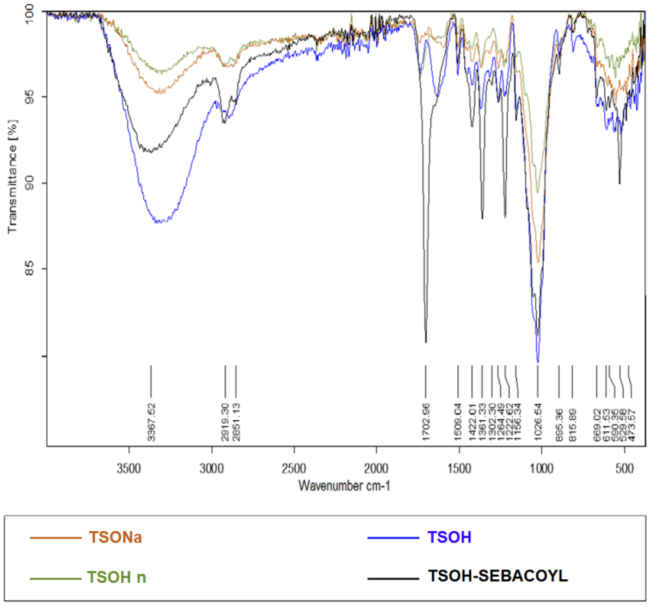

Figure 2: FT-IR spectra.

