

Adsorption of Paraquat dichloride from aqueous solution by activated carbon derived from used tires

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Abstract

The removal of pesticide from wastewater under different batch experimental conditions, using a car tire derived activated carbon was investigated. The pesticide utilized in the study was Paraquat dichloride (1,1-dimethyl-4,4-bipyridyl dichloride), which is a well known herbicide. The adsorbent was produced from the pyrolysis and activation of used tires (TAC). The performances of this adsorbent and a commercial activated carbon F300 (CAC) have been compared. It was determined that the adsorption of Paraquat was weakly pH dependent. The effects of particle size, carbon dosage, temperature and the initial concentration of the Paraquat were studied. Further experiments investigating the regeneration capabilities of the tire-supplied carbon were performed. The regenerated carbons that were washed with basic pH solution were found to have the best sorption capacity recovery.

It was found that the rate of sorption of Paraquat onto the carbon is very fast with almost 90% of the maximum possible adsorption taking place in the first 5 min. Nevertheless, the batch sorption kinetics was fitted for a first-order reversible reaction, a pseudo-first-order reaction and a pseudo-second-order reaction. The pseudo-second-order chemical reaction model appears to provide the best correlation. The applicability of the Langmuir isotherm for the present system has been evaluated at different temperatures. The isotherms show that the sorption capacity of CAC decreases with temperature and the dominant mechanism of CAC adsorption is physical sorption.

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1. Introduction

Pesticides have been detected in some water supplies since 1945 [1]. This class of water pollutants is of particular importance due to toxicity, carcinogenicity and mutagenic effects. The removal and disposal of pesticides is an extremely complex problem due to the large range of chemicals that are in use. There is no recognized universally applicable treatment that removes all pesticides. Conventional methods for the removal of pesticides from wastewater include UV treatment, chemical coagulation, sedimentation, filtration, disinfection and sorption onto solid substrates such as activated carbon. The latter topic was the subject of this study.

The term ‘activated carbon’ refers to a wide range of amorphous carbon-based materials that have been “activated” in

order to exhibit a high surface area. Commercial activated carbons are usually derived from natural materials such as coconut shell, wood or coal and are manufactured to produce precise surface properties. These materials are expensive and require elaborate reactivation and regeneration processes. Such processes often result in the degradation of the adsorption properties of the carbon, which subsequently affects the economic viability of the operation. There is a need for effective but low cost carbons that can be used on a once through basis for pollution control—an application that does not require the use of specialized activated carbons. One such material under consideration is derived from the used tires.

The disposal of scrap tires is a growing problem. For example, in the USA, it is estimated that the amount of scrap tires is 240 to 270 million t per year and that there is stockpile of 3000 million t awaiting disposal [2]. The main methods of scrap tire disposal are to land fills followed by illegal stock-

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piling and incineration. In the European Union the amount of scrap tires is of the order of 2 million t per year [2,3]. The treatment and disposal option for tires most commonly used throughout the European Union is to a land fill, representing approximately 46% of the total amount of waste tires. Recycling the recovered materials or energy represents approximately 31% while about 23% are re-treaded [4]. Japan generates approximately 0.7 million t of scrap tires per year. The majority are recycled. Reclaiming and re-treaded represents about 35%, energy recovery accounts for a further 34% and the remainder is land filled, stockpiled, or exported [2].

There exists, however, an alternative disposal process.

Several studies have shown that the activation of tire char can result in a product with a comparable surface area to commercially available activated carbon [5–7].

Similarly, activated tire char has exhibited promising wastewater remediation performance [8,9]. It could also have potential as a storage medium for methane [5].

Paraquat (1,1-dimethyl-4,4-bipyridyl dichloride) is one of the most widely used herbicides, and until recently held the largest share of the global herbicide market. Paraquat is sold in about 130 countries to kill weeds on farms, plantations, estates. It is also utilized in non-agricultural weed control. Paraquat is a quick acting, non-selective herbicide, which destroys green plant tissue [13]. It can be found in formulations with many other herbicides.

Paraquat is a highly toxic compound in the US EPA toxicity class 1. The lethal dose for Paraquat in humans is 35 mg kg⁻¹ [14]. In New Zealand the maximum allowable concentration of Paraquat in drinking water is 10 µg L⁻¹ [15].

Paraquat is highly persistent in soil. The bound residues may persist indefinitely and can be transported in runoff with the sediment. The reported half-life for Paraquat in one study ranged from 16 months (aerobic laboratory conditions) to 13 years (field study) [14]. Ultraviolet light, sunlight, and soil microorganisms can degrade Paraquat to products that are less toxic than the parent compound [14].

Previously, we studied the removal of hexavalent chromium and color (methylene blue) from wastewater using the adsorbents produced from waste tires and sawdust under a variety of conditions [11,12]. In this study, the adsorption kinetics of the tire-derived adsorbent for the removals of Paraquat under a wide range of conditions have been investigated. In addition, a well-known commercial activated carbon (CAC) F300 was used as a reference.

