OPTIMIZATION OF TEA WASTE ACTIVATED CARBON PREPARATION PARAMETERS FOR REMOVAL OF CIBACRON YELLOW DYE FROM TEXTILE WASTE WATERS

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ABSTRACT

Waste from tea, a beverage globally consumed is a common menace discarded to the environment thereby contributing to environmental pollution. The textile and paper industries have also been major culprits in the pollution of the environment through their indiscriminate discharge of dye solutions. These dyes are carcinogenic, mutagenic, and generally harmful to the entire eco-system; this has posed a major challenge to the general populace. This research has tried to harness potentials of waste from tea by converting it to adsorbent used for adsorption of Cibacron yellow dye (CBY). Chemical activation with potassium hydroxide was used for the conversion of the tea waste to viable activated carbon (WTC). Response surface methodology, a central composite design tool was used to optimize the WTC preparation parameters which were activation temperature, chemical impregnation ratio and activation time with targeted responses of yield and the percentage dye removal. About 21.30 and 95.07 % yield and CBY removal respectively, were obtained at optimum preparation conditions of 760 ^{o}C, 1.8 IR and 135 min. Langmuir isothermal was the most fitting model for the adsorption process than Freundlich model. The kinetic studies showed that pseudo-second-order kinetics described the adsorption process better than pseudo-first-order kinetic model. The WTC prepared at optimum conditions had surface area of 830 m^2/g with a total pore size of 0.563 cm^3/g. The activated carbon produced from tea waste was found to be a good adsorbent for removal of CBY from waste waters.

KEYWORDS: Optimization; isotherm; kinetics; activation; dye; adsorption.

INTRODUCTION

Dyeing as a process of adding colour to materials has been used to add value and beauty which is appreciated globally, but the uncontrolled discharge dyes to the environment harming the ecosystem is their detestable and irksome side. Dyes are widely used by many industries which include printing, textiles, leather, paper, plastics and dye synthesis. We have several thousands of dye products in the market with about 700,000 metric tons produced annually out of which 35,000–70,000 is discharged to the environment [1]. Unlike some pollutants that can easily be evacuated and treated, dyes are either slowly or non-degradable in nature and also harmful to the ecosystem [2].

Several attempts by researchers have been made in other to solve this problem of dye pollution through various methods. These includes: reverse osmosis, membrane separation, coagulation, chemical oxidation, biological treatments, photodegradation and adsorption [3]. Commercial activated carbon has been found very useful in adsorption process but it's expensive nature has prompted research into finding alternatives to it. The use of renewable materials for production of activated carbons so as to substitute for coal based commercial types is a welcome development, since their characteristics are comparable. Agricultural waste materials, clay, microorganism and many other substances have been tested and yielded fruitful results which can compete favorably with the commercial ones. These alternative substances are much available, cheaper and renewable [4].

The solidarity to find solution to this environmental menace and to globally make our environment a safer place of harbor has prompted this research by looking at potentials in our waste to create solution and wealth. Waste from used tea was harnessed to produce activated carbon for removal of Cibacron reactive yellow dye (CBY) from synthetic textile waste-waters. Preparation of activated carbon for high adsorption performance through good development of its pores and surface characteristics is influenced by its preparation conditions.

To obtain the optimum conditions for preparation of activated carbon from WTC for adsorption of CBY, a useful statistical model tool which enables comprehension of optimum parameters, experiment design technique was used. This technique using response surface methodology has been reported to have yielded good results in helping researchers to study interaction between two or more variables in various processes [5-7]

Therefore, in this work, some important activated carbon preparation conditions: activation temperature, chemical impregnation ratio IR, and activated time were concurrently studied using central composite design to find their optimum condition for preparation of activated from WTC for adsorption of CBY.

MATERIALS AND METHODS

Potassium hydroxide, sodium hydroxide, hydrochloric acid, and Cibacron reactive yellow dyes (Fig. 1) of analytical grade were purchased from Merck's Company in South Africa. Waste from tea was obtained from Sheraton Hilton hotel, Abuja Nigeria.

