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DYE ADSORPTION FROM INDUSTRIAL WASTEWATER ONTO TEMPLE GRASS ACTIVATED CARBON

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Abstract

This research is focused on Temple grass activated carbon for adsorption of dye from the industrial wastewater. The activated carbons were modified from the carbonization of dried Temple grass at 400°C with chemical activation. Three types of chemicals, such as sodium chloride (NaCl), potassium hydroxide (KOH), and phosphoric acid (H_3PO_4) were used for soaking for 1 h before pyrolysis at 700 ° C for 2 h. The modified activated carbon with NaCl activation has the highest specific surface area BET of 148 m^2/g, and smallest average pore of 25.72 °A. Therefore, the activated carbon with NaCl activation was used to study the dye adsorption. The influence of pH, contact time, initial feed concentration, adsorbent dose and temperature are investigated in batch experiments. The results show that the optimum conditions for removal dye from wastewater are found to be pH 2.0, contact time 90 min, adsorbent dose 1.0 g/100 mL, initial feed concentration 33.79 ppm and temperature 30 °C. The percentage removal at these optimum conditions was found to be 85.5%. The mechanism of dye adsorption on Temple grass activated carbon is according to Frundich's isotherm. This shows that the mechanic is a multilayer and irreversible adsorption, in which the adsorption constants, K_F, n_F are 3.26 L/mg and 16.10. The correlation coefficient (R^2) is 0.9765. Overall, the experimental results suggest that Temple grass activated material could be used as low cost alternative adsorbent for the treatment of dye containing industrial wastewater.

Keywords: Activated carbon, Dye adsorption, Sodium Chloride, Temple grass, Wastewater

Introduction

One of the best for wastewater treatment technologies around the world is adsorption. Now activated carbon is considered as a universal adsorbent for the removal of pollutant such as heavy metals and dyes from the wastewater due to its high surface areas, large adsorption capacities, fast adsorption kinetics and relative ease of regeneration. The most precursors used for the production of activated carbons are organic materials that are rich in carbon [1]. Natural and agricultural wastes are considered being very important raw materials for the activated carbon preparation, since they are renewable sources and low-cost. The agricultural wastes such as sugarcane bagasse [2], banana peel [3] and coconut shell [4] have been found to be suitable precursors owing to their high carbon and low ash contents. In this study, Temple grass from the football decorating was converted into the high value activated carbon, which may be used widely because of its exceptional adsorbent properties. Dyes are popularly used in textile, dyeing, printing, photography and etc. [5]. Reactive dyes are use in textile dyeing industries due to the superior fastness to applied fabric, high photolytic stability, high solubility and resistance to microbial attack [6]. Now in worldwide 10,000 types of commercially available textile dyes production reached approximately 7.10×10^5 metric tons every year [7]. The estimated amount of textile dyes discharged globally every year is 280,000 tons [8] leading to significant water pollution, a great problem in contemporary time. In many developing countries particularly in India, China, and Bangladesh, the dye-enriched textile wastewaters are not treated at all, they are just dumped into various water bodies, which are ultimately contributing to environmental degradation, killing aquatic lives, and harming human health [9]. Reactive dyes are the widely used dyes all over the world. Most of the dyeing operations of cellulosic fibers are done by reactive dyes which have the worldwide acceptance to the dyeing technologists. This water soluble dyes get exhausted on the cellulosic fiber in the presence of salt at basic pH. Under alkaline conditions fixation is carried out in which covalent bond forms between reactive

sites of fiber and cellulosic material [9]. But this alkaline condition also facilitates the reaction of reactive group with the dye liquor, resulting in deactivation or hydrolysis of the dye. Normally soda ash is used as the most commonly used alkali in the dyeing bath. The important point is not the type or amount of alkali, but the pH of the bath. However, dye fixation on cellulosic fibers is generally low (less than 70%), the results in a highly colored dye house effluent which is not favorable for the environmental grounds. As much as 50% of the total cost of a reactive dyeing process is attributed to the washing off stages to remove unfixed or hydrolyzed dyes and treatment of the resulting effluent [10]. This research is focused on Temple grass activated carbon for adsorption of dye from the industrial wastewater. Langmuir and Freundlich isotherms have been used to study the mechanism of reactive dye from wastewater adsorption.