2. Basic adsorption kinetics models

The adsorption kinetics models correlate the pollutant uptake rate, so these models are important in water treatment process design. In this study, the kinetics of Paraquat uptakes by the adsorbent derived from used tires have been measured.

2.1. First-order reversible reaction model

The sorption of Paraquat from liquid phase onto a porous solid may be considered as a reversible reaction [16]. A simple first-order reaction model can be expressed as



If this model is correct, the rate equation for the reaction is expressed as

$$\begin{aligned} \frac{dC_B}{dt} &= -\frac{dC_A}{dt} = k_1 C_A - k_2 C_B = C_{A_0} \frac{dX_A}{dt} \\ &= k_1 (C_{A_0} - C_{A_0} X_A) - k_2 (C_{B_0} + C_{A_0} X_A) \end{aligned} \quad (2)$$

Here, C_B (mg g⁻¹) is the concentration of Paraquat on the sorbent and C_A (mg L⁻¹) is the concentration of Paraquat in solution at any time. C_{B_0} and C_{A_0} are the initial concentrations of Paraquat on sorbent and solution, respectively. X_A is the fractional conversion of Paraquat, and k_1 and k_2 are the first-order rate constants. Under equilibrium conditions, the rates of forward and backward reactions are equal. Therefore,

$$\begin{aligned} K_C &= \frac{C_{B_e}}{C_{A_e}} = \frac{C - C_{A_0} X_{A_e}}{C - C_{A_0} X_{A_e}} = \frac{k_1}{k_2} \quad \text{or} \\ X_{A_e} &= \frac{K_C - (C_{B_0}/C_{A_0})}{K_C + 1} \end{aligned} \quad (3)$$

In the above equation ‘e’ represents equilibrium and K_C is the equilibrium constant. The rate equation in terms of equilibrium conversion can be obtained from Eqs. (2) and (3):

$$\frac{dX_A}{dt} = (k_1 + k_2)(X_{A_e} - X_A) \quad (4)$$

Integrating Eq. (4) and substituting for k_2 from Eq. (3), gives

$$-\ln \left(1 - \frac{X_A}{X_{A_e}} \right) = k_1 \left(1 + \frac{1}{K_C} \right) t \quad (5)$$

Thus Eq. (5) can be rewritten in a different form:

$$\ln[1 - U(t)] = -k_{\text{overall}} t \quad (6)$$

In which k_{overall} is the overall rate constant and

$$k_{\text{overall}} = k_1 \left(1 + \frac{1}{K_C} \right) = k_1 + k_2 \quad (7)$$

$$U(t) = \frac{C_{A_0} - C_A}{C_{A_0} - C_{A_e}} = \frac{X_A}{X_{A_e}} \quad (8)$$

$U(t)$ is called the fractional attainment of equilibrium.

2.2. Pseudo-first-order model

The sorption kinetics may be described by a pseudo-first-order according to Ho and McKay [17], and Namasivayam and Kardivelu [18]:

$$\frac{dq_t}{dt} = k'_1 (q_e - q_t) \quad (9)$$

where q_e is the amount of solute adsorbed upon equilibrium per unit weight of adsorbent (mg g^{-1}), q_t the amount of solute adsorbed at any time (mg g^{-1}), and k'_1 is the adsorption rate constant (min^{-1}).

Eq. (9) is integrated from $t = 0$ to $t > 0$ and then rearranged to obtain the following linear time dependence function:

$$\log(q_e - q_t) = \log(q_t) - \frac{k'_1}{2.303}t \quad (10)$$

2.3. Pseudo-second-order model

A pseudo-second-order model [17,19] may be used to describe the kinetics of adsorption:

$$\frac{dq_t}{dt} = k'_2(q_e - q_t)^2 \quad (11)$$

Integrating Eq. (11) from $t = 0$ to $t > 0$ and rearranging it to obtain a linearized form:

$$\frac{t}{q} = \frac{1}{k'_2 q_e^2} + \frac{1}{q_e}t \quad (12)$$

$$h = k'_2 q_e^2 \quad (13)$$

where h is the initial sorption rate ($\text{mg g}^{-1} \text{min}^{-1}$); k'_2 has a unit of $\text{g mg}^{-1} \text{min}^{-1}$.

3. Adsorption isotherm

Adsorption from aqueous solutions involves the concentration of the solute on the adsorbent surface. At equilibrium, no changes in the concentration of the solute can be observed in the solution or on the surface of the adsorbent. The constant temperature presentation of the sorption capacity of the adsorbent as a function of the equilibrium concentration is called an adsorption isotherm. The Langmuir model is often used to describe sorption of a solute from a liquid solution. The equation in its linearized form is shown below [11,12]:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (14)$$

where C_e is the equilibrium concentration (mg L^{-1}) and q_e the amount adsorbed at equilibrium (mg g^{-1}). Plotting C_e/q_e against C_e , a straight line, having a slope $1/q_m$ and an intercept $1/q_m b$, is obtained. q_m (mg g^{-1}) is the amount adsorbed per unit mass of adsorbent corresponding to complete coverage of the adsorptive sites, and b (L mg^{-1}) is the Langmuir constant.