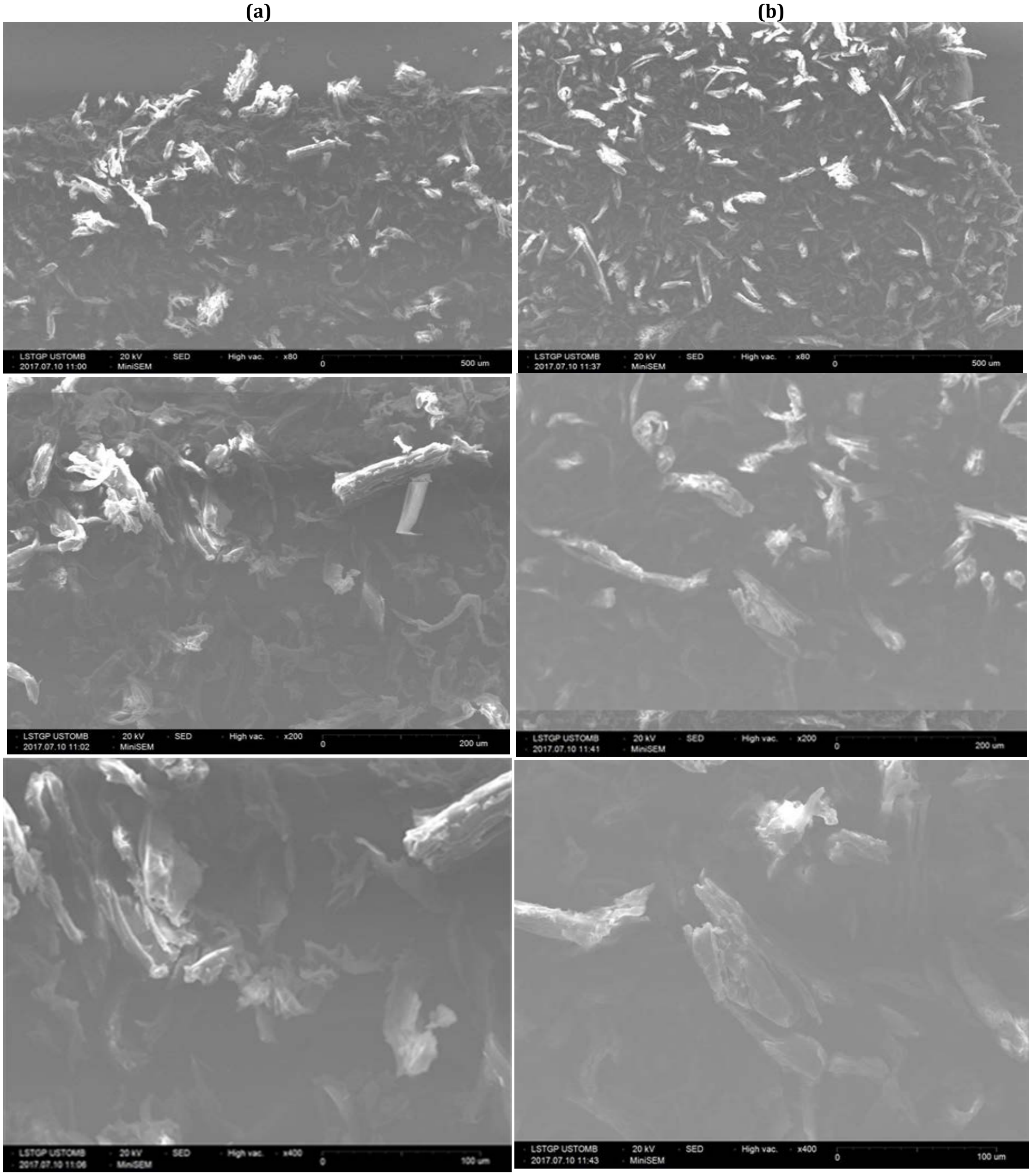

Figure 3: SEM images of TS–OH (a) and TS–Sebacoyl (b).

3.2. The effect of the contact time

The effect of the contact time on the removal dyes by TS–Sebacoyl, in the initial dyes with the concentration of $150\ mg\ L^{-1}$, has been shown in (Fig 4). The results revealed that the removal process was rather faster for TY than BY. Thus, a quite fast sorption of TY occurred between 2min to 4 hours at the elimination rate of dye, until 71%, was sequestered from the solution vs. 39% at 60 minutes for BY, for which the process was marked by a slower stage as the adsorbed amount of dye reached the equilibrium. Then, the sorption rate continued to increase at a relatively slow speed with the contact time until the maximum removal of the dyes. This was accomplished approximately after 2 h and18 h for TY and BY, with a maximum elimination rate of 90.13% and 39.50%; respectively. Similar behavior has been observed for the sorption of Acid Blue 25 into the base treated Shorea dasyphylla sawdust. The researchers have concluded that during the initial period of time, the removal of the dye by the material was fast followed by a slowdown. At the beginning of adsorption, the rate was fast because all the adsorption sites were vacant. However, as these sites were progressively covered, the rate of the adsorption decreased (Megat et al., 2012). In order to examine the controlling mechanism of the sorption process, pseudo-first order model and pseudo-second order kinetic models were used to analyze the experimental data. 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):

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

where k_1 (min^{-1}), andk_2 (g mg^{-1} min^{-1}) are the rate constants of the pseudo-first order and the pseudo-second order for the sorption process, respectively, q_e and q_t (mg g^{-1}) are the amounts of dye sorbed at the equilibrium and at time t (min), respectively. The equilibrium sorption capacity (q_e), the rate constants (k_1, k_2), and the coefficient (R^2) values were calculated from the linear plots. The parameters obtained for the two models have been presented in Table 1. The perfect correlation was however observed between the experimental data and the pseudo-second order kinetic model with the excellent correlation coefficients. Moreover, the calculated q_e values from the model completely agreed with the experimental sorption capacities, representing the effectiveness of the model. In the literature, many studies have shown that the adsorption kinetics of the numerous dyes in the various chemical treatments of the timber sawdust were well fitted in the pseudo-second order model. For example, the pseudo-second order was the best model for describing the adsorption kinetics of AB25 dye on base treated Shorea dasyphylla sawdust (Megat et al., 2012).