Materials and methods

Temple grass or Manila grass waste is a green waste which comprises food, forest, garden, agricultural and biological industrial wastes. It was obtained from decorating of the football field to remove other plants and then dried. The dried Temple grass was being carbonized in a furnace at 400 °C for 120 min. The carbonaceous material was cooled down and soaked in each solution 1 M H_3PO_4, 1 M KOH and 1 M NaCl for 60 min, followed by filtration with a stainless screen filter before activation in a furnace at 700 °C for 60 min. The activated material was cooled down and washed several times with hot water until pH 7 and then the sample was filtrated again with the stainless screen and dried in oven at 100 °C for 24 h. Finally, the sample was ground in a blender and sieved to a particle size of 150-300 μm. The materials were stored in a tight bottle ready to use as an adsorbent for reactive red adsorption. TGAC was called for an adsorbent in this work. A stock solution containing 50 ppm of Novacron Brilliant Red EC-3GL dye was prepared by dissolving reactive red in distilled water. Working solutions of desired concentrations were prepared by diluting the stock solution for making the standard curve. A dyeing wastewater collected from a textile dyeing factory in Samutprakarn was used to evaluate the effectiveness of the prepared Temple grass activated carbon in the treatment of wastewater. The pH of the dye solution was adjusted by using concentrated 6 M NaOH and 6 M HCl solutions.

Adsorption studies were conducted using a batch adsorption technique. A number of stoppered Duran glasses Erlenmeyer containing 100 mL of dye solution of at a desired concentration, pH and temperature was placed in a thermostatic shaker. In the studies, the amount of the activated material was used to treat 100 mL of the wastewater at a defined pH, concentration and temperature. The flasks were agitated at a shaking rate of 110 rpm for 3 h to ensure adsorption equilibrium was reached. Samples were filtered with Whatman No.1 and No.42 filter papers and dye content in the filtrate was analyzed with a UV-Visible spectrophotometer (HACH model DR 6000) at wavelength (λ_{max}) 610 nm. The average values were reported in this work for all experiments were carried out in duplicates.

The percentage of dye adsorption (%) in wastewater was calculated from the following equation:

$$\text{Dye adsorption}\,(\%) = \left(\frac{C_i - C_t}{C_i}\right)100 \tag{1}$$

where C_i is the initial concentration of dye in wastewater (mg/L), and C_t is the concentration of dye in wastewater (mg/L) at time t.

In order to optimize the design of an adsorption system to remove the dye from wastewater, it is important to establish the most appropriate correlations for equilibrium data for each system. Langmuir and Freundlich isotherm models were used to describe the non–linear equilibrium relationship between the dye adsorbed onto the activated carbon and that left in wastewater.

Adsorption isotherm: Langmuir theory was based on two assumptions that the forces of interaction between sorbed molecules are negligible and the adsorbed layer was single-molecular. The theory can be represented in equation (2) and the following linear form in equation (3):

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{2}$$

$$q_e = \frac{1}{q_{max}} + \frac{1}{q_{max} K_L C_e} \tag{3}$$

Where C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g), q_{max} is the maximum adsorption capacity and K_L is the Langmuir adsorption equilibrium constant.

