

Adsorption of Supranol Yellow 4GL from Aqueous Solution onto Activated Carbons Prepared from Seawater Algae

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ABSTRACT: Adsorbents prepared from seawater algae, viz. green *Ulva lactuca* (PGA) and brown *Systoceira stricta* (PBA), by chemical activation were successfully tested for the removal of Supranol Yellow 4GL dye from aqueous solutions. Impregnation in 20% phosphoric acid for 2 h at 170 °C and subsequent air activation at 600 °C for 3 h significantly enhanced the adsorption capacities of both algae relative to their inactivated states. Parameters influencing the adsorption capacity such as contact time, adsorbent dosage, pH and temperature were studied. Similar experiments were carried out with commercially available Merck activated carbon (MAC) for comparative purposes. Adsorption efficiencies were measured at a pH 2 and dosages of 8 g/l and 12 g/l for PGA and PBA, respectively. Batch adsorption experiments resulted in maximum adsorption capacities determined from Langmuir models of up to 263, 93 and 84 mg/g for PGA, PBA and MAC, respectively. BET, FT-IR analyses, iodine number and Methylene Blue index determination were also performed to characterize the prepared adsorbents. The adsorption kinetics were found to comply with the pseudo-second-order model with intra-particle diffusion being the rate-determining step. Thermodynamic analysis confirmed that the adsorption reaction was spontaneous and endothermic. These studies indicate that these seawater algae could be used as low-cost alternatives for the removal of dyes.

INTRODUCTION

Industrial activities in the 20th and 21st Centuries have increasingly caused environmental contamination with severe consequence to aquatic life and human health. In particular, dyes represent a highly visual class of pollutants which are intensively used in the paper, printing, leather, food and textile industries (Aksu 2005). Most synthetic dyestuffs have complex aromatic structures, making them resistant to environmental conditions such as solar light, pH effects and microbial attack (Akzu and Tezer 2005). Such dyes can be classified as anionic, cationic and non-ionic dyes (Fu and Viraraghavan 2001). Their direct discharge is easily visible and also toxic to aquatic life, being carcinogenic, mutagenic and capable of seriously affecting human health by damaging vital organs (O'Mahony *et al.* 2002; Özcan and Özcan 2004). Dye effluents are difficult

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to treat, resistant to many chemical compounds and oxidizing agents, and are not capable of biological degradation (Kargi and Ozmihci 2004). Hence, it is desirable to remove colour-causing contaminants from effluents before their discharge into the natural environment. Many methods have been used for wastewater treatment such as precipitation, oxidation, ultrafiltration, flotation and coagulation; however, these types of treatment are only applicable to a limited variety of dyes for technical reasons and the high cost (Gong *et al.* 2005; Robinson *et al.* 2002).

Adsorption appears to provide an alternative means of effecting the elimination of coloured pollutants on a large scale by using the unused resources of natural materials that are available in large quantities. Such adsorbents are potentially of low cost and could be used instead of commercial activated carbon, which although having a large adsorptive capacity remains costly (Cooney 1999; Liversidge *et al.* 1997). In the present study, attention has been focused on two Mediterranean algae, viz. *Ulva lactuca* and *Systoceire stricta* found in north western Algeria, as an alternative for an activated carbon preparation. Preliminary studies performed on the untreated powdered algae revealed their interesting adsorptive properties towards Supranol Yellow 4GL dye.

MATERIALS AND METHODS

Raw material selection and activation

Both *Ulva lactuca* and *Systoceire stricta* algae were selected due to their abundance on the Algerian coast. The seawater algae were washed with distilled water and dried in sunlight for a week before treatment in the laboratory. Prior to use, they were dried in an oven overnight at 115 °C and then ground using a jar mill (Vierzen grinder) to a particle size capable of passing through a 0.071 mm sieve. The reagents used were of A.R. grade (Merck, Germany). Stock solutions were prepared by dissolving the appropriate amount of Supranol Yellow 4GL supplied by the Soitex Textile Company, Tlemcen, Algeria in distilled water according to standard procedures.

The preparation process of the activated carbon consisted of impregnation in 20% phosphoric acid solution followed by activation. Firstly, impregnation was carried out over a period of 150 min at 170 °C to dehydrate and stabilize the precursor. Secondly, the impregnated precursor was filtered, dried in an oven at 110 °C for 24 h and finally pyrolyzed at 600 °C for 3 h. Finally, after cooling to room temperature, the pyrolyzed material was washed with 0.1 N HCl followed by several washings with distilled water until the wash water when tested with lead acetate showed the absence of phosphate anions.

Adsorbent characterization

The specific surface areas of the activated carbons obtained from seawater algae as well as that of the commercial sample (Merck) were determined via BET area measurements employing a Micromeritics ASAP 2000 instrument.