The waste tea was washed thoroughly with hot distilled water to remove some impurities until a pH 6.8-7 was attained and then dried. The dried waste tea sieved to 500 μm-1.00 mm particle sizes, was mixed with potassium hydroxide and then activated at the corresponding temperature as determined by the Design of Experiment shown in Table 1. Inert atmosphere of the furnace during activation was maintained by passing nitrogen (99.99%) into it at flow rate of 150 ml min^{-1}. The activated waste tea was washed with distilled water until neutrality of pH

6.8-7 was attained. Then, the sample was dried in an oven for 6 h at 110 ^{o}C before packaged in an air tight container for further use. The ranges of preparation parameters used were temperature (500-800 ^{o}C), activation time (60-150 min) and chemical impregnation ratio IR, (0.3-2.50). The chemical impregnation ration was done using the following relationship:

$$IR = \frac{\text{weight of potassium hydroxide pellets}}{\text{weight of dried waste tea}} \quad (1)$$
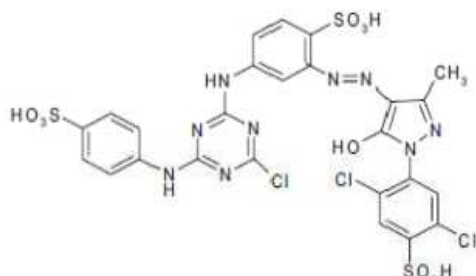
Scheme 1: molecular structure of CBY

WTC Design of Experiments using Response Surface Methodology

A popular class of second order design central composite design amongst others like three-level factorial design and Box-Behnken design was used for the RSM optimization studies to analyse effects of the preparation parameters activation temperature, IR and activation time towards their responses yield and percentage removal [5] . According to a 2^3 full factorial CCD, a total of 20 experiments were obtained consisting of eight factorial points, six axial points (±α, 0, 0), (0, ±α, 0), (0, 0, ± α), and six replicates at the center points (0,0,0). Reproducibility of the data and experimental error are determined through usage of the center points. The rotatability α which is the distance of the axial point from center was 1.682. It was obtained from the relationship $(n_p)^{0.25}$ (where $n_p = 2k$, number of points in the cube portion part of the design and k is the number of factors. The independent variables were the activation temperature x_1, activation time x_2 and chemical impregnation ratio IR x_3; while the depended variables (responses) were the yield of WTC and percentage removal of CBY. An optimal model predictor quadratic equation was used to determine the responses, it is given as:

$$Y = b_o + \sum_{i=1}^{n} b_{ii}x_i + \left(\sum_{i=1}^{n} b_{ii}x_i\right)^2 + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} b_{ij}x_ix_j \quad (2)$$

where Y is the predicted response, b_o is the constant coefficients, b_{ii} the quadratic coefficients, b_{ij} the interaction coefficients and x_i, x_j are the coded values of the variables considered. A statistical software Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) was used to determine the regression analysis for the responses. Some statistical techniques were used to adjudge the reliability of the software to the responses equations obtained. These were coefficient of variability R^2, probability P-value (95% confidence level) and Fisher's test. The independent variables with their coded levels for the central composite design are presented in Table 2.

Table 1 Experimental design matrix for preparation of WTC

Run	Level			Activated carbon preparation variable			Waste tea AC yield, Y_1 (%)	Cibacron yellow removal, Y_2 (%)
				Activation temperature, x_2 (^{o}C)	Activation time, x_3 (min)	IR, x_1		
1	-1	-1	-1	560.81	78.24	0.75	27.35	33.45
2	1	-1	-1	739.19	78.24	0.75	23.45	42.87
3	-1	1	-1	560.81	131.76	0.75	27.70	17.80
4	1	1	-1	739.19	131.76	0.75	30.75	91.34
5	-1	-1	1	560.81	78.24	2.05	36.40	37.98
6	1	-1	1	739.19	78.24	2.05	23.45	70.76
7	-1	1	1	560.81	131.76	2.05	39.10	28.98
8	1	1	1	739.19	131.76	2.05	27.35	90.76
9	-1.682	0	0	500.00	105.00	1.40	32.45	28.98
10	1.682	0	0	800.00	105.00	1.40	31.20	98.32
11	0	-1.682	0	650.00	60.00	1.40	31.35	31.78
12	0	1.682	0	650.00	150.00	1.40	34.65	40.23
13	0	0	-1.682	650.00	105.00	0.30	28.00	20.00
14	0	0	1.682	650.00	105.00	2.50	35.30	64.78
15	0	0	0	650.00	105.00	1.40	37.23	29.11
16	0	0	0	650.00	105.00	1.40	35.92	30.09
17	0	0	0	650.00	105.00	1.40	36.82	27.69
18	0	0	0	650.00	105.00	1.40	37.50	30.05
19	0	0	0	650.00	105.00	1.40	37.20	31.65
20	0	0	0	650.00	105.00	1.40	37.20	31.66