Freundlich adsorption isotherm is an empirical model considers heterogeneous adsorptive energies on the adsorbent surface and is expressed as follows:

$$q_e = K_F C_e^{1/n} \quad (4)$$

The amount of solute adsorbed, q_e is related the equilibrium concentration of solute in solution, C_e. This expression can be linearized to give the following equation:

$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e \quad (5)$$

where K_F is a constant for the system, related to the bonding energy. K_F can be defined as the adsorption or distribution coefficient and respects the quantity of dye adsorbed onto carbon adsorbent for a unit equilibrium concentration. The constant K_F and $1/n_F$ were determined by linear regression from the plot of log q_e against log C_e. K_F is a measure of degree or strength of adsorption. Small value K_F indicates the minimal adsorption and large value indicates the more adsorption [11]. The value of n_F discloses the adsorption pattern. The favorable adsorption is understood from the values of $1 < n_F < 10$ while irreversible adsorption is noticed from $n_F > 10$ and unfavorable adsorption from $n_F < 1$.

Results and discussion

From the analysis properties of activated carbon with surface area analyzer (model: Quantachrome/Autosorb-1, Thermo Finnigan/ Sorptomatic 1990) are shown in Table 1.

Table 1 Properties of Temple grass activated carbon with chemical activation at 700 °C

Property	Temple grass activated carbon (TGAC)		
	TGAC-NaCl	TGAC-KOH	TGAC-H_3PO_4
Surface area (m^2/g)			
- Multiple point BET	148.6	83.91	120.9
- Single point BET	145.1	80.84	118.0
- Langmuir Surface Area	228.5	132.3	186.0
Total Pore volume (cc/g)	0.09925	0.06996	0.08401
Average Pore diameter (°A)	25.72	33.35	27.79

Table 1 show that NaCl activation of TGAC has a higher surface area than those of KOH and H_3PO_4. This is expected as a high surface area results in a high dye adsorption. This can be explained from the increase in the number of adsorption sites. The NaCl is widely used in the production of activated carbon because of low energy costs and high carbon yields as well as easy recovery of the activating agents. A salt catalyst of the activation agent to promote bond cleavage, dehydration and condensation is better than acidic or alkaline catalyst.

Fourier transform infrared spectroscopy (FTIR) was used to determine the surface organic structures of the activated carbon by vibrational frequency changes in the functional groups. The spectra were acquired using FTIR spectrometer (model: Perkin Elmer Spectum100). The FTIR spectra analysis of before and after dye from wastewater adsorption adsorbed TGAC-NaCl were shown in Figure 1 and Table 2. The FTIR spectra revealed that various functional groups detected on the surface of TGAC before and after adsorption. There are some peaks were disappeared, shifted and new peaks were detect in the dye adsorbed TGAC-NaCl. As seen in Figure 1 and Table 2, three significant frequencies at 3750, 1538, 1039 which indicated the bonds –OH, -C=C- and –C-O- group were changed. These three significant frequencies in the spectrum indicate the possible involvement of the respective functional group on the surface of TGAC in dye adsorption process.