The iodine number, defined as the number of mg of iodine adsorbed per g activated carbon, was determined at a residual concentration of 0.02 N. This was followed by a determination of the Methylene Blue index, which indicates the extent to which micropores and mesopores were present in the prepared activated carbons, using the method reported by Bestani *et al.* (2008).

The zero point charge of the carbon (pH_{zpc}), defined as the pH at which positive or negative charge were absent from the surface of the activated carbon, was determined as follows. A known volume (50 mL) of a 0.01 M aqueous solution of NaCl was placed in each of a series of stoppered

conical flasks. The pH of the solution in each flask was adjusted using 0.01 M NaOH or 0.01 M HCl, respectively, following which 0.15 g of activated carbon was added to each flask and the resulting suspensions stirred for 48 h when the final pH value was measured.

Finally, IR spectroscopic analysis was used to identify the principal chemical functions present on the surfaces of the adsorbents. The corresponding IR spectra were determined using a Perkin-Elmer spectrometer employing KBr samples.

Adsorption of Supranol Yellow 4GL dye

Batch sorption experiments of Supranol Yellow 4GL dye onto the activated carbon samples were conducted as a function of the initial dye concentrations (100–1000 mg/ℓ range), adsorbent dosage (2–20 mg/ℓ range), contact time (30–480 min range) and pH (2–12 range) in a series of capped 200 ml Erlenmeyer flasks at a fixed temperature. For such sorption studies, a 25 ml volume of a dye solution of known initial concentration was mixed with a known amount of adsorbent. The resulting suspension was then agitated magnetically at a constant speed of 150 rpm until equilibrium had been reached, the time necessary to attain equilibrium having been ascertained from previous kinetic experiments. After the adsorption process had occurred, the resulting solution in each flask was centrifuged at 4000 rpm and the supernatant analyzed using a UV–vis 2121 Optizen spectrophotometer at a λ_{max} value of 405 nm. Solutions were diluted as required so that their absorbance remained within the linear calibration range. Experiments were carried out in triplicate at room temperature. The equilibrium adsorption capacities (q_e) at different dye concentrations were determined according to mass balance using the following relationship:

$$q_e = \frac{(C_0 - C_e)V}{1000m} \quad (1)$$

where C_0 is the initial dye concentration (mg/ℓ), C_e is the equilibrium dye concentration (mg/ℓ), V is the volume of the liquid phase (ml) and m is the mass of the activated carbon sample (mg).

RESULTS AND DISCUSSION

Surface areas of the prepared samples

The prepared adsorbents were characterized via BET analysis of the N_2 adsorption isotherms at -196°C which yielded the specific surface area, S_{BET} (m^2/g), of the studied materials. Such specific surface areas can be calculated directly from the linearized BET isotherm in the relative pressure range $0.0554 < P/P_0 < 0.278$. The corresponding values for the samples are listed in Table 1 where the data show that the PGA, PBA and MAC samples were mainly microporous but with some mesopore content, in agreement with the Methylene Blue values obtained. The values of the iodine numbers are also listed in Table 1. The iodine number is a fundamental parameter for characterizing the performance of an activated carbon since it provides a good approximation of the entire surface area available for the adsorption of the lower weight molecular compounds, especially the microporosity. In contrast, the Methylene Blue index as obtained via the standard Chemviron Carbon Company TM-11 method characterizes the mesoporosity of a given activated carbon.

TABLE 1. Various Properties of Samples Studied

Properties	Adsorbents		
	PGA	PBA	MAC
BET specific surface area (m ² /g)	882.88	516	1031
Iodine number (mg/g)	710.7	550.96	828
Methylene Blue index (mg/g)	168.80	177.55	172.75
pH _{zpc}	6.76	6.88	6.45

Determination of surface functional groups

The IR spectra of the activated carbons derived from the marine algae are depicted in Figures 1 and 2, respectively. FT-IR analyses employing KBr pellets were performed for both PGA and PBA to determine the functional groups likely to interact with Supranol Yellow 4GL during uptake. Both figures show a number of absorption peaks, indicating the complex structure of the material used in this study. The characteristic FT-IR wavenumbers for the PBA and PGA adsorbents are summarized in Table 2 overleaf.