Table 2 Independent variables and their coded levels for the central composite design

Variables (factors)	Code	Unit	Coded variable levels				
			-α	-1	0	+1	+α
Activation temperature	X_1	^{o}C	500	560.81	650	739.19	800
Activation time	X_2	min	60	78.24	105	131.76	150
Impregnation ratio, IR	X_3	-	0.3	0.75	1.4	2.05	2.50

The CBY percentage removal by WTC was determined through a batch adsorption experiment. In a set of 250 mL Erlenmeyer flasks containing 200 mL of 200 mg/L of CBY concentration, 0.2 g of WTC was measured into each flasks. At the natural of the dye solution maintained, the flasks were placed in water-bath isothermal shaker at 130 rpm speed until equilibrium was attained. The dynamic equilibrium of the CBY in the solution was determine with the aid of UV-Vis spectrophotometer (Shimadzu UV/Vis 1600, Japan) at maximum wavelength, λ_{max}=420 nm. The CBY removal (%) was calculated as follows:

$$\text{CBY removal (\%)} = \frac{\text{initial CBY concentration} - \text{final CBY concentration}}{\text{initial CBY concentration}} \times 100 \quad (3)$$

The percentage yield of the WTC produced was calculated from the following relationship:

$$\text{Yield of WTC (\%)} = \frac{\text{weight (g) of dried WTC produced}}{\text{weight (g) dried precursor used}} \times 100 \quad (4)$$

Characterization of WTC

Brunauer Emmett Teller (BET) analysis was carried out to determine the surface area and porosity of the WTC. The BET was carried out by nitrogen adsorption-desorption method using nitrogen temperature (-196 ^{o}C) with an autosorb BET apparatus, Micrometrics ASAP 2020, surface area and porosity analyzer. The analysis procedure was automated and operated with static volumetric techniques. The samples were first degassed at 200°C for 2 h before each measurement was recorded.

Batch equilibrium and kinetic studies

The equilibrium studies were carried out for adsorption of CBY on WTC while effects of contact time, initial dye concentration and solution pH on the dye removal were investigated. The studies were conducted in a set of Erlenmeyer flasks (250 mL) containing 200 mL of different initial concentrations (50-250 mg/L). 0.2 g of WTC was added to the flasks

and placed in a water-bath shaker at 30 ^{o}C with a speed of 130 rpm until equilibrium was attained. Similarly, the water-bath shaker temperature was adjusted to 40 and 50 ^{o}C and the procedure was repeated same different initial dye concentration (50-250 mg/L). The concentration of the dye before, during and after the equilibrium and kinetic studies were determine with the aid of UV-Vis spectrophotometer (Shimadzu UV/Vis 1601 spectrophotometer, Japan) at maximum wavelength of 420 nm. The amount of the dye adsorbed at time t, at equilibrium Q_e (mg/g) was calculated using the following equation:

$$Q_e = \frac{(C_o - C_e)V}{W} \qquad (5)$$

where C_o and C_e (mg/L) are the liquid-phase concentration of the dye at the initial and equilibrium respectively; V (L) is the volume of the solution; and W (g) is the mass of the dry adsorbent used.

The effect of solution pH on CBY adsorption on WTC was carried out by varying the initial pH of the solution from 3-12. In a set of Erlenmeyer flasks containing 200 mL of 100 mg/L CBY solution, 0.2 g of WTC was added and the pH was adjusted by adding either 0.1 M hydrochloric acid or 0.1 M sodium hydroxide which was measured using pH meter (Model Delta 320, Mettler Toledo, China). The flasks were placed in an isothermal water-bath shaker (30 ^{o}C) at 130 rpm for 24 h and the CBY percentage removal was determined using the equation:

$$CBY \text{ removal } (\%) = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (6)$$