4. Experimental methods

4.1. Material preparation and characterization

Pyrolysis of the tire-derived scrap was carried out in an isothermal reactor heated by a tubular furnace (i.d. = 61 mm, $L = 55$ cm). Fig. 1 shows the schematic diagram of the equipment. At the beginning of each run, 100 g of small pieces ($3 \text{ cm} \times 2.5 \text{ cm} \times 0.5 \text{ cm}$) of used tires were placed in a steel reactor tube (o.d. = 44 mm, $L = 24.5$ cm) supported on a 1 mm mesh located in the middle of the longer steel tube (o.d. = 60 mm, $L = 79$ cm). Nitrogen was used as the purging gas. It flows through the sample bed at 200 mL min^{-1} . The reactor was heated to the desired temperature (900°C) at a heating rate of $20^\circ\text{C min}^{-1}$. The holding time was 2 h. After the pyrolysis process, the product was activated at the same temperature for 2 h using CO_2 as an oxidizing agent. Then the reactor was cooled down to room temperature and the sample removed for weighing and characterization.

The adsorbents made in this work were characterized by scanning electron microscope (SEM) (see Figs. 2 and 3). These figures show that the adsorbent from used tires has an irregular and porous surface. The BET surface area measurements revealed that the surface area of the activated carbon from the used tire is $832 \text{ m}^2 \text{ g}^{-1}$. The CAC surface area was $1050 \text{ m}^2 \text{ g}^{-1}$.

Tests were performed on the tire-derived activated carbon (TAC) to determine the composition and physical properties of the product. A Phillips PW 1050 X-ray diffractometer was used to carry out the test. The results (see Fig. 4) of the X-ray diffraction confirm that the tire activated carbon does

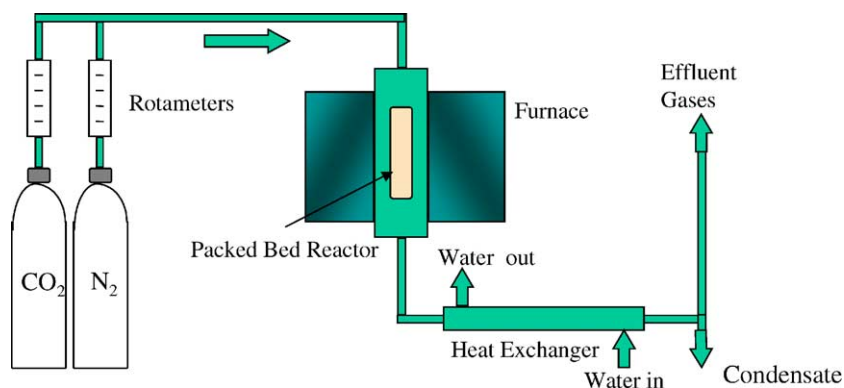


Fig. 1. Schematic diagram of the pyrolysis and activation process.

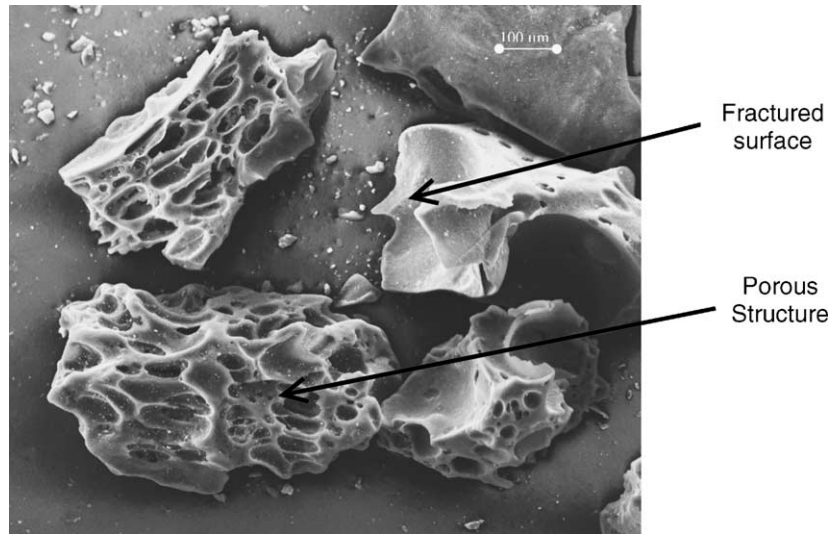


Fig. 2. Porous structure of a tire-derived activated carbon.