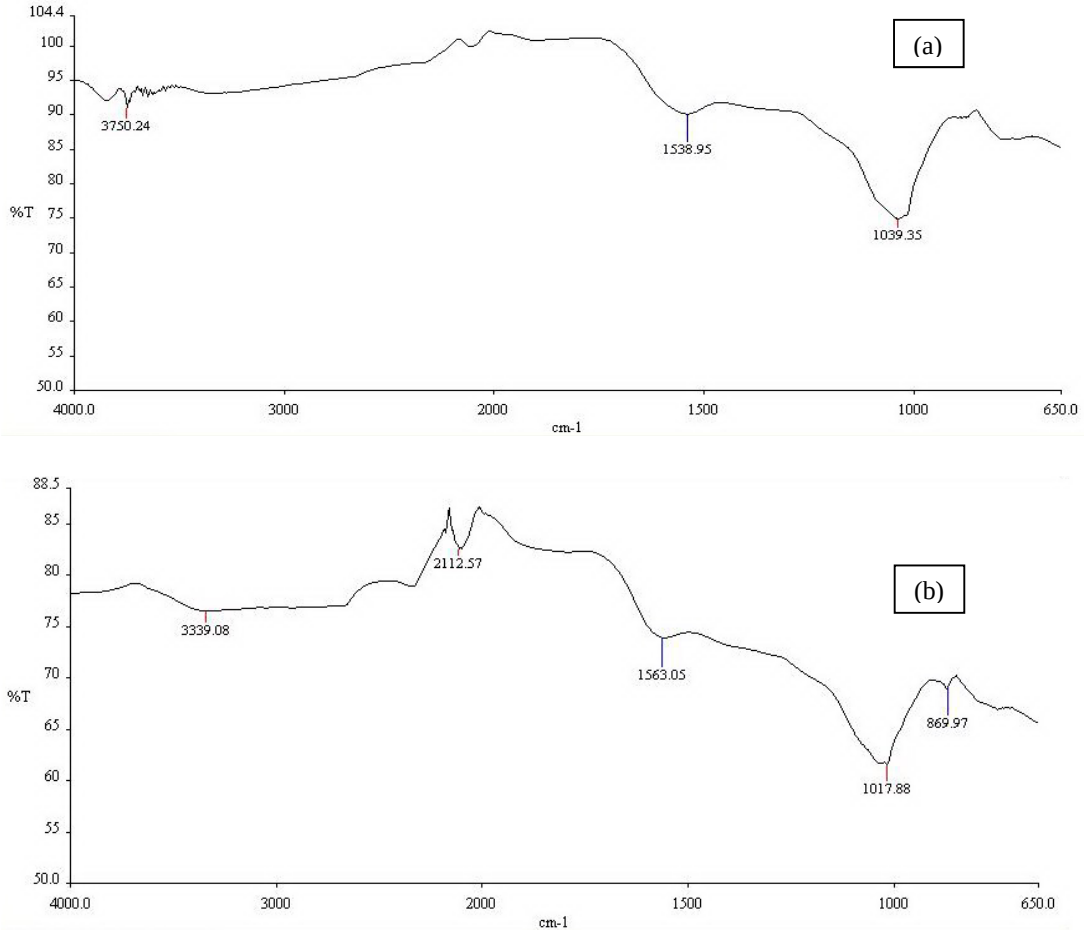

Figure 1 FTIR spectrum of (a) before and (b) after adsorption of dye from wastewater on TGAC-NaCl

Table 2 Bands assigned to the surface functional groups of TGCA-NaCl before and after dye from wastewater adsorption

IR peak	Frequency (cm^{-1})		Assignment of bond stretching
	Before adsorption	After adsorption	
1	3750	3339	-O-H in alcohols, acids, phenol, and –N-H in amines and amide
2	-	2112	-C-H in $–CH_3$ and $-CH_2$
3	1538	1563	-C=C- in aromatic rings, -C=O in highly conjugated carbonyl groups, and –C-H deformations in alkanes
4	1039	1017	-C-O- in alcohols, phenols, ethers, esters, acid, epoxides, lactones and carboxylic anhydrides
5	-	869	-C-C- deformations and out of plane –C-H deformation in aromatic rings

Effect of pH for dye from wastewater adsorption on TGAC-NaCl

The aqueous solution pH has been presented a significant influence on the adsorptive uptake of dye molecules due to its impact on both the surface binding-sites of the adsorbent and the ionization process of the dye molecule. The effect of pH was investigated for values between 1.0-12.0 and the results are displayed in Figure 2. The maximum dye adsorbed on TGAC was pH 2.0. As the pH of the solution increased, the dye adsorption decreased considerably. The same behavior was observed for the adsorption of various textile dyes on agricultural waste. The ionic forms of the dye in solution and the surface electrical charge of the carbon depend on the solution pH. Therefore, the interaction between the dye and adsorption is mainly affected by ionization states of the functional groups on the dye molecule and adsorbent surface. The enhancement of dye uptake at acidic pH values may be explained in term of electrostatic interaction between the adsorbent (TGAC) and the adsorbate (dye).