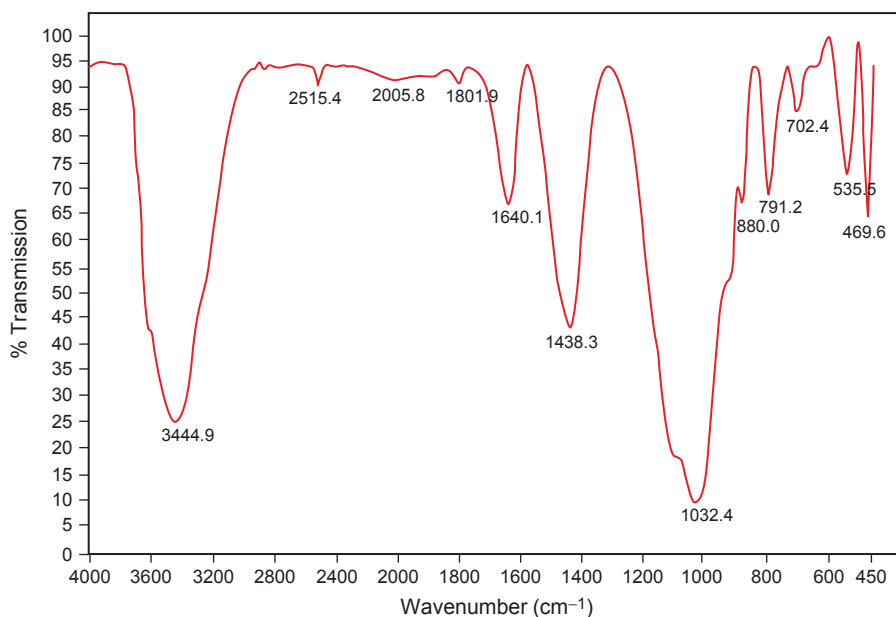


Figure 1. FT-IR spectrum of brown alga chemically activated with H₃PO₄ (PBA).

Effect of contact time

Tests were conducted in batch mode to assess the contact time necessary for each adsorption system to attain equilibrium. In subsequent experiments, each system was allowed to equilibrate for time periods in excess of this value. To determine the equilibrium time, 25 ml of a solution

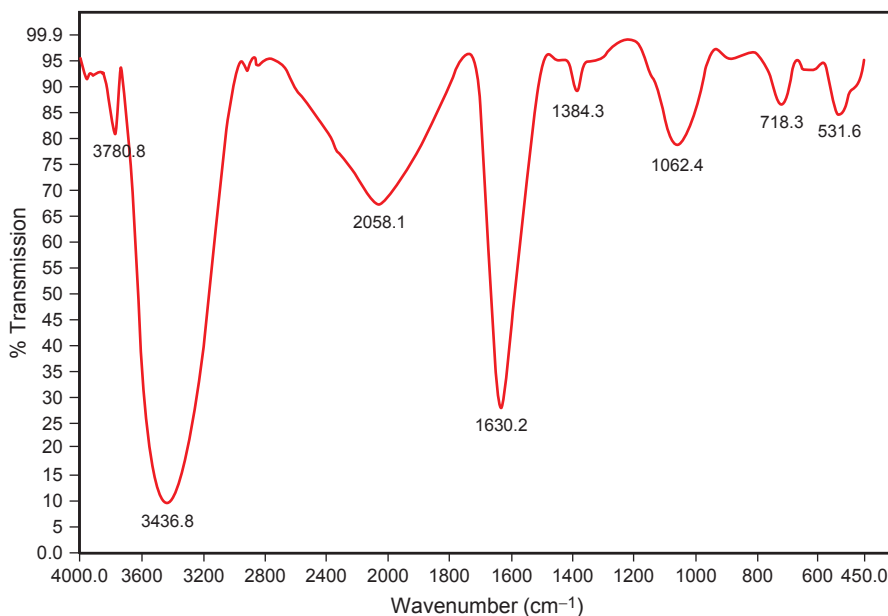


Figure 2. FT-IR spectrum of green algae chemically activated with H_3PO_4 (PGA).

TABLE 2. Characteristic FT-IR Wavenumbers^a for the PBA and PGA Adsorbents

PBA		PGA	
Wavenumber (cm ⁻¹)	Assignment	Wavenumber (cm ⁻¹)	Assignment
3445 (st)	$\nu(OH)$ for hydrogen-bonded alcohols	3780 (m)	$\nu(OH)$ for monomeric alcohols, phenols, N-H amine stretches
1640 (m)	$\nu(C=O)$ carbonyl group for ketones and carboxylic acid	3445 (st)	$\nu(OH)$ for hydrogen-bonded alcohols
1438 (st)	$\nu(COO^-)$ carboxylate ion	1630 (st)	$\nu(C=O)$ carbonyl group for ketones and carboxylic acid
1032 (st)	$\nu(C-O)$ stretches	1384 (w)	$\nu(COO^-)$ carboxylate ion
		1062 (m)	$\nu(C-O)$ stretches

^aAbbreviations: st: strong; m: medium; w: weak.

with a known arbitrarily selected concentration was mixed with a known dosage of PGA, PBA or MAC, with the resulting mixtures being agitated for time intervals ranging from 30 min to 360 min. After such agitation, the solutions were filtered and the resulting supernatants analyzed to determine the equilibrium concentration of Supranol Yellow 4GL. The data depicted in Figure 3 overleaf show that the percentage removal of Supranol Yellow 4GL by all three adsorbents increased with time until equilibrium was attained. Similar results have been reported in the literature for dye removal by other workers (McKay *et al.* 1985; El Nemr *et al.* 2009).