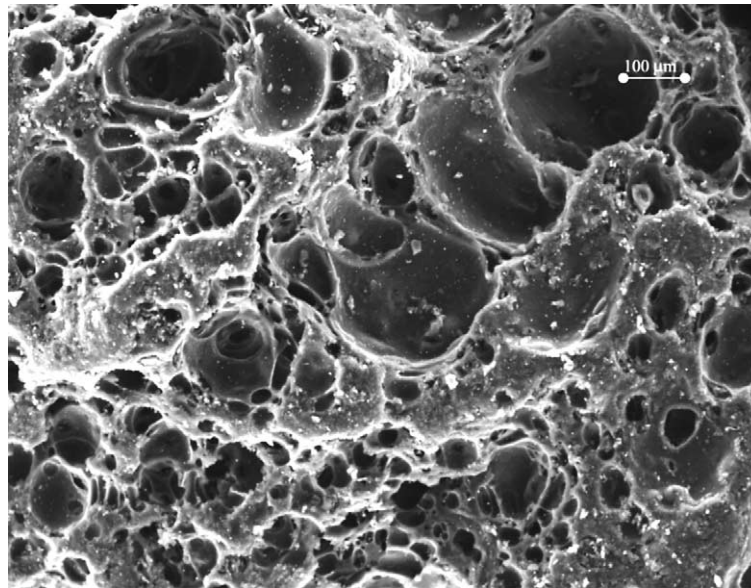


Fig. 3. Surface structure of a tire-derived activated carbon.

not have a crystalline structure. The structure of the carbon is most likely amorphous.

An energy dispersive spectrometer (EDS) was also used to analyze tire-derived material. Tires are primarily composed of vulcanized rubber, rubberized fabric containing reinforcing textile cords, steel or fabric belts and steel-wire reinforced rubber heads [10]. Styrene-butadiene rubber (SBR) is still the most important synthetic rubber used in the industry today although natural rubber is also used in tires to some degree. Carbon black, extender oil, sulfur, zinc oxide and stearic acid are also added in tire manufacture. Carbon black is used to strengthen the rubber and to improve its abrasion resistance. The bulk of a tire is organic and carbonaceous in nature thus provides an ideal source for the production of activated carbon [20].

The EDS analysis provided a rudimentary composition for the tire-derived activated carbon. Fig. 5 is one section of the plot. The compositions from the peak areas are calculated as shown in Table 1. It was found that carbon, sulfur and oxygen were the only common components in the TAC. Other minor constituents that were determined in the analysis included sodium, silicon, zinc, sodium, calcium, iron and vanadium.

Table 1
EDS composition of TAC

Element	Composition (wt.%)
Carbon	96.86
Oxygen	2.03
Sulfur	1.39

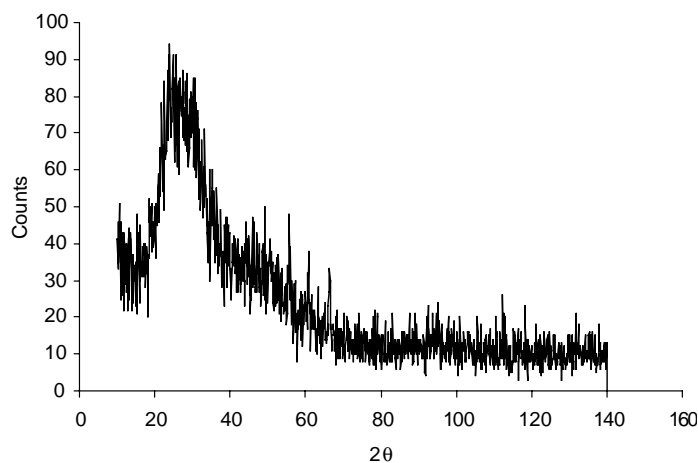


Fig. 4. X-ray diffraction (XRD) of TAC.

The origins of the other constituents in the carbon can be determined by considering the process and materials used in tire manufacture. The sulfur is a result of the vulcanization process. Many of the heavy metals are added to the tire for strength or are naturally present in the long-chained organic components that rubber is composed of.

4.2. Adsorption

The measurement of adsorption kinetics of the carbon was carried out by shaking 1 g of carbon with 200 mL of Paraquat solution of known concentration in 250 mL conical flask placed in a thermostat in a shaking flask. The removal kinetics of the Paraquat was investigated by taking samples of the solution after the desired contact time and the filtrate were analyzed for its Paraquat concentration. A spectrophotometer was employed at a wavelength of 282 nm. Twelve vials for each experimental case were used to avoid inaccuracies due to volume change caused by sampling. A

Hewlett-Packard 8452A diode array spectrophotometer was used to carry out these tests. The pH was adjusted either with 0.1 M HCl or 0.1 M NaOH as required. At least five experiments were carried out for each condition with a variation of less than 4%. The same procedure has been used to study the effect of initial concentration, pH, temperature and particle size.

The equilibrium isotherm was determined by mixing 0.2 g of carbon with 50 mL of Paraquat solution in a 125 mL conical flask at the required temperature. Each isotherm consisted of six different Paraquat concentrations from 100 to 1000 mg L⁻¹. The flasks containing Paraquat solution and carbon were placed in a shaker and agitated for 48 h at the required temperature and at a fixed agitation speed of 150 rpm. The equilibrium concentrations were measured using a spectrophotometer. At least five experiments were carried out for each condition with a variation of less than 3% in concentration detected.