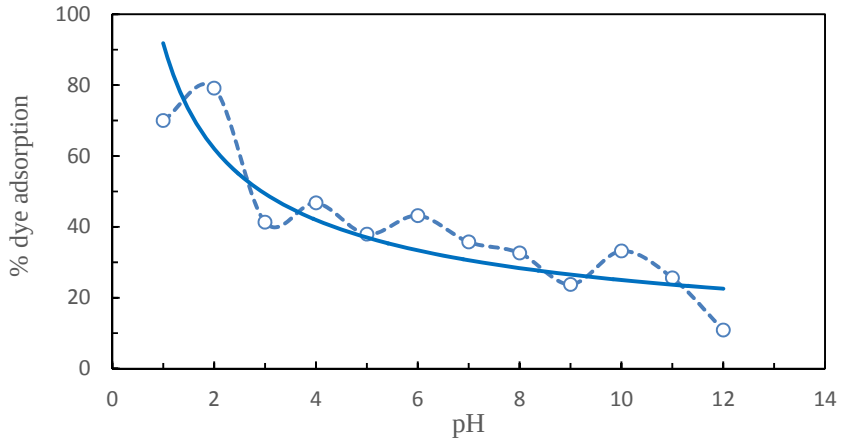

Figure 2 Effect of pH on the removal dye from wastewater concentration 33.79 ppm, adsorbent dose 1.0 g/100 mL, temperature 30 °C, and contact time 60 min

Effect of contact time for dye adsorption on TGAC

The effect of contact time for dye adsorption on TGAC from aqueous solution is shown in Figure 3. The maximum adsorption of dye by activated carbon was attained within 90 min. The percentage of dye adsorption was rapid in the beginning but it gradually decreased with time until reached equilibrium. A similar reported that the rate of adsorption was higher in the beginning, due to larger surface area of the adsorbent [12]. After adsorption, the rate of dye uptake might be controlled by the rate of dye transported from the exterior to interior sites of adsorbent particle and some dye adsorptions can be reversible from the adsorbent for slightly decrease adsorption at 90 min adsorption later. That means the adsorption is irreversible in equilibrium stage.

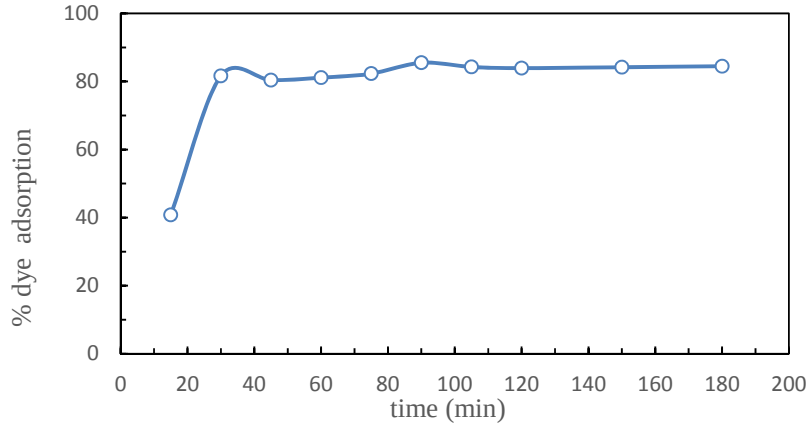

Figure 3 Effect of contact time on the removal dye (initial dye concentration in wastewater 33.79 ppm, adsorbent dose 1.0 g/100 mL, temperature 30 °C, and pH 2.0)

Effect of adsorbent dosage for dye adsorption on TGAC-NaCl

The adsorbent dosage is an important parameter for the adsorption process because this determines the capacity of an adsorbent for a given initial concentration of adsorbate. The effect of TGAC dose on the adsorption of dye of wastewater is presented in Figure 4. The results shows that the dye adsorption increase to a certain limit and then it constants. An increase in adsorption with adsorbent dosage can be attributed to increased surface area and the availability of some adsorption sites. But the amount adsorbed per unit mass of the adsorbent decreased considerably. The decrease in unit adsorption with increasing dose of adsorbent may be due to the adsorption sites remaining unsaturated during the adsorption process. Hence, remaining part of the experimental was carried out with the adsorbent dose off 1.0 g/ 100 mL (w/v).

