BATCH ADSORPTION OF REACTIVE RED 120 FROM WASTE WATERS USING ACTIVATED CARBON FROM WASTE TEA

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ABSTRACT
Recalcitrant anionic Reactive red 120 dye's removal from waste water was studied by production of activated carbon produced from waste tea. The efficacy and efficiency of this low cost material was investigated to serve as a substitute to the pricey commercial activated carbon. The activated carbon from waste tea (WTC) was prepared through chemical activation in Nitrogen atmosphere and removal of Reactive Red 120 (RR120) was tested through batch adsorption process. Initial dye concentration (50-300 mg/L), temperature (30-50 $^{\circ}$C), contact time and initial pH 3-12 were parameters considered during the experiment. Langmuir isotherm and pseudo-second-order kinetic were the best models that the fitted adsorption process compared with Freundlich and Temkin isotherm, and pseudo-first-order kinetic models that were also tested. The thermodynamic studies of the adsorption process revealed that the process was spontaneous, endothermic and intra-particle diffusion was rate controlling mechanism. The WTC prepared had good surface area and was found to be effective for adsorption of RR120.

KEY WORDS: Waste tea, Activated carbon, Reactive red 120, Adsorption, Kinetics, Isotherms, Thermodynamics

INTRODUCTION

Adsorption process application for elimination of pollutants from waste waters has proven to be effective, eco-friendly and technically feasible amongst other processes like osmosis, coagulation, photocatalytic degradation, membrane separation, dialysis and foam flotation. Organic and inorganic pollutants in form of gases, liquids and dissolved solids can also be removed appropriately using adsorption process with the aid of adsorbents [1]. The impediment to this process is the high cost of commercial activated carbon which limits the applicability of the process [2]. There has been immense research into finding alternative to the commercial activated carbon through harnessing the potentials of various materials such as agricultural wastes, clay, zeolite, oxides of metals and so on [3,4]. Population growth and man's technological advancement especially in the dyeing industry has been accompanied with pollution increase. Quite a number of dyes to a tune of about 100,000 types are in the markets which are further classified according to their chemical components [5]. Reactive dyes which are majorly azo-based chromophores combined with different classes of reactive groups are distinct from other types in that they can bind to textile fibres like cotton to form covalent bonds. They are usually brightly colored with simple applicability, water fast and have low consumption of energy; they are stable to light, heat and oxidizing agent and biologically non-degradable even though they are used extensively in textile industries [6].

Waste tea often times is discarded thereby contributing to pollution of the environment, but recent trend in research shows that it can be converted to activated carbon for adsorption [7]. But its application for removal of Reactive Red 120 dyes (RR120) from waste water is yet to be explored and reported. Therefore, this study is aimed at harnessing the potential of converting waste tea to activated carbon through chemical activation for the removal of reactive red 120 dyes from waste water.

MATERIALS AND METHODS

Materials

Potassium hydroxide, sodium hydroxide, hydrochloric acid, and reactive red 120 dye (RR120) used (Merck and Sigma-Aldrich products) were obtained from Port-Harcourt Nigeria and used without further purification. Stock solution of RR120 was prepared by dissolving it in distilled water to the required solution without any pH adjustment. The molecular formula of RR120 is $C_{44}C_{l2}H_{24}N_{14}Na_6O_{20}S_6$, molecular weight of 1469.98 and the molecular structure is shown in Fig. 1. Waste tea was collected from Shiroro Hotels Minna, Nigeria; it was washed thoroughly with hot distilled water to remove the adhered impurities until it was colourless, then dried at 110 $^{\circ}$C over night in an oven and then packaged for further use.
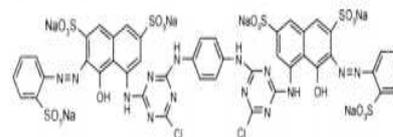
Fig. 1 Molecular structure of Reactive Red 120

Preparation of waste tea activated carbon.