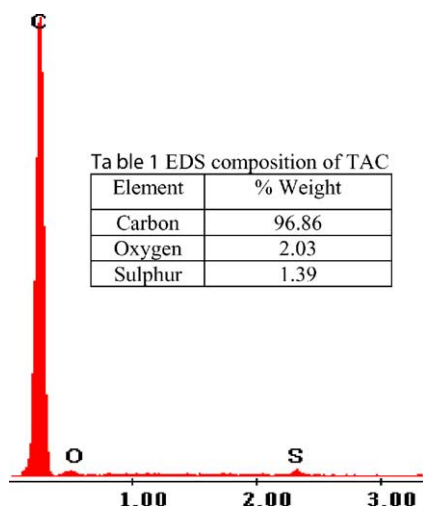


Fig. 5. EDS graph from a sample of TAC.

5. Results and discussion

5.1. Effect of particle size

The effect of particle size on the sorption of Paraquat solution was studied using three size fractions of TAC (average particle size = 0.11, 0.38 and 0.9 mm). Experimental results for these experiments are shown in Fig. 6. The results show that the sorption of Paraquat onto TAC is very fast with almost 90% of the sorption taking place in the first 5 min. The equilibrium sorption capacities after 3 h for the different size fractions were 7.25, 6.95 and 6.81 mg g⁻¹ for particle fractions 0.11, 0.38 and 0.9 mm, respectively. The sorption capacity of the TAC did not change much with decreasing the particle size. Hence, the effect of intra-particle diffusion on the adsorption can be neglected for the particles of average size below 0.9 mm.

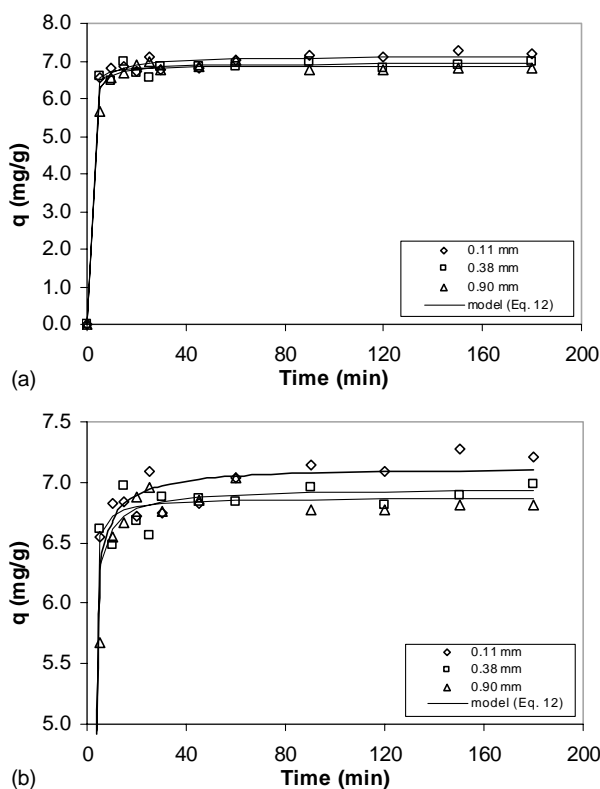


Fig. 6. (a) and (b) Effect of particle size on sorption of Paraquat on TAC.

The data from Fig. 6a and b below were correlated using first-order reversible, pseudo-first-order and pseudo-second-order models (Eqs. (6), (10) and (12)). Linear plots of t/q versus t shows the applicability of the second-order model (Eq. (12)) to the system of Paraquat and the TAC for particle sizes ranging from 0.11 to 0.9 mm. The data obtained from the second-order plot and the correlation coefficients (r^2) are shown in Table 2. The trend lines plotted in Fig. 6a and b are derived from the constants in this table.

5.2. Effect of activated carbon dosage

Fig. 7 shows the quantity of Paraquat sorbed for dosage sizes of 0.1, 0.2, 0.4, 0.8, 1.2, 1.6 and 2.0 g of TAC after 60 and 150 min. It was found that increasing the dosage of activated carbon increases the quantity of Paraquat sorbed from the solution as expected due to the great capacity of the adsorbent already shown in Fig. 6. The increase in sorption can be attributed to the increase in external surface areas,

Table 2
Data illustrating the effect of particle size on adsorption kinetics

Sample	Diameter (mm)	q_e (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	r^2
1	0.11	7.25	0.1005	0.9997
2	0.38	6.95	0.9791	0.9998
3	0.9	6.81	0.0826	0.9999