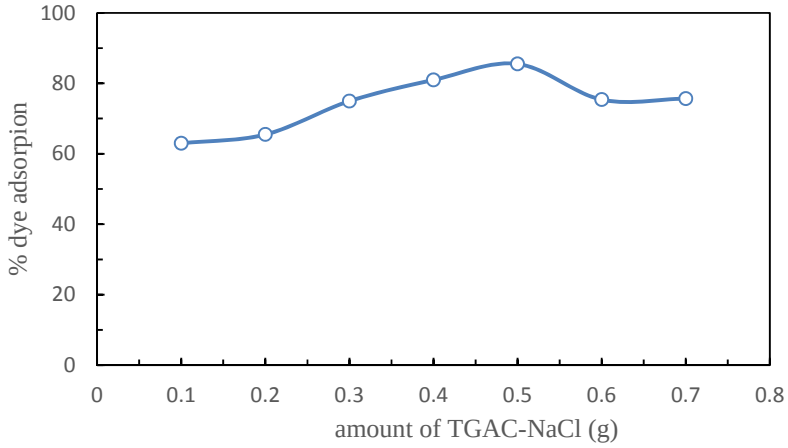

Figure 4 Effect of adsorbent dose on the removal dye concentration of wastewater 33.79 ppm in volume 100 mL, temperature 30 °C, pH 2.0 and contact time 90 min

Effect of concentration for dye adsorption from wastewater on TGAC-NaCl

Figure 5 shows the effect of dye concentration in wastewater by dilution for maximum uptake on TGAC. The adsorption percentage was found to decrease with increase concentration. This may be due to the saturation of surface area and active sites of adsorbent. Similar resulted was reported for reactive dye adsorption on sugarcane bagasse pith activated carbon [12]. The experimental results showed 96.82 % of dye (at initial dye concentration 5.16 ppm) adsorption by 1.0 g of TGAC-NaCl. This result is very interesting, since high concentration of adsorbate was attained maximum adsorption even at low adsorbent dosage. Hence, our Temple grass activated carbon is the better adsorbent for the removal of reactive red from wastewater.

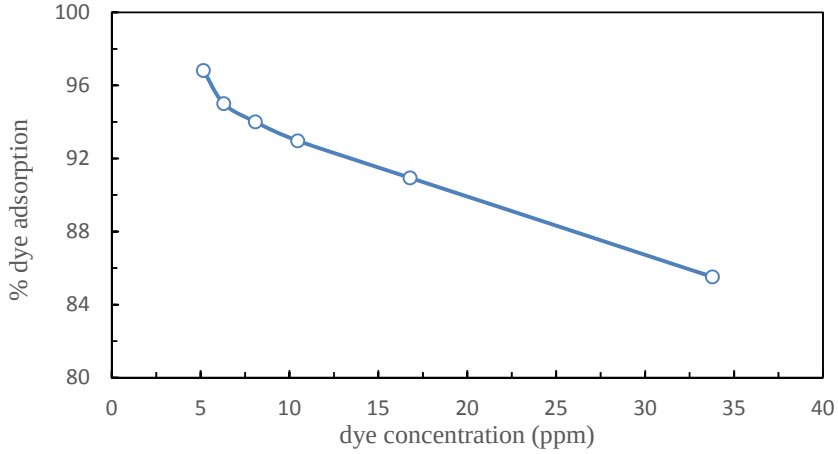

Figure 5 Effect of initial concentration on the dye adsorption (adsorbent dose 1.0 g/100 mL, temperature 30 °C, pH 2.0 and contact time 90 min)