The packaged dried waste tea was sieved to 250-500 μm sizes and then impregnated with potassium hydroxide at an impregnation ratio of 2.05:1 g/g. The mixture was dried after some hours and then loaded in a rectangular furnace for 2 h at 850 $^{\circ}$C with heating rate of 10 $^{\circ}$C/min under purified nitrogen (99.99%) atmosphere of 100 cm^3/min flow rate. The cooled sample was washed with distilled water until a pH of 6.8-7 was attained, dried at 110 $^{\circ}$C and finally packaged for use.

Characterization of waste tea activated carbon

Brunauer Emmett Teller (BET) was used to determine the surface area and porosity of the WTC, and pH point of zero charge (pHzpc) was also determined.

The BET was carried by nitrogen adsorption-desorption method using nitrogen temperature (-196 $^{\circ}$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 $^{\circ}$C for 2 h before each measurement was recorded.

The pH zero surface charge pHzpc of the WTC characteristics was carried out by using the solid addition method [8]. Three initial concentrations of KNO_3 (0.1, 0.01, 0.001 mol/dm^3) of 40 mL each were measured into eighteen 100 mL conical flasks with glass stoppers and 0.2g of WTC added. The pHs of the prepared KNO_3 solutions were adjusted between 2 and 12 with either 0.1 M of KOH or 0.1 M H_2SO_4. The samples were shaken for 24 h at 135 rpm. At the expiration of time, when equilibrium was established between the KNO_3 solution and the WTC, the final pH readings were noted. The final pH values were plotted against the initial pH values of the solution and at the point where plateau like feature occurred on the plot, the corresponding pH reading was noted and taken as the pHzpc of WTC. This method is similar to Babic et al and Cerovic et al [9].

Batch equilibrium studies
Adsorption studies were performed in a set of 15 Erlenmeyer flasks (250 mL) with 200 mL of dye solutions at different initial concentration (50-300 mg/L) in them. About 0.2 g (1-3 mm) of WTC adsorbent was added, mixed and placed in water bath isothermal shaker at 30 ^{o}C for 24 h to attain equilibrium. Similar procedure was repeated with another set of flasks were used containing same dye concentration at 40 ^{o}C and 50 ^{o}C. The flasks were afterwards removed from the shaker for determination of final concentration of the solution using UV-vis spectrophotometer (Shimadzu UV/Vis 1601 spectrophotometer, Japan) at maximum wavelength of 536 nm. The amount of the dye adsorbed at time t, at equilibrium Q_e (mg/g) was calculated using the following equation 1:

$$Q_e = \frac{(C_o - C_e)V}{W} \qquad\qquad 1$$

where C_o and C_e (mg/L) are the liquid-phase concentration of the dye at the initial and equilibrium respectively; V is the volume of the solution (L); and W is the mass of the dry adsorbent used (g).
Studies on the effect of initial pH on the adsorption of the RR120 dye by WTC was carried out by adjusting the pH of the solution with 0.1 M HCl and 0.1 M NaOH solutions. The experiment was conducted in a set of 250 mL Erlenmeyer flasks charged with 200 mg/L and 0.20 g of the dye concentration and WTC, respectively at a temperature of 30 ^{o}C for 24 h.

Batch kinetic studies
Adsorption kinetic experiments were conducted in a similar way to the equilibrium studies. Concentration of the dye solution was determined at pre-set intervals of time. The amount of the dye adsorbed at time t, Q_t (mg/g) was calculated using equation 2:

$$Q_t = \frac{(C_o - C_t)V}{W} \qquad\qquad 2$$

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

RESULTS AND DISCUSSION
Characterization of the activated carbon
The Brunauer Emmett Teller analysis of WTC is summarized in Table 1. The relatively high surface area and pore volume were attributed to the intercalation of potassium metal from intermediate reaction of KOH with carbon [10].