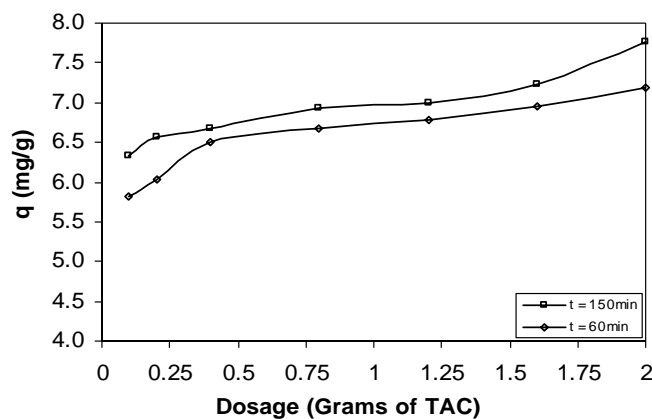


Fig. 7. Effect of TAC dosage on the sorption of Paraquat.

which, in turn, means an increase in number of available sites for Paraquat uptake. The increased external surface area provides more adsorptive sites for the sorption reaction to occur. There is no significant deviation in sorption capacity between 60 and 150 min, indicating that the sorption process is nearly at equilibrium.

Increasing the dosage size of the TAC did not increase the adsorption capacity proportionally. As the dosage was increased only limited increases in sorption capacity were detected because the sorption system reached the equilibrium.

5.3. Effect of initial concentration

The removal of Paraquat by adsorption on TAC and CAC has been shown to occur rapidly for all initial concentrations. On changing the initial concentration of Paraquat solution from 10 to 40 mg L⁻¹ the amount adsorbed increases from 1.66 to 7.28 mg g⁻¹ at 25 °C, pH = 7 and average particle size of 0.65 mm for the TAC (Fig. 8). While for the CAC the amount adsorbed increases from 1.59 to 7.51 mg g⁻¹ (Fig. 9). From Figs. 8 and 9 one can see that with lower initial concentration of adsorbate the amount of adsorbate attained on the solid phase is smaller than the amount attained when higher initial concentrations are used.

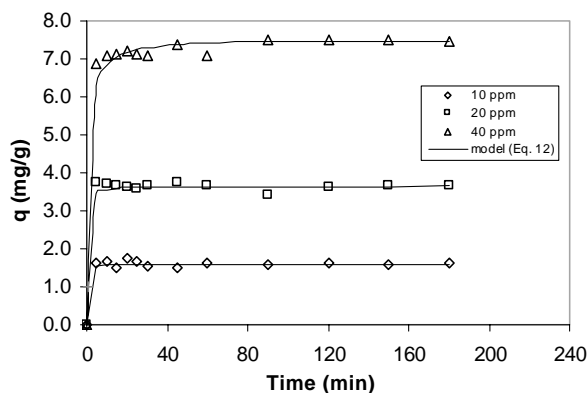


Fig. 8. Effect of initial concentrations on the sorption of Paraquat on TAC (note that 1 ppm = 1 mg L⁻¹).

Table 3
Data on the effect of initial concentration

Sample	C_i (mg L ⁻¹)	q_e (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	Percentage removed	r^2
TAC	10	1.66	2.9912	82.9	0.9995
TAC	20	3.62	0.3663	90.6	0.9984
TAC	40	7.28	0.0848	87.7	0.9997
CAC	10	1.59	6.4506	79.6	0.9979
CAC	20	3.65	1.1000	91.3	0.9989
CAC	40	7.51	0.1354	92.9	0.9988

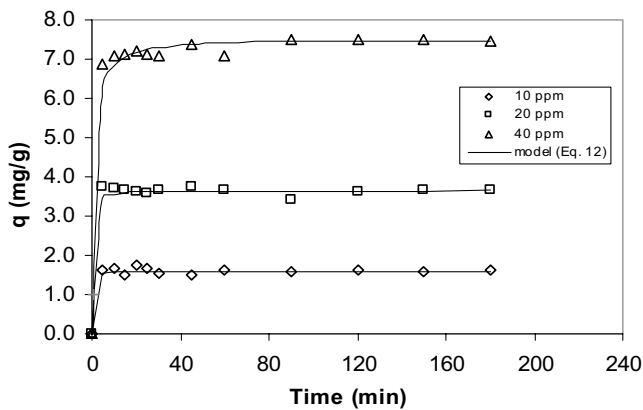


Fig. 9. Effect of initial concentrations on the sorption of Paraquat on CAC (note that 1 ppm = 1 mg L⁻¹).

The data followed a second-order rate equation (Eq. (12)). The q_e values were calculated based on second-order curve and presented in Table 3. The TAC shows comparable performance to CAC for all the three initial concentrations.