Effect of Temperature for dye in wastewater adsorption on TGAC-NaCl

The effect of wastewater temperature was studied by conducting the experiment at different temperatures 30, 35, 40, 45 and 50 °C and at optimum conditions, i.e., with a solution of 50 ppm of dye concentration in wastewater at a fixed pH 2, contact-time 90 min, dosage of 1.0 g/100 mL for TGAC-NaCl and results obtained as shown in Figure 6. The dye adsorption of wastewater highly decreased with increasing temperature from 30 °C to 35 °C and then adsorption remain constant with temperature increase. For the effect of temperature at equilibrium adsorption in this work seems no significant difference between studied temperatures in range 35 – 50 °C. The high dye adsorption of wastewater should be done at room temperature (30 °C) for saving energy and cost.

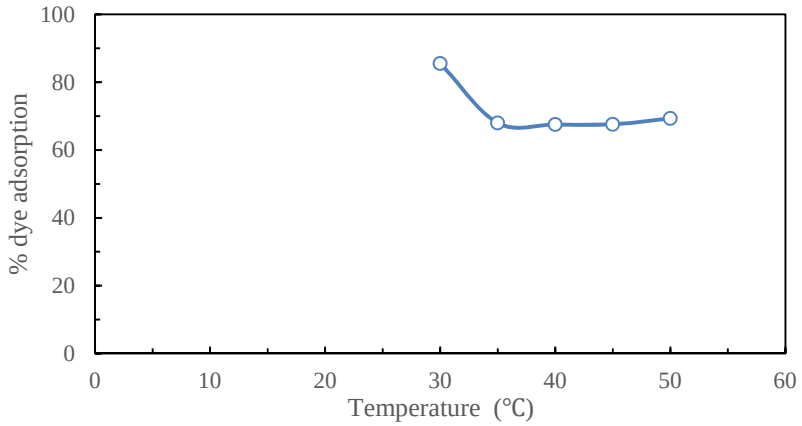

Figure 6 Effect of temperature on the removal of dye from wastewater (initial dye concentration in wastewater 33.79 ppm, adsorbent dose 1 g/100 mL, pH 2.0 and contact time 90 min)

Adsorption isotherm

Adsorption is the adhesion of atom, ions, biomolecules or molecules of gas, liquid, or dissolved solid to surface. This process creates a film of adsorbate on the surface of the adsorbent. Adsorption equilibrium isotherm model equations such as Langmuir and Freundlich were used in this study to describe the experimental adsorption data. It is important to find the best-fit isotherm to evaluate the efficacy of prepared adsorbent to develop suitable industrial adsorption system designs. The applicability of the isotherm equations is compared by considering the correlation coefficient, R^2.

Langmuir adsorption isotherm explains that the during adsorption process the uptake of dye occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed dyes. It clarifies that the surface binding was primarily by physical forces and implicit in its deviation was assumption that all sites possess identical affinity for the adsobate. Its use was extended to empirically explain the equilibrium relationships between the bulk liquid and solid phases. The experimental data produced a straight line fit with a fair correlation coefficient as shown in Figure 7 (R^2 = 0.8513) indicating the non-acceptability of the model for studied reactive dye from wastewater adsorption system.