Table 1 The BET analysis of 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)
794.6	214.8	27.03	519.28	65.35	0.502	0.281	55.98	2.41

The result for experimental determination of pHzpc from various KNO_3 concentrations used (Fig. not shown) was 7.4 ±1.
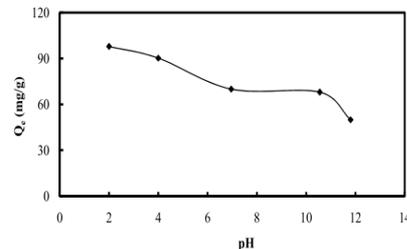
Fig. 2 Effect of pH on adsorption of RR120 on WTC
The effect of pH on the adsorption of RR120 on WTC at a pH of 2-12 for 24 h was investigated. The results in Fig.2 showed that maximum adsorption was obtained at the lowest pH 2 while the lowest was at pH 12. The high adsorption can be attributed to electrostatic attraction between the negative charges of the adsorbent surface and the protonated hydrogen ions in the acidic dye solution. As the pH of the solution increases, adsorption was found to be decreasing; this was due to extinction of the positive hydrogen ions thereby promoting activities of electrostatic repulsion between the negative charges of both the anionic dye and the WTC surface [11]

Effect of initial dye concentration
Initial concentration from 50-300 mg/L was varied to study the adsorption of RR120 by WTC. Dynamic equilibrium was achieved faster at low initial concentrations of the dye while longer time was taken for higher concentrations of the dye to attain equilibrium. It took 250 min for initial concentrations of 50-150 mg/L while 200-300 mg/L dye concentration attained equilibrium at 610 min. However, equilibrium concentrations were measured at 1440 min. The result on effect of initial concentration on adsorption of RR120 is presented in Fig.3. It was also observed that the adsorption capacity at equilibrium increases from 36.20 to 212.62 mg/g with initial dye concentration from 50-300 mg/L. Therefore, it can be said that adsorption of RR120 on WTC can be improved upon by increase in initial dye concentration. Similar trend was observed in the adsorption of reactive blue 15 dyes from aqueous solution on cross-linked chitosan beads [12]
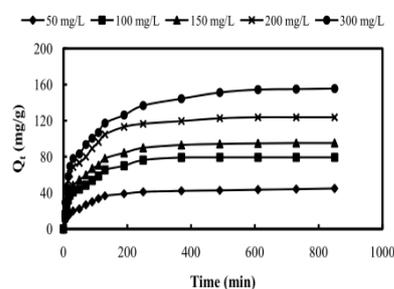
Fig. 3 Effect of temperature on adsorption of RR120 on WTC
Valuable information can be obtained about enthalpy during adsorption when a temperature dependence study on the process is undertaken. Therefore, temperature of the process was maintained at 30, 40, and 50 ^{o}C for effective study of temperature effect on the adsorption isotherms. Adsorption capacity was found to be increasing with increase in temperature

of the process signifying the endothermic nature of the process.
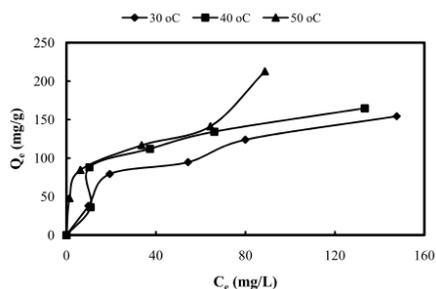
Fig. 4 Effect of temperature on adsorption of RR120 on WTC

Adsorption isotherm

The distribution of adsorbate between the liquid phase and the solid phase when adsorption process reaches equilibrium is provided during adsorption isotherm studies. This information helps an Engineer to optimize the design parameters for adsorption system for adsorption process. It also helps to establish the most appropriate correlation for equilibrium curves. The equilibrium characteristics of this adsorption study were described through Langmuir, Freundlich and Temkin equations.

The Langmuir isotherm [13] can be linearized as:

$$\frac{1}{Q_e} = \frac{1}{Q_m C_e b} + \frac{1}{Q_m} \qquad 3$$

where C_e is the equilibrium concentration of the RR120 adsorbed mg/L, Q_e is the amount of RR120 adsorbed mg/g, Q_m and b (Langmuir constants), the monolayer adsorption capacity and affinity of adsorbent towards adsorbate respectively.