5.4. Effect of temperature

Samples of TAC (Fig. 10) and CAC (Fig. 11) were tested at 25, 35 and 45 °C over a 3 h period. The initial concentration of the Paraquat solutions was 40 mg L⁻¹ and pH was 7. The TAC and CAC particle sizes were 0.65 mm. The amount of Paraquat adsorbed on TAC at 25, 35 and 45 °C after 3 h are 7.28, 6.99 and 6.99 mg g⁻¹, respectively. In the adsorp-

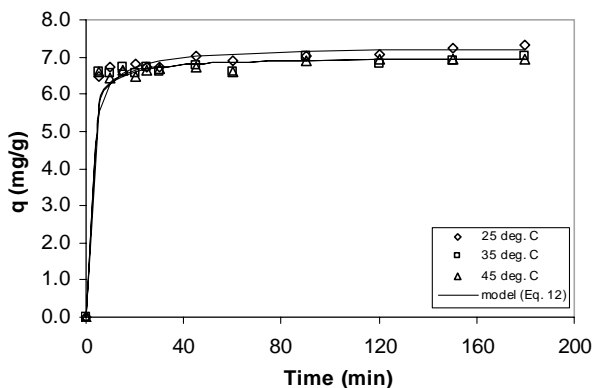


Fig. 10. Effect of temperature on the sorption of Paraquat on TAC.

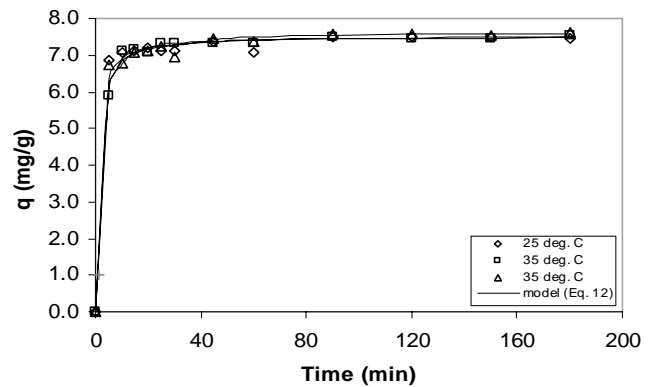


Fig. 11. Effect of temperature on the sorption of Paraquat on CAC.

tion runs for CAC, the equilibrium sorption capacities were 7.52, 7.52, and 7.64 mg g⁻¹ at 25, 35 and 45 °C, respectively. The total amount adsorbed of Paraquat on TAC and CAC was not affected significantly with the increasing of temperature from 25 to 45 °C. The TAC shows comparable sorption capacities to the CAC. The adsorption kinetics for all the systems studied fit the pseudo-second-order model (Eq. (12)) with regression analysis producing correlation coefficients of almost 1 as shown in Table 4.

5.5. Effect of pH

The effect of pH on the adsorption of Paraquat using TAC (Fig. 12) and CAC (Fig. 13) was also studied. The pHs of

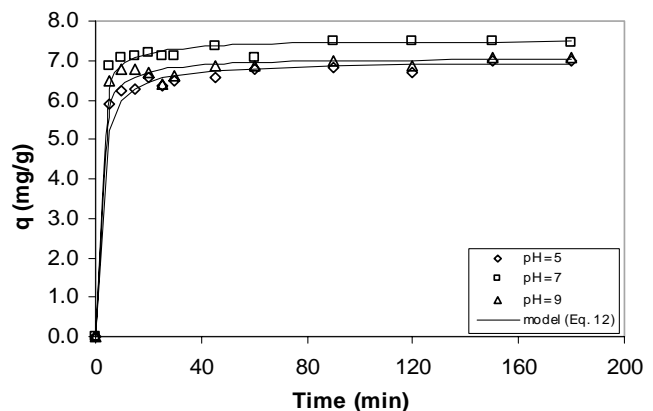


Fig. 12. Effect of pH on the sorption of Paraquat on TAC.

Table 4
Data illustrating the effect of temperature on the adsorption kinetics

Sample	T ($^{\circ}\text{C}$)	q_e (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	h ($\text{mg g}^{-1} \text{min}^{-1}$)	r^2
TAC	25	7.28	0.0848	4.49	0.9994
TAC	35	6.99	0.1338	6.53	0.9995
TAC	45	6.99	0.1248	6.11	0.9998
CAC	25	7.51	0.1354	7.66	0.9997
CAC	35	7.52	0.1444	8.18	0.9990
CAC	45	7.64	0.1037	6.05	0.9990

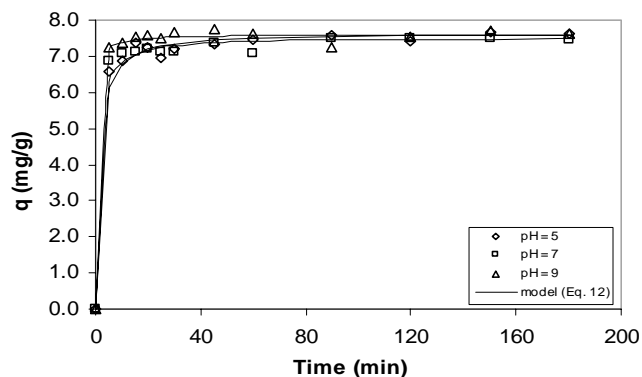


Fig. 13. Effect of pH on the sorption of Paraquat on CAC.

the Paraquat solutions used were 5, 7 and 9. The initial concentration of the Paraquat solutions was 40 mg L^{-1} and temperature was 25°C . The TAC and CAC particle size was 0.65 mm . The results (Table 5) show that the sorption of Paraquat on TAC and CAC is weakly pH dependent because the amount adsorbed at equilibrium was almost constant for both carbons for all pHs tested. The data was best modeled using the second-order model (Eq. (12)). The sorption capacity data for TAC and CAC are very close.