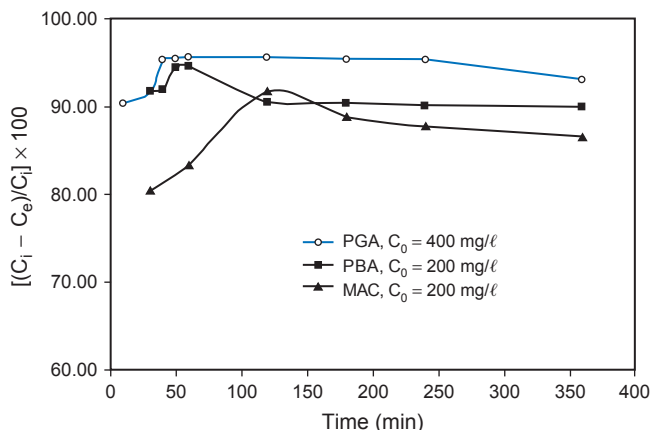


Figure 3. Influence of time on the adsorption of Supranol Yellow 4GL.

Effect of pH

Due to the charge on the adsorbate and the adsorbent, the pH of the adsorption medium is a critical parameter influencing the whole adsorption process, particularly dye uptake (McKay *et al.* 1985; El Nemr *et al.* 2009; Jain and Shrivastava 2008). The surface charge on the adsorbent can be modified by changing the pH value of the contacting solution. To determine the optimum pH conditions for the adsorption of Supranol Yellow 4GL onto PGA, PBA and MAC, the initial pH of the solution in contact with each adsorbent was varied from 2 to 12 by adding either 0.1 N NaOH or 0.1 N HCl solutions, employing a fixed initial concentration of adsorbate (200 mg/l) and a contact time of 1 h for both PGA and PBA, and 2 h for MAC. As shown in Figure 4, a consistent increase in adsorption capacity for all three considered adsorbents was observed at pH 2. However, with increasing pH, a significant decrease in the dye uptake was observed for both MAC and PBA but the amount adsorbed was only slightly affected even at high pH values with PGA (Khenifi *et al.* 2007; Bouberka *et al.* 2006). The increase in dye uptake at low pH may be due to the high

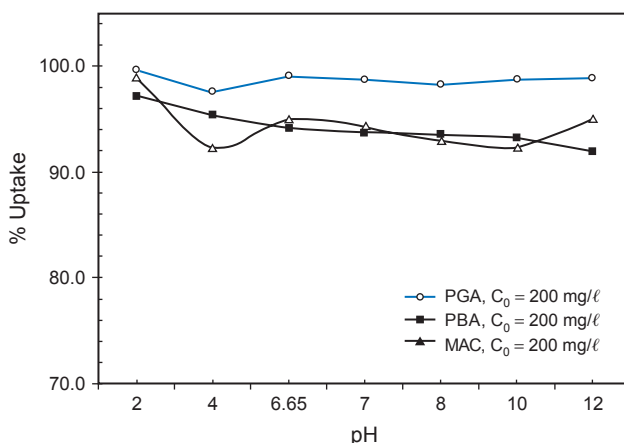


Figure 4. Influence of pH on the adsorption of Supranol Yellow 4GL.

concentration of H^+ ions in the aqueous solution competing with the dye molecules for the available sites on the adsorbent surface, a process which would be favoured by the electrostatic attraction between the surface of the positively charged adsorbent and the negatively charged dye molecules. Under these conditions, the adsorption of an anionic dye such as Supranol Yellow 4GL would be more effective in an acidic environment (Özcan and Özcan 2004).

Effect of adsorbent dosage

Of the factors influencing the adsorption properties, the amount of the activated carbon is particularly important because it determines the sorbent–sorbate equilibrium in the system and can also be used to predict the treatment cost of activated carbon per unit of dye solution. The dependence of the adsorption of Supranol Yellow 4GL on the adsorbent dosage was studied by varying the amount of PGA, PBA or MAC within the range 2–20 mg/l, maintaining all other parameters constant. As shown in Figure 5, the maximum uptake was attained at an adsorbent dosage of 4 g/l for PGA and PBA, and at an adsorbent dosage of 8 g/l for MAC when virtually 100% of the dye was removed. The results also show that the adsorbent concentrations strongly affected the percentage removal of the dye from aqueous solution. This can be attributed to the availability of a greater number of adsorption sites with increasing adsorbent dosage.