RESULTS AND DISCUSSION
Design of Experiments using Response surface methodology
The final CCD model obtained for both yield Y_1 and percentage removal Y_2 with significant terms was quadratic as suggested by the software, they are given as:

$$Y_1 = 37.06 - 2.02x_1 + 1.45x_2 + 2.15x_3 - 2.33x_1^2 - 1.92x_2^2 - 2.39x_3^2 + 1.02x_1x_2 - 2.98x_1x_3 - 0.13x_2x_3 \qquad (7)$$

$$Y_2 = 29.93 + 21.54x_1 + 4.25x_2 + 8.66x_3 + 12.59x_1^2 + 2.81x_2^2 + 5.07x_3^2 + 11.64x_1x_2 + 1.45x_1x_3 - 2.73x_2x_3 \qquad (8)$$

The response model equations obtained represents optimum correlation between the WTC preparation parameters and the responses. The model equations were arrived at according to sequential model of sum of squares based on the highest order of polynomials and the models were not aliased with significance observed at additional terms. At that point, the experimental error were minimal and with efficient data reproducible which were all determine by 15-20 runs of the experimental design layout. The WTC yield and CBY percentage removals obtained were in the ranges of 23.45-39.10 % and 17.80-98.32 %, respectively. The complete experimental design with the preparation parameters and responses are presented in Table 1.

Analysis of variance ANOVA was further conducted to ascertain the validity of these models. Table 3 and 4 are for the ANOVA results for WTC yield and CBY removal, respectively. The Fishers variance ratio F-value test, which has a condition of significance as Prob. > F less than 0.05, was

conducted [8]. The results of the models showed that both models were significant since their F-values were 8.52, 28.02 and Prob. > F values 0.0012, 0.0001 for WTC yield and CBY removal, respectively were within the confines. The WTC yield model significant and insignificant terms were x_1, x_2, x_3, x_1^2, x_2^2, x_3^2, x_2x_3 and x_1x_2, x_2x_3 respectively; the significant terms x_1, x_2, x_3, x_1^2, x_3^2, x_1x_2 and insignificant terms of x_2^2, x_1x_3, x_2x_3 were for the CBY removal model. The correlation coefficients between the predicted and experimental data for the two models were 0.944 for yield and 0.961 for the CBY removal. The plots of the experimental against the predicted values of the two responses are shown in Fig. 2 and Fig. 3.

Table 3 Analysis of variance for response surface quadratic model for WTC yield

Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob > F	Comment
Model	406.39	9	45.15	8.52	0.0012	Not Significant
x_1	55.99	1	55.99	10.57	0.0087	
x_2	28.71	1	28.71	5.42	0.0422	
x_3	62.98	1	62.98	11.89	0.0062	
x_1^2	78.45	1	78.45	14.81	0.0032	
x_2^2	53.00	1	53.00	10.01	0.0101	
x_3^2	82.66	1	82.66	15.61	0.0027	
x_1x_2	8.30	1	8.30	1.57	0.2391	
x_1x_3	71.10	1	71.10	13.42	0.0044	
x_2x_3	0.14	1	0.14	0.03	0.8751	
Residual	52.97	10	5.30	-	-	
Lack of Fit	51.39	5	10.28	32.55	0.0008	Not Significant
Pure Error	1.58	5	0.32	-	-	

Table 4 Analysis of variance for response surface quadratic model for CBY removal

| Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob > F	Comment
Model	11285.07	9	1253.9	28.02	< 0.0001	Not Significant
x_1	6334.97	1	6334.97	141.55	< 0.0001	
x_2	246.59	1	246.59	5.51	0.0408	
x_3	1025.28	1	1025.28	22.91	0.0007	
x_1^2	2283.61	1	2283.61	51.03	< 0.0001	
x_2^2	114.12	1	114.12	2.55	0.1414	
x_3^2	370.66	1	370.66	8.28	0.0164	
x_1x_2	1083.92	1	1083.92	24.22	0.0006	
x_1x_3	16.82	1	16.82	0.38	0.5535	
x_2x_3	59.51	1	59.51	1.33	0.2757	
Residual	447.54	10	44.75	-	-	
Lack of Fit	435.94	5	87.19	37.56	0.0006	Not Significant
Pure Error	11.61	5	2.32	-	-	
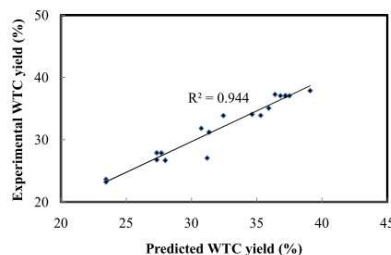
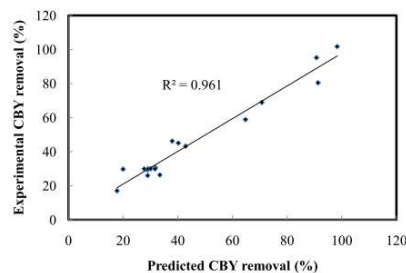