5.6. Regeneration

Experiments were performed to determine the optimum regeneration technique. Contaminated carbons were regenerated by treatment with a base, an acid and a combination of an acid and a base. At least five experiments were carried out for each condition with a variation of less than 4% in concentration measurement. The regenerated carbons were then tested with a fresh Paraquat solution to determine their sorption capacities.

Table 5
Data illustrating the effect of pH on the adsorption kinetics

Sample	pH	q_e (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	h ($\text{mg g}^{-1} \text{min}^{-1}$)	r^2
TAC	5	6.99	0.0852	4.16	0.9994
TAC	7	7.28	0.0848	4.49	0.9994
TAC	9	7.06	0.1283	6.40	0.9997
CAC	5	7.65	0.1028	6.02	0.9997
CAC	7	7.52	0.1354	7.66	0.9997
CAC	9	7.60	0.4389	25.38	0.9994

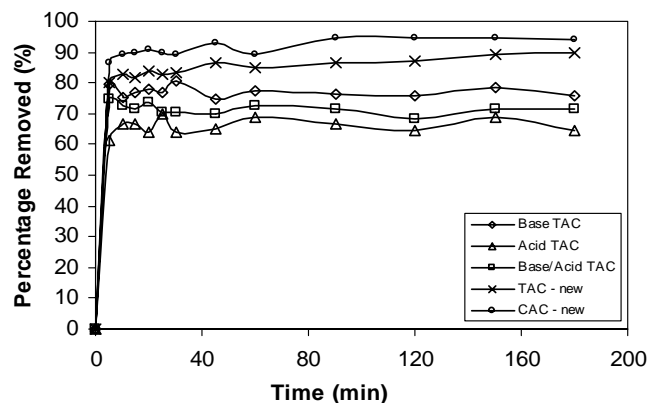


Fig. 14. Performance of the regenerated activated carbon in the adsorption of Paraquat.

The carbon regenerated in the basic conditions had the highest sorption capacity of all the regenerated carbons. The sorption capacities were 5.26 , 6.16 and 5.70 mg g^{-1} for the acid, base and acid–base systems regeneration, respectively. The sorption capacity of the best-regenerated TAC was still 14% lower than new TAC (Fig. 14).

5.7. Adsorption isotherms

A series of isotherms are shown in Fig. 15 for the sorption of Paraquat from aqueous solution onto TAC and CAC at different concentrations and temperatures. Fig. 15 shows the applicability of the isotherm to the Langmuir model. From Table 6, it can be seen that for CAC the sorption capacity decreases with temperature. This result confirms the exothermic nature of Paraquat adsorption on CAC. Increasing the temperature of the adsorption increases the overall energy of the Paraquat molecules and thus they are able to

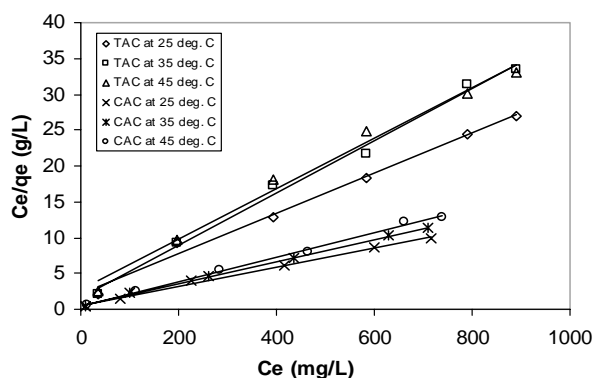


Fig. 15. Application of the Langmuir isotherm to the adsorption data.

Table 6
Sorption capacities of TAC and CAC for Paraquat adsorption for Langmuir isotherm calculations

Sample	T ($^{\circ}\text{C}$)	q_m (mg g^{-1})	b (L mg^{-1})	r^2
TAC	25	33.7	0.014	0.9927
TAC	35	27.8	0.019	0.9917
TAC	45	28.7	0.011	0.9877
CAC	25	75.8	0.023	0.9946
CAC	35	68.0	0.023	0.9910
CAC	45	61.0	0.027	0.9887

free themselves of the active sites. While for the TAC there was no obvious trend.

6. Conclusions

In this paper, the adsorbent materials derived through a laboratory scale pyrolysis and activation of the used tires has been tested. These adsorbents have comparable performance to a commercial activated carbon. The carbon produced from used tires is reasonably effective (85% removal) at $\text{pH} = 7$ and at temperature of 25°C . The temperature dependence is evident from these experimental results. The pseudo-second-order chemical reaction model provides the best correlation of the Paraquat adsorption kinetics. The regenerated tire-carbon has been found to be capable of removing Paraquat to a considerable extent.

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