Table 1. Kinetics constants for TY and BY dyes sorption onto TS–Sebacoyl

	Qe (exp)	Pseudo-first order model			Pseudo-second ordermodel		
Dye	mg g^{-1}	Qe mg g^{-1}	K_1 min^{-1}	R^2	Qe mg g^{-1}	K_2 $gmg^{-1}min^{-1}$	R^2
TY	135.2083	51.999	0.0023	0.842	142.8	0.0002	0.995
BY	59.2592	6.558	0.0004	0.946	62.5	0.0003	0.996

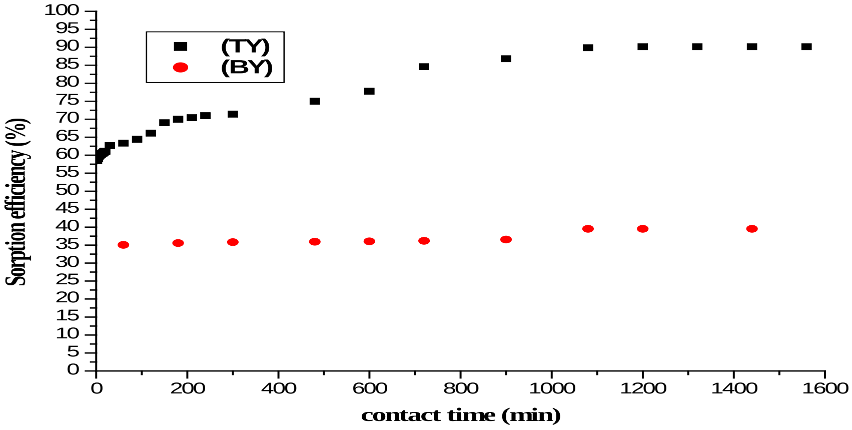

Figure 4: Effect of contact time on the sorption rate of TY and BY dyes by TS–Sebacoyl

3.3. The effects of pH

The pH of the solution had a significant impact on the amount of TY that could be adsorbed. pH can influence the dissociation of the adsorption sites and the solution chemistry of TY, particularly the degree of the ionization. The maximum amount of the adsorption was observed at an acidic condition, but decreased with the increase in pH values (Fig. 5). Beyond pH = 5, the removal rate of TY by the adsorbent support tended to stabilize to reach a level of 67.63% at pH = 10.03. A similar finding was reported in Acid Red 37 (AR 37) and Acid Blue 25 (AB 25) adsorption by chitosan and chemically modified chitosan (Azlan et al., 2009). At a low pH, the concentration of H^+ in the bulk solution would be high, and the functional groups of TS–Sebacoyl would be protonated, thus enhancing the electrostatic attraction between the adsorbent and TY. In the aqueous solution, the sulfonate groups of TY were dissociated and converted to anionic form. As the pH increased, the number of positively charged adsorbent surface was reduced. This would not favor the adsorption of TY due to the reduction in the electrostatic attractions. In addition, due to the presence of various functional groups in TS–Sebacoyl as demonstrated by FTIR spectra, other adsorption mechanisms such as hydrogen bonding and chemical adsorption could not be ruled out. On the other hand, (Fig 5) shows the adsorption of BY was clearly independent from the initial solution pH, in the pH range = 2 to 10, which proved that the pH of the solution did not affect the removal of BY by the TS-Sebacoyl adsorbent, and the removal rate of BY reached to 43.58%

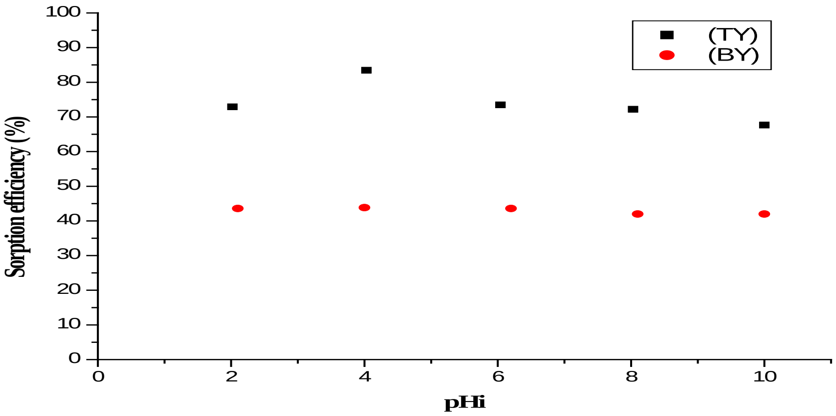

Figure 5: The effect of pH on the sorption rate of TY and BY dyes by TS–Sebacoyl.