Fig. 2 Experimental against predicted WTC yield

Fig. 3 Experimental against predicted CBY removal

The three parameters activation temperature x_1, activation time x_2 and impregnation ratio IR x_3, all contributed positively in the preparation of the WTC and its usage for removal of CBY from synthetic solution as shown in Table 1.

The yield of WTC increased with decrease in activation temperature. This was attributed to loss of some volatile component of the carbon at elevated temperatures and further loss of carbon in form of CO and CO_2. The 3D response surface for interaction between activation time against temperature with IR fixed at zero level (IR=1.4) is shown in Fig. 4, while that of IR against activation temperature at time fixed at zero level (t=105 min) is shown in Fig. 5. Decrease of WTC yield was equally observed at some high IR which may also be attributed to oxidation of the carbon material.
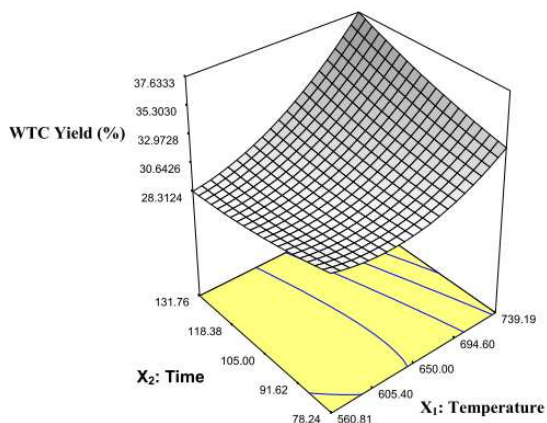

Fig. 4 The 3D response surface plot of activation time against temperature at IR fixed at zero level (IR=1.4) for WTC yield
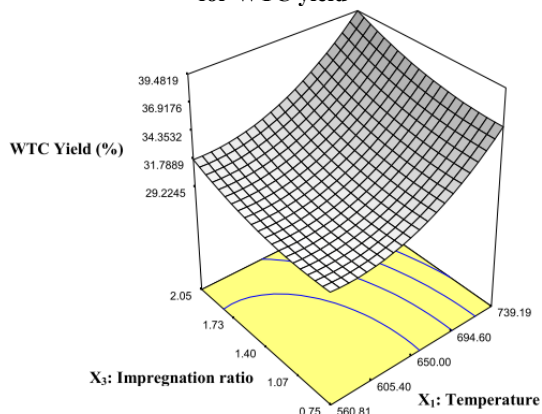

Fig. 5 The 3D response surface plot of IR against temperature at time fixed at zero level (t=105 min) for WTC yield

Temperature played significant role in the removal of CBY from solution. Good removal of CBY was observed at high activation temperature of the process. This was because potassium compounds activating agents intercalates carbon materials at elevated temperatures which lead to development of good pores and surface area in the carbon. Loss of oxidized carbon materials in form of CO and CO_2 also helps in the development of pores; increase in IR, increased the chances of more oxidation which was observed to have lead to improved removal of CBY at increased IR. Similar observation was made when AB25 was removed by WTAC prepared using potassium acetate as activating agent [4]. The reverse was the case with the activation time which

contributed latent effect on the adsorption process. The 3D response surface plot for IR against activation temperature at fixed zero level of activation time (t=105 min) is shown in Fig.6
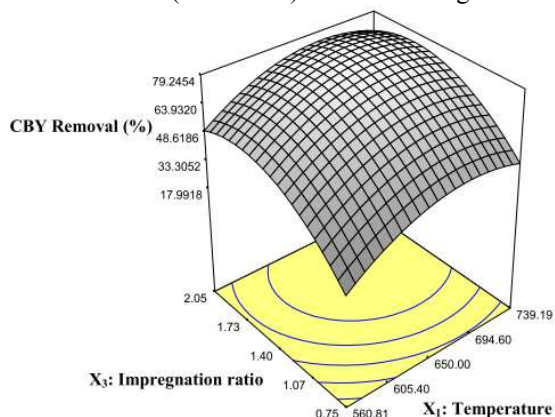