A plot of $1/Q_e$ against $1/C_e$ gave a fitted curve (Fig. not shown), and the Langmuir constants were generated from the plot of sorption data. The results of essential characteristics of Langmuir isotherm expressed in dimensionless separation factor R_L, calculated for all concentrations at various temperatures investigated revealed that the entire adsorption processes were favorable since their values were in the range of $0 < R_L < 1$. The R_L equation [14] is given by:

$$R_L = \frac{1}{(1 + b C_o)} \qquad 4$$

where b is the Langmuir constant and C_o the highest dye concentration mg/L.

The Freundlich isotherm [15], an empirical equation based on heterogeneous surface can be expressed in linear form as:

$$\log Q_e = \log K_F + \frac{1}{n \log C_e} \qquad 5$$

A plot of Log Qe against Log Ce enables the constants K_F and exponent n to be determined (Fig. not shown). Where K_F is the adsorption of distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for an equilibrium concentration. The slope 1/n, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero.

It can be seen from the results in Table 2 based on correlation coefficient R^2 that Langmuir isotherm model best described the adsorption of RR120 on WTC which was further supported by the favourable nature of values obtained for essential of Langmuir model, R_L.

Table 2 Langmuir, Freundlich and Temkin isotherm model constants and correlation coefficients for adsorption of RR120 on WTC

Temperature (^{o}C)	b(L/mg)	Q_m (mg/g)	R_L	R^2
Langmuir isotherm				
30	0.024	200	0.1212	0.966
40	0.0256	250	0.1159	0.939
50	0.0635	250	0.0497	0.979
Temperature (^{o}C)	K_F	1/n		R^2
Freundlich isotherm				
30	43.85	0.471		0.916
40	20.94	0.434		0.688
50	15.31	0.311		0.943
Temperature (^{o}C)	A_T(L/mg)	b_T kJ/mol		R^2
Temkin isotherm				
30	0.2890	63.84		0.951
40	0.4496	65.29		0.847
50	2.3822	83.19		0.822

The maximum adsorption capacity of WTC for removal of RR120 was 250 mg/g. This is comparable with those of reported in the literature such as adsorption of Reactive black 5 and Reactive yellow 176 with adsorption capacities of 4.38 and 3.65 mg/g respectively [16]; and adsorption capacity of 81.97 mg/g for removal of Reactive red 120 by cetylpyridinium-bentonite [17].

Temkin and Pyzhev isotherm model was also used to study the isotherm nature of RR120 adsorption on WTC. It takes into account adsorbing species-adsorbate interaction. The isotherm assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-interactions, and also that adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energies. The model can be expressed linearly as:

$$Q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \qquad 6$$

A plot of Q_e against $\ln C_e$ (Fig. not shown), enables the determination of isotherm constants b_T and A_T through the slope of RT/b_T and intercept of $RT/b_T \ln A_T$. The results of the parameters obtained as shown on Table 2 revealed that the model did not describe well the adsorption process; the correlation coefficient R^2 values were lower than all the other models considered.

Adsorption kinetics

The mechanism of adsorption was investigated using the pseudo-first-order and pseudo-second-order adsorption models.

The Lagergren and Svenka rate equation which is the first rate equation developed for sorption in liquid/solid systems is based on solid capacity. The pseudo-first-order model [18] can be expressed as:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \qquad 7$$

where Q_e and Q_t are the amount of dye adsorbed (mg/g) at equilibrium and at time t respectively; K_1 is the rate constant of adsorption which can be obtained from the plots of $\ln(Q_e - Q_t)$ against t at various temperature of operation as shown in Fig. 5.
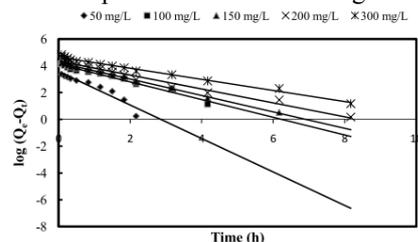
Fig. 5 Pseudo-first-order kinetics of RR120 adsorption onto WTC at various initial conditions (30 ^{o}C)

The pseudo-second-order equation [19,20] can be expressed linearly as:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{K_2} Q_e^2 \qquad \qquad 8$$

A linear plot of t/Q_t against t as shown in Fig. 6, gives a slope of $1/Q_e$ and an intercept $1/K_2Q_e^2$ where K_2, rate constant of adsorption can be determined.