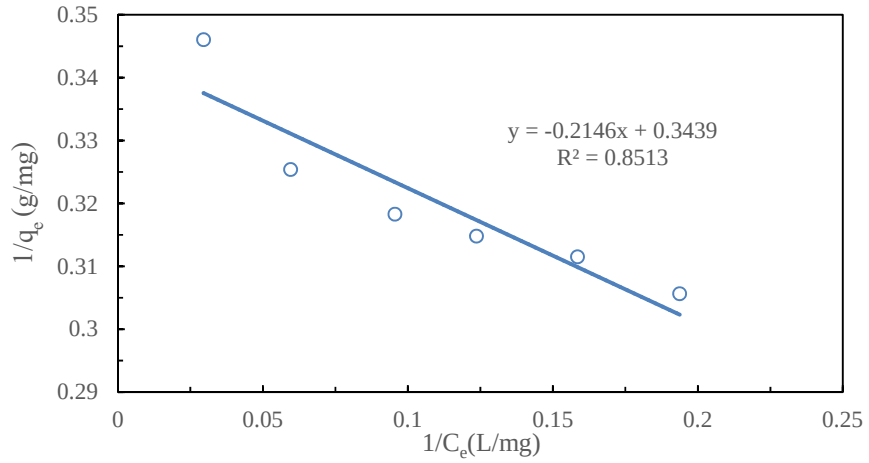

Figure 7 Langmuir isotherm of dye from wastewater adsorption on TGAC-NaCl

The Freundlich equation was also employed for the adsorption of dye on the adsorbent, Temple grass activated carbon. This isotherm model can be used for heterogeneous systems with interaction between the molecules adsorbed. A plot of log q_e vs log C_e is shown in Figure 8, where the values of K_F and $1/n_F$ were determined from the intercept and slope of the linear regressions. The experimental data to Freundlich's adsorption isotherm model lead to good linearization (R^2 = 0.9765) indicating the acceptability of this isotherm model. Therefore, in this study the Freundlich model produced reasonably good agreement isotherm data. The value of Freundlich constant, n_F, indicate the nature of the adsorption process as in given Table 2. The values of n_F with the initial dye concentration of wastewater shown in 16.10 was observed to be in range more than 10 and confirm that the ongoing adsorption process is irreversible.

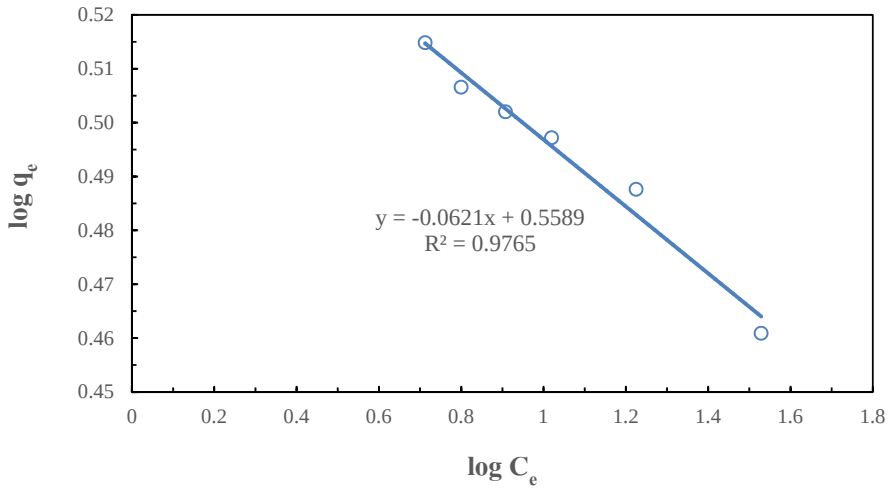

Figure 8 Freundlich isotherm of dye from wastewater adsorption on TGAC-NaCl

Table 2 The values of n_F

n_F value	Nature of adsorption process
$n_F > 10$	Irreversible
$1 < n_F < 10$	Favorable
$n_F = 1$	Linear
$n_F < 1$	Unfavorable

Conclusion

The results of the study indicated that with increase in the contact time percent adsorption of dye increases, the dye adsorption was rapid during initial period of time and equilibrium was reached in 90 minutes at pH 2.0. The results also showed that with increase in the adsorbent doses and temperature percent adsorption of dye adsorption increases until 1.0 g in 100 mL solution volume at room temperature. Thus it can be concluded that the agricultural waste Temple grass is an activated material as an adsorbent to consider for removal of dye since it is effective, low cost, and abundant and can be obtained locally. Thus reducing reactive dye from wastewater environmental pollution can be lowered

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