

Removal of microcystin-LR from aqueous solutions using % burn-off activated carbon of waste wood material

S. Hena, N. Ismail, A. M. Isaam, A. Ahmad and S. A. Bhawani

ABSTRACT

The activated carbon (AC), prepared at different burn-off rates, showed a high uptake of methylene blue. At 93% burn-off, methylene blue uptake was 620 mg/g. Adsorption capacity of microcystin-LR onto rubber wood AC was investigated in a batch system by considering the effects of various parameters like contact time, initial concentration, pH and temperature. Microcystin-LR removal is pH dependent and found to be highest at pH 2.5. Increases in adsorption capacity with increase in temperature indicate that the adsorption reaction is endothermic. Based on this study, the thermodynamic parameters like standard Gibb's free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) were evaluated. A pseudo second order model was found to explain the kinetics of microcystin-LR adsorption most effectively. The rate of intraparticle diffusion was also evaluated. The Langmuir and Freundlich isotherms were used to describe the adsorption equilibrium studies of rubber wood AC at different temperatures. The Langmuir isotherm shows better fit than Freundlich isotherms in the temperature range studied. The results show that the rubber wood AC can be efficiently used for the removal of microcystin-LR from water. In order to investigate the possibility of regeneration and reuse of exhausted adsorbent, desorption studies were also performed.

Key words | activated carbon, adsorption, kinetics, microcystin-LR, thermodynamics, waste wood material

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INTRODUCTION

With increasing discharge of wastewater containing nitrogen and phosphorus to rivers and lakes, harmful cyanobacteria blooms in natural waters have become a growing environmental problem world-wide (Kaebernick & Neilan 2000; Haider *et al.* 2003).

Microcystins are a family of cyclic heptapeptides hepatotoxins produced by several commonly occurring species of cyanobacteria, including *Microcystis*, *Nostoc*, *Anabaena* and *Planktothrix* (Falconer 2005). Microcystin-LR is the most common *Microcystis* toxin found in drinking water supplies.

Several human health problems and fatalities from microcystins poisoning have been documented, a toxic incident involving the death of 50 people occurred in Brazil in 1996 (Pouria *et al.* 1998).

Microcystins are problematic since they are chemically stable in water (Jones & Orr 1994; Tsuji *et al.* 1994). The most common method to control cyanobacterial blooms is by dosing with copper based algacides. While this invariably destroys the blue-green cells, it is no longer considered an effective treatment method as it promotes blue-green tolerant species, destroys zooplankton, and releases toxins upon cell lysis (McKnight *et al.* 1983; Jones & Orr 1994). Traditional water treatment methods of coagulation, flocculation, sedimentation and filtration are ineffective at removing dissolved (extracellular) cyanotoxins (Newcombe & Nicholson 2004; Grutzmacher *et al.* 2010; Nishi *et al.* 2012). Microfiltration and ultrafiltration are adequate for removing cyanobacterial cells, but not cyanotoxins. This is due to their large pore size and high

molecular weight cut-off of the membranes (Ribau Teixeira & Rosa 2005; Lee & Walker 2008). Treatment using chlorination and ozonation requires high doses and long contact times, and there is the possibility of generating toxic byproducts such as trihalomethanes (Drikas *et al.* 2001; Shawwa & Smith 2001; Dixon *et al.* 2010). Biological methods typically require a reaction time of hours to days (Saitou *et al.* 2002; Harada *et al.* 2004; Grutzmacher *et al.* 2010) and are thus not viable. Activated carbon (AC) adsorption has been shown to be an effective and low cost technology for drinking water purification in many studies if the application is optimized (Campinas & Rosa 2010). Water treatment studies conducted at the laboratory and pilot plant-scale have concluded that AC filtration is effective in removing the cyanobacterial toxins from drinking water due to the presence of the largest volume of mesopores (Huang *et al.* 2007).

AC removes microcystin-LR efficiently via adsorption (Newcombe *et al.* 2003; Wang *et al.* 2007). Generally, peptides exhibit hydrophobic properties in aqueous media, signifying that the primary interaction between microcystin-LR (m-LR) and an AC is via hydrophobic forces. Simultaneously, during adsorption the polar surface sites on the AC also experience electrostatic interactions with their charged groups of m-LR. Lahti & Hiisvirta (1989) previously reported that small doses of powdered AC do not significantly affect m-LR adsorption in solution, whereas Donati *et al.* (1994) demonstrated the rate and effectiveness of m-LR adsorption by several wood based powdered ACs and presented its removal as a direct proportionality of adsorbent mesopore volume. The previous studies demonstrated that wood based ACs contain both micropores and mesopores, while the coconut and sugar cane bagasse carbons contain micropores only and consequently wood based carbons adsorb more microcystin (Pendleton *et al.* 2001). However, excess loading of natural organic material causes a reduction of the adsorption capacity for microcystins (Lambert *et al.* 1996).