The two models showed that they were applicable to describing the adsorption process as a result of the linearity of the plots. But the correlation coefficients of pseudo-second-order kinetics were above 0.996 at all concentrations studied which was above the highest R^2 value (0.991) of pseudo-first-order coefficients. This confirmed that the adsorption process followed second-order kinetic model. That is to say chemical sorption was rate controlling step which may involve valency forces through sharing or exchange of electrons between dye anions and adsorbent. Azazian theoretically put forward an equation to support claims that the rate coefficient K_1 from pseudo-first-order model is not the intrinsic adsorption rate constant but a combination of adsorption K_a and desorption K_d rate constants. The equation is thus:

$$K_1 = K_a C_o + K_d \qquad \qquad 9$$

The equation buttress the point that the rate coefficient must be in linear form it pseudo-first-order describes adsorption process [21]. Results on Table 3 shows that the initial concentration C_o relation with K_1 coefficient values were not linear but rather were found to be increasing in concentration while K1 values were decreasing to 200 mg/L.

Table 3 Kinetic parameters of RR120 adsorbed onto WTC at different initial concentrations

C_o (mg/L)	$Q_e$exp (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		Q_e cal (mg/g)	K_1 (h^{-1})	R^2	Qe cal (mg/g)	K_2 (g/mgh)	R^2
50	47.889	28.16	2.002	0.976	50	0.400	0.999
100	84.545	85.03	1.676	0.939	90.91	0.040	0.998
150	116.603	106.38	1.004	0.958	125	0.021	0.997
200	141.175	122.49	0.894	0.974	166.67	0.012	0.997
300	212.622	199.74	1.103	0.991	250	0.008	0.998
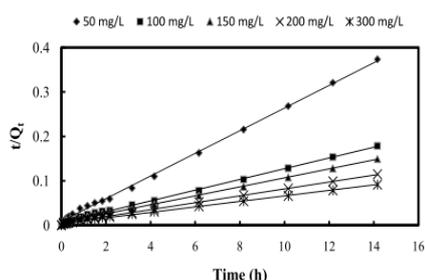
Fig.6 Pseudo-second-order kinetics of RR120 adsorption on WTC at various initial conditions (30 °C)

Adsorption thermodynamics

Thermodynamic parameters of adsorption of RR120 on WTC were undertaken at various temperatures of 30, 40 and 50 °C. This was done to determine the spontaneity of the adsorption process. The equation used is expressed as:

$$\Delta G = -RT \ln K_o \qquad \qquad 10$$

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.

Van't Hoff equation was used to determine the average standard enthalpy change, the equation is expressed as:

$$\ln K_o = \frac{-\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad \qquad 11$$

A plot of InKo against 1/T gives a graph (Fig. not shown) where we can obtain ΔS from the intercept and ΔH from the slope.

Table 4 Thermodynamic parameters of RR120 adsorption on WTC

Concentration mg/L	ΔH (J/mol)	ΔS (J/mol)	ΔG (J/mol)		
			303 K	313 K	323 K
50	90938.5	307.87	-3402.16	-3141	-9501.41
100	49634.6	175.84	-3550.57	-5583.67	-6991.72
150	28616.8	99.6	-1395.64	-2857.81	-3336.46
200	14507.9	51.78	-1099.84	-1843.51	-2109.84
300	34478.2	113.4	-111.134	-548.979	-2346.23

The thermodynamics parameters obtained at various temperatures investigated are reported in Table 4. The negative values obtained for change of Gibbs free energy (ΔG), showed that the adsorption of RR120 on WTC was spontaneous in nature. The positive values of enthalpy (ΔH) obtained showed that the adsorption process was endothermic in nature and the positive values of entropy (ΔS) also confirmed the favorability of the adsorption at elevated temperatures. The absolute of change of Gibbs free energy for physical adsorption is -20 to 0 KJ/mol which is smaller than that of chemisorptions -80 to -400 KJ/mol [22]. Results of Gibbs free energy of this study as presented in Table 4 further affirmed that adsorption process was physical in nature and was more favorable at high temperatures. Similar result was reported on removal of 2,4-dichlorophenoxyacetic acid by corn cub activated carbon [23].