Fig. 6 The 3D response surface plot of IR against temperature at time fixed at zero level (t=105 min) for CBY removal

Process Optimization

The statistical software was used to obtain the optimum preparation parameters in relation to the responses considered. The Design Expert software considered the unit factor effect, two factors interaction and quadratic factors impact on the resulting models which ordinarily are tedious or impossible with maximum accuracy to execute manually. The percentage yield and removal of 21.30 and 95.07 % respectively were obtained at optimum preparation parameters of 760 $^{\mathrm{o}}$C, 1.8 IR and 135 min. The insignificant error for the responses as presented in Table 5 for yield and removal showed that the experimental data was in agreement with the predicted data.

Table 5 Model validation

Model Desirability	X_1 $^{\mathrm{o}}$C	X_2 min	X_3 IR	WTC yield (%)			CBY removal (%)		
				Predicted	Experimental	Error	Predicted	Experimental	Error
1.0	760	135	1.8	22.38	21.30	4.83	96.00	95.07	0.97

The BET characterization of the WTC

At optimum conditions, the WTC prepared characterized was mesoporous in nature and had good surface area. Summary of the characterization result is shown in Table 6.

Table 6 The BET characterization of the WTC

S_{BET} (m^2/g)	S_{ext} (m^2/g)	S_{ext}/S_{BET} (%)	S_{mic} (m^2/g)	S_{mic}/S_{BET} (%)	V_{tot} (cm^3/g)	V_{mic} (cm^3/g)	V_{mic}/V_{tot} (%)	D_p (nm)
830	281.22	33.88	584.76	70.45	0.524	0.332	63.36	2.54

Effect of initial dye concentration and pH of the solution on CBY adsorption by WTC

Adsorption of CBY was found to be more favorable at lower pH where the surface of WTC was covered by numerous protons in the solution thereby attracting the negatively charged solute (Fig. not shown).

Numerous vacant active sites of the WTC at low initial concentrations favored rapid adsorption of the CBY pollutant from solution while the removal was slower at higher initial dye concentration. Profiles for the initial concentration effect on the adsorption process are shown in Fig. 7. The percentage of adsorption at higher initial dye concentration was larger than at lower concentration; this was attributed to increase in mass transfer or presence of innumerable molecules of the targeted solute at

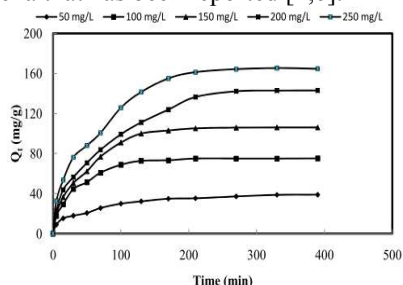higher concentrations. This behavior is similar to phenomena that has been reported [4,6].

Fig. 7 Effect of initial concentration on adsorption of CBY on WTC at 30°C

ADSORPTION ISOTHERM

Adsorbate distribution between the liquid and solid phase was studied using Langmuir, Freundlich and Temkin isotherms.

The non-linear form of the Langmuir isotherm model [9] is given as:

$$Q_e = \frac{Q_m C_e b}{(1 + b C_e)} \qquad (9)$$

where Q_e is the amount of CBY adsorbed mg/g, C_e is the equilibrium concentration of CBY adsorbed mg/L, Q_m is the monolayer adsorption capacity and b is the affinity of adsorbent towards adsorbate.

A plot of Q_e against C_e gave a fitted curve, and the Langmuir constants (Q_m and b) were generated from the plot of sorption data; Fig. 8 and Table 7 shows the Langmuir plots and its parameters obtained.