3.4. Sorption isotherms

The sorption isotherms of anionic dyes TY and BY onto TS–Sebacoyl have been reported in (Fig.6). The adsorption of dyes increased with the increasing initial concentration to reach the equilibrium. A great difference was observed in the adsorbed quantity of the two dyes by the material which was represented graphically by a very weak slope of the curve of the BY than that of the TY. The experimental data were analyzed by using Langmuir and Freundlich isotherm models. The linear form of Langmuir' isotherm model has been given by the following equation:

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

The Freundlich isotherm equation could be written in the linear form as given below:

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

where x/m (qe.mg g^{-1}) is the amount of dye adsorbed per gram of sorbent, Q0(qmaxmg g^{-1}) is the maximum sorption capacity per gram of adsorbent, Ce (mg L^{-1}) is the equilibrium concentration of dye in solution, and b(L mg^{-1}) is the Langmuir constant related to the energy of adsorption, K(L g^{-1}) is the relative adsorption capacity constant of the adsorbent and 1/n is the intensity of the adsorption constant.The calculated results of the Langmuir and Freundlich isotherm constants have been given in (Table 2). It was found that the adsorption of TY or BY on the TS-Sebacoyl were correlated well (R > 0.99) with the Langmuir equation.

Table 2: Langmuir andFreundlich isotherm constants and the correlation coefficients.

	Freundlich constants			Langmuir constants		
Dye	n	K_F L g^{-1}	R^2	Qemgg^{-1}	bLmg^{-1}	R^2
TY	1.703	24.215	0.975	1408.450	0.0039	0.990
BY	4.347	29.994	0.926	140.845	0.0196	0.999

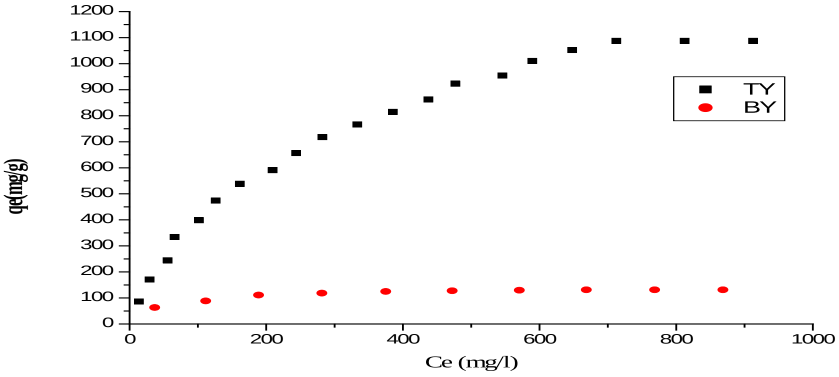

Figure 6. The sorption isotherm for TY and BY dyes onto TS–Sebacoyl.

3.5. Thermodynamic parameters

The adsorption of the two dyes at two concentrations onto TS–Sebacoyl adsorbent was studied at three temperatures to determine the thermodynamic parameters, and the results have been summarized in (Table 3) and (Table 4). The dyes's uptake increased with an increase in temperature, indicating an endothermic process. The thermodynamic parameters ΔG, ΔH, and ΔS have represented by Eqs (5), (6) (Zhu et al., 2010):

$$\Delta G^0 = -RT.\log KL \qquad (5)$$

$$\log K_L = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \qquad (6)$$

Where T is the temperature (K), R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), and KL is the Langmuir equilibrium constant (L mg^{-1}). The vant'Hoff plot of log KL versus 1/T gave straight lines. The calculated slope and intercept from the plot were used to determine ΔH and ΔS; respectively. The negative values of ΔG at all the temperatures indicated that the adsorption process was spontaneous, and TY, BY had a good affinity for TS–Sebacoyl surface. The positive value of ΔH confirmed that the adsorption process was endothermic. The positive value of ΔS indicated an increase in randomness at the solid/solution interface after the adsorption on TS–Sebacoylsurface.