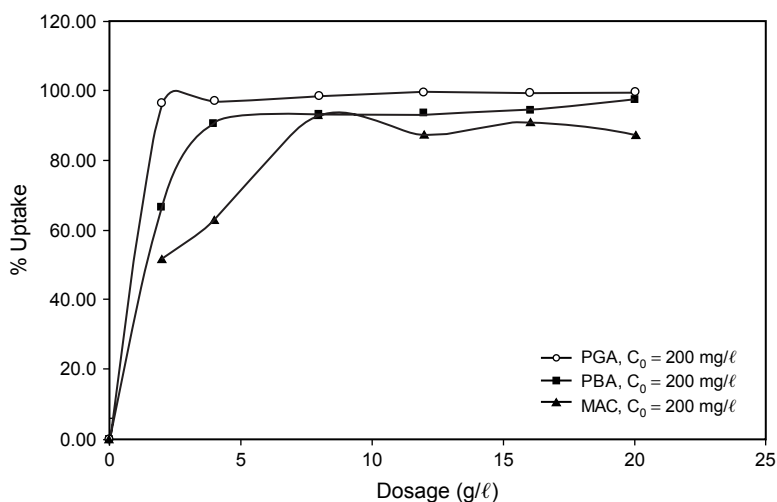


Figure 5. Influence of adsorbent dosage on the adsorption of Supranol Yellow 4GL.

Adsorption isotherm for Supranol Yellow 4L

In order to evaluate the applicability of adsorption as a means of removing Supranol Yellow 4L dye from aqueous solutions, two frequently used single-component adsorption isotherm models were considered in this study to describe the interaction between the adsorbate and the adsorbents, viz. the Langmuir and Freundlich isotherms. Both models represent the affinity of the adsorbate for the adsorption sites on the adsorbent surface. The Langmuir model, which assumes that adsorption occurs at specific homogeneous sites within the adsorbent, may be expressed by the equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L b} + \frac{C_e}{b} \quad (2)$$

The linear plot of C_e/q_e versus C_e allows both the maximum adsorption capacity corresponding to complete monolayer coverage b (mg/g) and the Langmuir constant K_L (ℓ/mg) to be obtained.

The Freundlich model has been widely used to describe adsorption data where the dye uptake occurs on a heterogeneous adsorbent surface. In this case, it is assumed that the stronger binding sites are occupied first and that the binding strength decreases with an increasing degree of site occupation. The Freundlich model may be expressed by the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

In this case, the parameters K_F and n can be obtained from the intercept and slope of the plot of $\log q_e$ versus $\log C_e$. Figures 6 and 7 show the application of the linearized forms of both models to the experimental data obtained. These data were well fitted by the Langmuir isotherm with correlation coefficients, R^2 , attaining values of 0.98, 0.99 and 0.99 for PBA, PGA and MAC, respectively. Application of the Freundlich model to the same data gave an R^2 value of 0.98 for PBA but exhibited relatively poor agreement with the experimental data for PGA ($R^2 = 0.86$) and MAC ($R^2 = 0.60$). The important constants and parameters for both isotherms and those found in the literature (Bouberka *et al.* 2006; Khenifi *et al.* 2007) are tabulated overleaf in Table 3. It may be observed that maximum adsorption capacities were obtained for the chemically activated seawater algae, whilst the lowest value was that for the Merck activated carbon. The highest values of b provide clear evidence that activation by phosphoric acid improved the sorptive ability of the seawater algae compared to the untreated ones (values not shown).

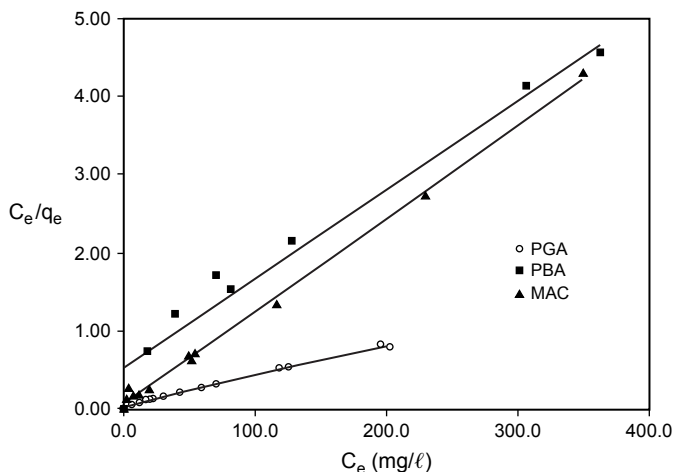


Figure 6. Linearized Langmuir adsorption isotherms for Supranol Yellow.