The non-linear form of the Freundlich model equation [10] is given as:

$$Q_e = k_f C_e^{1/n} \qquad (10)$$

where Q_e is the amount of dye adsorbed at equilibrium, mg/g; C_e is the equilibrium concentration of the adsorbate, mg/L; K_f and n are the Freundlich equilibrium coefficients. The value of n gives information on favorability of adsorption process and K_f is the adsorption capacity of the adsorbate.

The model plots and its parameters are presented in Fig. 8 and Table 7, respectively. Good fitted curves were obtained from the plots of Q_e against C_e signifying that the model described the adsorption process as well. The 1/n values obtained showed that the surface of WTC was heterogeneous as the values were between 0 and 1, although the degree of heterogeneity was less since the values were further away from zero (0.513-0.777). A similar result of heterogeneous behavior of adsorbents during adsorption has been reported [10].

A non-linear form of Temkin and Pyzhev model was used to describe adsorbate-adsorbent interaction. The model equation is expressed as [12]:

$$Q_e = B \ln(K_T C_e) \qquad (11)$$

where K_T is the equilibrium binding constant corresponding to the maximum binding energy, B is related to the heat of adsorption, Q_e is the experimental adsorption capacity (mg/g), C_e is the concentration of the CBY adsorbed at equilibrium position (mg/L);

$$B = \frac{RT}{b_T} \qquad (12)$$

where $1/b_T$ indicates the adsorption potential of the adsorbent; R is the universal gas constant (8.314 J/kmol); and T is the temperature in Kelvin (K).

This model is based on the assumption that the increase of coverage due to adsorbate-adsorbent interactions leads to decrease in heat of adsorption of all molecules in the layer and that adsorption is characterized by a uniform distribution of binding energies up to some maximum binding energy [12]. A plot of Q_e against C_e at various temperatures of operation gave good curves which are shown in Fig.8 Evaluation of the three isotherms revealed that all the models described the adsorption process but some level of variance. The least and the best fitted models were Temkin and Langmuir models, respectively. The variation was revealed by the correlation coefficient values of the various models as presented in Table 7. It can be said that CBY adsorption on WTC was described by monolayer coverage phenomenon and the adsorbent surface was heterogeneous.

Table 7 Langmuir, Freundlich and Temkin isotherm models for Cibacron yellow adsorption on WTC

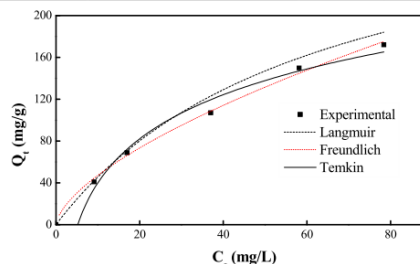| Isotherms	Parameters	Cibacron yellow		
		30 °C	40 °C	50 °C
Langmuir	Qm (mg/g)	200	250	333.33
	b (L/mg)	0.1471	0.0215	0.0132
	R²	0.940	0.904	0.969
Freundlich	KF	30.62	7.129	5.662
	1/n	0.513	0.743	0.777
	R²	0.969	0.904	0.953
Temkin	AT	49.82	39.35	37.48
	BT (kJ/mol)	0.9999	0.9999	0.0078
	R²	0.825	0.787	0.984

Fig. 8 Langmuir, Freundlich and Temkin isotherms for the CBY dye adsorption at 30°C

ADSORPTION KINETIC MODELS

Pseudo-first order model

The pseudo-first-order model equation [13] can be expressed non-linearly as:

$$Q_t = Q_e(1 - e^{-K_1 t}) \qquad (13)$$

where Q_e and Q_t are the amount of CBY adsorbed (mg/g) at equilibrium and at time t (h) respectively; k_1 is the rate constant of adsorption (h⁻¹). First-order kinetic model parameters were obtained as graphs of Q_t against Q_e were plotted at various temperatures studied (Figs. Not shown). The parameters are presented in Table 8

Table 8 Pseudo-first and second order kinetic parameters

Dye conc. (mg/L)	Qexp (mg/g)	Pseudo-first-order parameters			Pseudo-second-order parameters		
		K₁ (h⁻¹)	Qcal	R²	K₂ (10⁴)	Qcal	R²
50	37.15	0.0454	38.798	0.927	6.08	42.176	0.974
100	75.03	0.0129	78.903	0.984	4.86	82.532	0.991
150	105.83	0.0135	118.71	0.983	2.53	120.542	0.986
200	142.15	0.0167	154.87	0.976	94.1	169.349	0.985
250	164.24	0.0195	182.37	0.947	1.09	190.365	0.981