Table 3. Thermodynamic parameters of TY adsorption

C_i mg l^{-1}	ΔS^0 J mol^{-1} k^{-1}	ΔH^0 KJ mol^{-1}	qemgg^{-1}			ΔG^0KJmol^{-1}		
			298 K	308K	318K	298K	308K	318K
1000	113,3484	15,19068	648,95	686,45	731,25	-18,58714	-19,72063	-20,85411
500	82,49337	6,78096	285	295	305,83	-17,80206	-18,627	-19,45193

Table 4. Thermodynamic parameters of BY adsorption

C_i	ΔS^0 J mol^{-1} k^{-1}	ΔH^0	qe mg g^{-1}			ΔG^0 KJ mol^{-1}		
mg l^{-1}		KJ mol^{-1}	298 K	308K	318K	298K	308K	318K
1000	46,536	1,1634	144,44444	146,2963	148,14815	-12,70433	-13,16969	-13,63505
500	53,22555	2,27694	97,222222	99,074074	101,85185	-13,58427	-14,11653	-14,64878

3.6. Desorption and reusability

The examinations on the desorption have focused on the elucidating the nature of the adsorption process, and in order to make the treatment process more economical, the recovery of the dyes as well as the regeneration of the adsorbent were allowed (Fig.7). The elimination of these dyes in the first use of the adsorbent gave a maximum level equal to 92.5% for TY and 67.03% for BY, and after the regeneration of this material with sodium chloride (1M), the reuse of this material for the three cycles gave the stable and appreciable removal rates of the order of 85.83% and 65.11%; respectively for TY and BY. This result was very important for the economic reasons because it allowed to deduce that this adsorbent could be reused with the same efficiency.

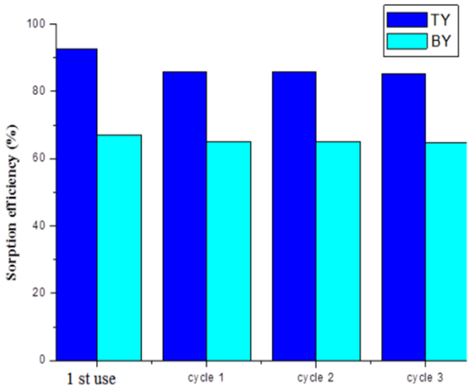

Figure 7. Percentages of TY and BY dyes removal by TS–Sebacoyl sorbent over three repeated adsorption–desorption cycles.

4. CONCLUSION

In the present study, the sorption of two acid dyes onto the chemically modified TS–Sebacoyl adsorbent was investigated. As the findings represented, the TS–Sebacoyl could be effectively applied in dye solutions with a wide range of pH. The kinetic examinations showed that the sorption process was based on the pseudo-second order model. The sorption isotherms were appropriately fitted by the Langmuir isotherm model, and the removal process took place because of the electrostatic attraction between the adsorbent and the dyes. Although, TS–Sebacoyl's dyes' removal efficiency was not affected by the ionic strength. The elimination of TY gave better results because the maximum quantity eliminated was 10 times greater than that of BY. This result could be interpreted by the difference in the molecular structures of the two dyes. Indeed, BY is a linear conjugate molecule and it is of a large size, which is its disadvantage considering its adsorption by the adsorbent support. On the other hand, TY has nitrogen atoms in its center, which impose a lack of flatness on the molecule. The TY dye is therefore a non-linear tetrahedral molecule with one of the nitrogen atoms in the center, which would facilitate the penetration of this molecule through the adsorbent support. The results of the calculation of thermodynamic parameters represented that the removal process was of the endothermic and spontaneous nature. Finally, using the material to remove the dyes for three repeated times did not reduce its capacity for the dyes' sorption. The overall findings represented that TS–Sebacoyl can be efficiently applied as an adsorbent to remove the acid dyes from the colored wastewaters.

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