Kinetics of adsorption of Supranol Yellow 4GL

In order to describe the mechanism of chemical reaction, diffusion and mass transfer, several kinetic models are usually employed to test the experimental data for dye adsorption onto

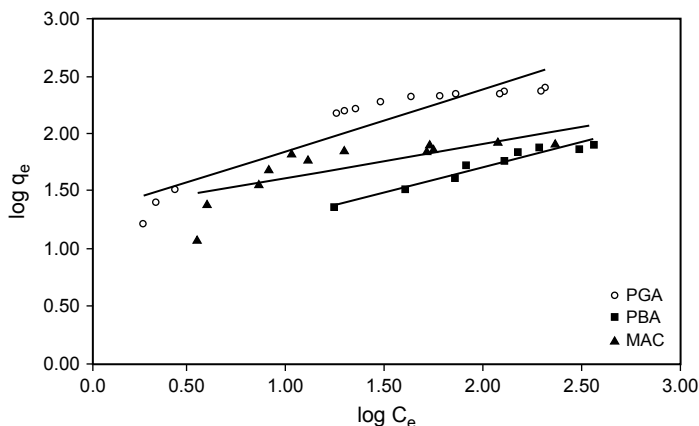


Figure 7. Linearized Freundlich adsorption isotherms for Supranol Yellow.

TABLE 3. Langmuir and Freundlich Isotherms Parameters for the Adsorption of Supranol Yellow 4L by the Prepared Adsorbents and Other Literature Data

Isotherm parameters	Adsorbents					
	PBA ^a	PGA ^a	MAC ^a	Montmorillonite ^b	Organic clay ^c	
Langmuir model	b (mg/g)	93.45	263.15	84.03	58.47	54.0
	K_L (l/g)	0.015	0.060	0.152	0.0062	0.074
	R^2	0.97	0.99	0.99	0.987	0.99
Freundlich model	K_F (l/g)	16.58	17.09	0.22	–	0.09
	n	3.71	1.69	3.36	–	0.27
	R^2	0.98	0.86	0.60	–	0.91

^aThis study. ^bBouberka *et al.* (2006). ^cKhenifi *et al.* (2007).

low-cost adsorbents (Bhattacharyya and Sharma 2005; Do 1998; Ho and McKay 1999, 2003; Waranusantigul 2003). In the present study, the applicability of the pseudo-first-order and pseudo-second-order kinetic models together with the intra-particle diffusion model were tested for the sorption of Supranol Yellow 4GL onto all the prepared adsorbents.

The linear form of the pseudo-first-order kinetic model may be written as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

where q_e and q_t (mg/g) are the amounts of dye adsorbed onto the adsorbent at equilibrium and at time t , respectively, and k_1 (min^{-1}) is the rate constant for first-order adsorption. The applicability of this kinetic model is demonstrated if the plot of $\log(q_e - q_t)$ versus t is linear allowing the values of q_e and k_1 to be determined from the intercept and slope of the plot, respectively. The low values of R^2 (Table 4 overleaf) and the difference between q_{exp} and q_{calc} indicate that this model was not well suited for describing the adsorption of Supranol Yellow 4GL dye.

TABLE 4. Kinetic Parameters for the Adsorption of Supranol Yellow 4L by Various Prepared Activated Carbons

Adsorbents	Pseudo-first order			Pseudo-second order			Intra-particle diffusion				
	q_e (mg/g)	q_{calc} (mg/g)	k_1 (min^{-1})	R^2	q_{calc} (mg/g)	k_2 [g/(mg min)]	h [mg/(g min)]	R^2	k_{int} [mg/(g $\text{min}^{1/2}$)]	C	R^2
PGA											
$C_0 = 700$ mg/ ℓ	58.19	1.30	0.059	0.90	58.14	0.012	416.66	0.99	0.098		54.311 0.96
$C_0 = 800$ mg/ ℓ	66.34	4.70	0.091	0.90	66.60	0.040	178.57	1.00	0.114		65.582 0.97
PBA											
$C_0 = 400$ mg/ ℓ	47.13	9.46	0.099	0.98	47.85	0.024	55.50	1.00	0.132		46.125 0.96
$C_0 = 500$ mg/ ℓ	61.25	3.30	0.025	0.80	61.35	0.032	119.04	0.99	0.184		52.118 0.99
MAC											
$C_0 = 550$ mg/ ℓ	67.28	27.32	0.029	0.90	70.42	0.002	10.92	0.99	1.372		52.177 0.99
$C_0 = 600$ mg/ ℓ	71.71	44.22	0.032	0.98	78.12	0.001	7.17	0.99	1.561		54.695 0.98

The linear form of the pseudo-second-order equation may be written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where k_2 is the rate constant for pseudo-second-order adsorption [$\text{g}/(\text{mg min})$] while the initial adsorption rate h [$\text{mg}/(\text{g min})$] is given by $h = k_2 q_e^2$. The linear form of the plot of t/q_t versus t depicted in Figure 8 and the higher correlation coefficient ($R^2 = 0.99$) listed in Table 4 clearly indicate that the adsorption kinetics of Supranol Yellow 4GL from aqueous solutions onto all the adsorbents considered were well fitted by the pseudo-second-order model. This is also confirmed by the experimental value of q_e and the calculated value $q_{e\text{calc}}$ which are quite close to each other, as shown in Table 4. Similar phenomena have been observed in the adsorption of Acid dyes (El-Geundi 1991; Chiou *et al.* 2004; Martin and Iwuco 1982; Bulut and Aydin 2006).