Pseudo-second-order model

The non-linear form of pseudo-second order equilibrium adsorption model [14] is expressed as:

$$Q_t = \frac{K_2 Q_e^2 t}{(1 + K_2 Q_e t)} \qquad (14)$$

where k_2 (g/mgh) is the rate constant of second order adsorption. Plots of Q_t versus t at various temperatures studied gave very good curves as shown in Fig. 9. The parameters generated from the plots are presented in Table 8

The graphs and parameters obtained from the two models showed that they both described CBY adsorption on WTC adequately. The fitted curves of the two models plots and their high correlation coefficients values of >0.900 were proofs even though results of correlation coefficient is not a sufficient criteria for selection of an adsorption kinetic model [15]. In comparison, pseudo-second-order model fitted the experimental data more than pseudo-first-order as adjudged by its higher correlation coefficient values.
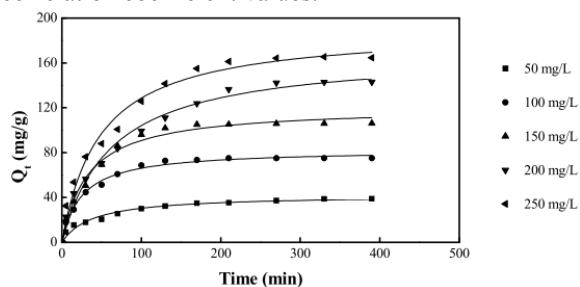

Fig. 9 Pseudo-second-order kinetics at 30°C for CBY adsorption on WTC

ADSORPTION THERMODYNAMICS

Thermodynamics studies were conducted at different temperatures of 30, 40 and 50 °C on CBY adsorption on WTC to determine some thermodynamic parameters of the process. Spontaneous nature of the process was evaluated using the following equation:

$$\Delta G = -RT \ln K_o \qquad (15)$$

where R is the universal gas constant (8.314 J/Kmol); T, the absolute temperature (K); K_o is the distribution coefficient expressed as $K_o = Q_e/C_e$; and ΔG is the Gibbs free energy.

The enthalpy change ΔH, was evaluated using the Van't Hoff equation which is expressed as:

$$\ln K_o = \frac{-\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (16)$$

The degree of dispersion ΔS, and ΔH were determined from the intercept and slope respectively, of a plot of $\ln K_o$ against $1/T$ graphs (Fig. not shown).

Table 9 Thermodynamic parameters of CBY adsorption on WTC

Concentration (mg/L)	ΔH (kJ/mol)	ΔS (J/mol)	ΔG (kJ/mol)		
			303 K	313 K	323 K
50	84.461	285.92	-2.688	-3.906	-8.322
100	43.491	150.73	-2.972	-2.049	-5.978
150	35.858	124.71	-2.251	-2.443	-4.716
200	39.558	137.35	-2.266	-2.956	-4.971
250	50.865	172.52	-1.667	-2.547	-5.063

The negative values obtained for the Gibbs free energy evaluation showed that CBY adsorption on WTC was spontaneous and physical in nature. Physical adsorption process occurs when the absolute value of change of Gibbs free energy between -20 to 0 kJ/mol while chemisorptions is between -80 to -400 kJ/mol [16]. The adsorption process was characterized with randomness and endothermic activities. The endothermic nature was revealed by positive values of the enthalpy change of the process ΔH. Similarly, in the adsorption of Congo red on modified hectorite, the adsorption was endothermic in nature and the surface of the hectorite was organized in a more random fashion [17].

CONCLUSION

The study shows that CCD can be used to adequately optimize preparation conditions and responses for production of activated carbon from tea waste for adsorption of CBY from synthetic waste waters. The adsorption process was pH dependent and endothermic in nature. Kinetic studies showed that both pseudo-first and pseudo-second-order kinetic models both described the process but the second order model gave the best fitting. Langmuir isotherm described the process more than Freundlich and Temkin isotherms investigated. The percentage yield of WTC and removal of CBY were 21.30 % and 95.07 % respectively, at optimum preparation conditions of 760 °C, 135 min and 1.8 IR.

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