Intraparticle diffusion model

The thermodynamics of the process was studied by testing the possibility of intraparticle diffusion model which can be expressed as:

$$Q_t = k_{ip} t^{0.5} + C \qquad \qquad 13$$

where K_{ip} (mg/g.min$^{0.5}$) is the intra-particle diffusion rate constant and C gives idea on the boundary thickness. A plot of Q_t against $t^{0.5}$ of various initial dye concentrations gave linear plots for both the boundary layer diffusion and intraparticle diffusion. The results of the plot is shown on Table 5

Table 5 Intraparticle diffusion model results

Temp °C	Concentration mg/L	Boundary layer diffusion			Intra-particle diffusion		
		K_{i1} (mg/g.min$^{0.5}$)	C	R^2	K_{i2} (mg/g.min$^{0.5}$)	C	R^2
30	50	2.878	3.139	0.993	0.332	37.93	0.571
	100	4.687	10.92	0.951	0.474	67.22	0.596
	150	6.045	10.10	0.952	0.617	78.84	0.767
	200	7.917	16.08	0.915	0.703	105.1	0.882
	300	8.417	22.65	0.949	1.842	106.1	0.89
40	50	2.897	3.804	0.945	0.085	34.06	0.54
	100	7.668	6.581	0.951	0.227	2.37	0.56
	150	7.900	9.489	0.978	0.529	99.27	0.565
	200	10.34	9.427	0.967	0.341	125.7	0.455
	300	11.11	16.26	0.974	1.747	131.9	0.802
50	50	3.194	17.77	0.908	0.112	45.89	0.261
	100	7.995	0.812	0.965	0.834	69.45	0.423
	150	9.323	0.999	0.978	2.528	69.76	0.655
	200	9.919	10.17	0.959	3.471	75.53	0.754
	300	18.23	2.686	0.983	4.09	136.3	0.714

Must reactions usually have mechanisms or steps between the starting reactants and products. Therefore, a need arises as to which of the steps is rate-controlling. In the adsorption process undertaken, the steps involved were movement (mass transfer) of solute from the water to the surface of the adsorbent (WTC) across the boundary layer and then diffusion into the pores of the WTC.

In batch reactors, intra-particle diffusion is commonly the rate limiting step while for continuous flow systems; the rate limiting step is often found as film diffusion. The multilinearities of the plots as

observed (Fig. not shown) showed that intra-particle diffusion was not the only rate controlling step since different features were observed on the plots. The gradual horizontal shape represented the intraparticle rate limiting portion while the sharper steep sloppy side was the boundary layer diffusion side.

The results of the analysis of the two proposed rate-controlling steps with their parameters k_{i1} and k_{i2} for boundary layer and intra-particle diffusion respectively, are presented in Table 5. The intra-particle diffusion portion had thicker boundary layer than boundary layer diffusion side according to the calculated values of C. Also, the k_{i1} values were distinctively larger than the k_{i2} values signifying that intra-particle diffusion was the rate controlling step for the adsorption of RR120 on WTC.

CONCLUSION

This study has shown that the activated carbon prepared from waste tea WTC is a good potential adsorbent for removal of RR120 from polluted waters with good adsorption capacity of 250 mg/g which is comparable with other adsorbents found in literature. The anionic dye removal was at its best at pH 3. Langmuir isotherm model was successfully tested and was found to be adequately predicting the adsorption process more than Freundlich model. The adsorption process followed the pseudo-second-order rate more than pseudo-first-order rate model. The adsorbent WTC can be used to substitute commercial activated carbon for the removal of RR120 from waste waters.

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