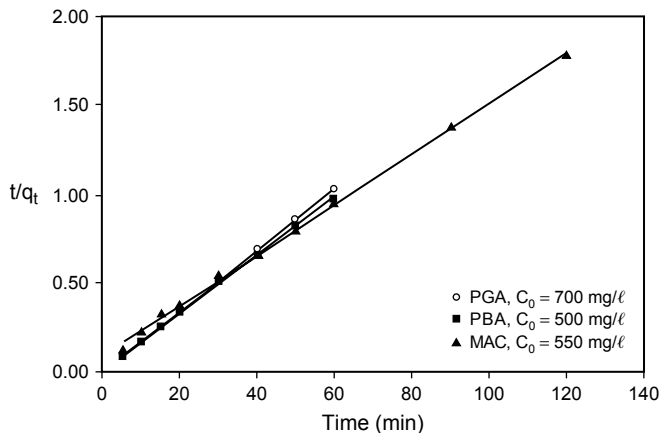


Figure 8. Pseudo-second-order kinetic plots for Supranol Yellow 4GL adsorption at pH 2.

In addition to the above models, several intra-particle models can be used to describe the factors controlling the sorption rate. These include bulk diffusion (diffusion of the solute from the solution to the film surrounding the particle), external mass-transfer resistance (diffusion from the film to the particle surface) and intra-particle mass-transfer resistance (diffusion from the surface to the internal sites) (Findon *et al.* 1993). When intra-particle mass-transfer resistance is the rate-limiting step, the sorption process may then be described as being particle-diffusion controlled. Equation (6) has been used to model intra-particle diffusion (Okieimen *et al.* 1986; McKay and Poots 1980, 2006; Weber and Morris 1963):

$$q_t = k_{\text{int}} t^{0.5} + C \quad (6)$$

where C is the intercept and k_{int} is the intra-particle diffusion rate constant [$\text{mg}/(\text{g min}^{0.5})$] directly evaluated from the slope of the linear plot of q_t versus $t^{1/2}$ as shown overleaf in Figure 9. In some circumstances, such a plot may be multi-linear, indicating that two or more steps occur (Hameed 2009; Wang *et al.* 2008; Ahmad *et al.* 2007).

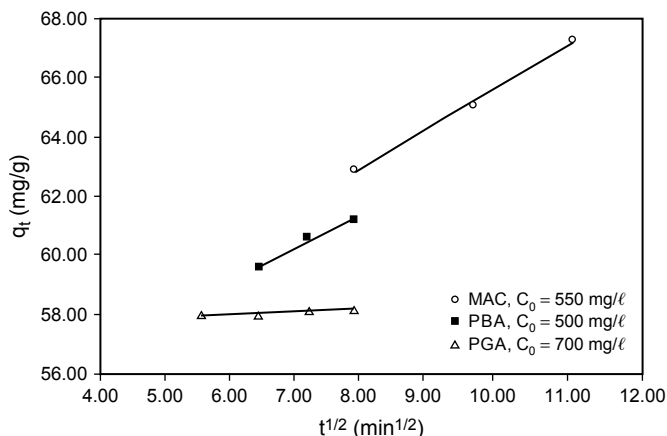


Figure 9. Intra-particle diffusion plots for Supranol Yellow 4GL adsorption at pH 2 and room temperature.

Table 4 lists the values of k_{int} and C obtained in the present work. It will be seen that these parameters increased with increasing initial adsorbate concentration. The increase in the C values corresponds to the increase in thickness of the boundary layer.

Thermodynamic parameters

In order to determine the spontaneity of the adsorption process and the enthalpy change thereby generated, thermodynamic parameters such as the standard enthalpy change (ΔH^0), the standard entropy change (ΔS^0) and the Gibbs' free energy change (ΔG^0) should be determined. These parameters can be estimated from the values of the equilibrium constants as a function of temperature and may be related by the following equation (Zubeyde *et al.* 2009; Hameed 2007; Shahryari *et al.* 2010):

$$\Delta G^0 = T\Delta S^0 - \Delta H^0 \quad (7)$$

Values of K_L obtained from applying the Langmuir model to data obtained at different temperatures can be used to evaluate ΔG^0 which is given by the following relationship:

$$\Delta G^0 = -RT \ln K_L \quad (8)$$

where R is the universal gas constant [8.314 J/(mol K)], T is the absolute temperature (K) and $K_L = (C_{Ac}/C_{eq})$ where C_{Ac} is the amount of dye adsorbed onto the material at equilibrium (mg/l) and C_e is the equilibrium concentration (mg/l). The standard enthalpy and entropy changes may be calculated from the following equation:

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (9)$$

The slope and intercept of the plot of $\ln K_L$ and $1/T$ (Figure 10 overleaf) was used to evaluate ΔH^0 and ΔS^0 , respectively.

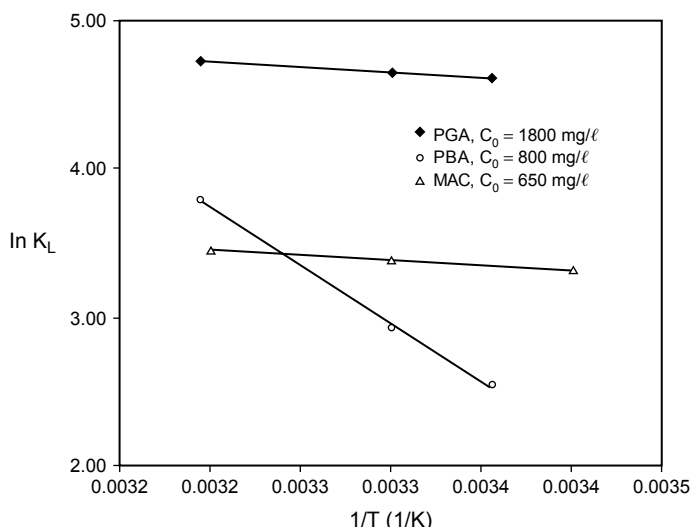


Figure 10. Plots of $\ln K_L$ versus $1/T$ for the estimation of thermodynamic parameters.

TABLE 5. Thermodynamic Parameters for the Adsorption of Supranol Yellow 4GL

Adsorbent	C_0 (mg/l)	T (K)	K_L	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 [kJ/(mol K)]
PGA	1800	298	100.7	-11.4	6.07	0.05
		303	104.7	-11.7		
		313	113.3	-12.3		
PBA	500	298	12.6	-6.29	65.23	0.24
		303	31.2	-7.37		
		313	138.5	-9.86		
MAC	650	298	27.37	-27.5	0.0072	0.51
		303	29.45	-28.1		
		313	31.62	-28.7		

The values of all the thermodynamic parameters are listed in Table 5. The positive value of ΔH^0 indicates the endothermic nature of the process, thereby suggesting that the adsorption process was physical in nature (Tan *et al.* 2008; Gupta *et al.* 2003). The negative values for ΔG^0 listed in Table 5 confirm the spontaneity of the adsorption process of Supranol Yellow 4GL by all three adsorbents and also indicate that the process became more efficient with increasing temperature. Furthermore, the positive values of ΔS^0 listed demonstrate the affinity of all considered adsorbents towards the adsorption of Supranol Yellow 4GL ions from aqueous solution through the increase in the degrees of freedom at the solid/liquid interface during adsorption (Chen *et al.* 2007; Cestari *et al.* 2004).

CONCLUSIONS

This study has shown that activated carbons prepared from seawater algae are effective adsorbents for the removal of a textile dye from aqueous solutions relative to the commercial carbon available

from Merck. A decrease in pH to 2 strongly influenced the adsorption process which attained a maximum uptake of 95%, 94.5% and 83.5% for PGA, PBA and the Merck activated carbon, respectively, a result which accords with the pH_{zpc} values of these materials. With both activated carbons based on the seawater algae examined, equilibrium was attained within 60 min. The experimental data for adsorption onto all three adsorbents considered were well fitted by the Langmuir isotherm model, with maximum adsorption capacities of 263.15 mg/g, 93.45 mg/g and 83.03 mg/g for PGA, PBA and MAC, respectively. Kinetic studies showed that the adsorption process obeyed the pseudo-second-order rate model, thereby suggesting that the adsorption process was physical with intra-particle diffusion being the rate-determining step. The positive value of ΔH^0 reflected the endothermic nature of the process which could be associated with physical adsorption. Negative values of ΔG^0 confirmed the spontaneity of the adsorption of Supranol Yellow 4GL by all three adsorbents and also indicated that interfacial transfer became more efficient with increasing temperature. Finally, the positive values of ΔS^0 supported the existence of an affinity between the dye molecules and all three adsorbents considered. The fact that the values of ΔS^0 were less than unity indicated the reversibility of the process. Finally, the significant adsorption of Supranol Yellow 4GL by the prepared adsorbents shows that such materials are suitable for adsorbing large molecules such as dyes, thereby suggesting their utility in the treatment of textile industry effluents.

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