Agricultural byproducts, like sawdust, are generally used as a fuel; however the bulkiness of sawdust and its tendency towards incomplete combustion are its drawbacks as an effective fuel. Adsorption on to low cost adsorbents, such as AC of waste wood material from furniture factories now offers an attractive and inexpensive option for the removal

of m-LR. The abundance and availability of rubber wood sawdust makes it economically feasible.

To date, many studies have been published with respect to the evaluation of AC prepared from different biomass, such as pine wood, sugar cane bagasse and coconut shell for the removal of m-LR (Pendleton *et al.* 2001; Huang *et al.* 2007; Júnior *et al.* 2008). However, no studies have been conducted relating the rubber wood AC adsorption of m-LR. The main objective of this study was to practically explore the adsorption capacity of the AC prepared from the waste wood material of a rubber wood furniture factory towards microcystin-LR. The adsorption capacity of the resulting AC was firstly verified for methylene blue.

This paper deals with the investigation of m-LR removal from aqueous solution by adsorption onto AC produced from waste rubber wood sawdust. The adsorption isotherms, kinetics and its mechanism at different temperatures are discussed.

EXPERIMENTAL PROCEDURE

Materials

The waste wood materials used in this study were collected from a rubber wood furniture factory in Malaysia. All the reagents used were of analytical grade, supplied by Sigma-Aldrich. The m-LR was supplied by Fluka, Switzerland and was used without further purification. The pH of the solution was varied using either hydrochloric acid or sodium hydroxide. All aqueous solutions were prepared using organic molecule free Milli-Q water (18 M Ω resistance).

Adsorbent preparation

The waste wood material is an economically low value product and considered as a possible raw material for the preparation of AC. Waste rubber wood chips were repeatedly washed with deionized water and dried in a hot vacuum oven at 373 K for 24 h. The dried wood chips were crushed and sieved to yield a particle size of 20–25 mesh and then carbonized in a furnace for two hours in a stream of nitrogen gas at 823 K to drive off volatile

compounds and develop a porous structure. The carbon thus produced was crushed to a size of 2 mm and repeatedly washed with organic molecule free Milli-Q water and dried at 378 K for 10 h. The resulting particles were activated by gasification with carbon dioxide at 850 °C for 30, 50, 70 and 90 min to burn-offs 21, 46, 79 and 93%, respectively. The prepared AC samples were distinguished as RWAC21, RWAC46, RWAC79 and RWAC93, where RWAC represented 'rubber wood AC' and the number represented weight loss percent of the prepared rubber wood AC upon activation.

Methylene blue test

The adsorption of methylene blue is usually used to test the adsorption properties of an AC, especially its adsorption capacity. The methylene blue test was performed to determine the adsorption capacities of ACs obtained from waste rubber wood chips through the burning-off procedure. A methylene blue test was conducted in temperature controlled shaker flasks of 100 mL capacity and fixed adsorbent dosage of 0.1 g. Fifty milliliters of methylene blue aqueous solution of concentration in the range of 100–1,000 mg/L were used in a batch equilibrium experiment. The agitation speed of the shaker was fixed at 200 rpm for all batch experiments. The adsorption study of methylene blue was carried out at 298 K for 48 h to obtain the equilibrium (as shown in Figure 1). After equilibrium was reached, the samples were centrifuged and analyzed for their methylene blue content using an ultraviolet (UV) spectrophotometer (Kumar *et al.* 2011). The equilibrium

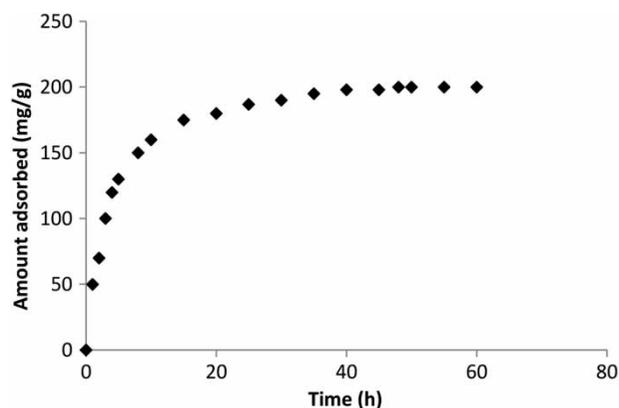


Figure 1 | Effect of contact time on methylene blue adsorption onto RWAC93.

adsorption capacity was calculated using Equation (1), below:

$$q_e = (C_0 - C_e) V/M \quad (1)$$

where q_e (mg/g) is the equilibrium adsorption capacity, C_0 and C_e are the initial and equilibrium concentration (mg/L) of methylene blue in solution, V (L) is the volume and M (g) is the weight of the adsorbent.

Batch adsorption studies

Batch studies were carried out in a temperature-controlled shaker using 10 mL of adsorbate solution and a fixed adsorbent dosage of 10 mg/L, at 200 rpm. Samples were separated at different time intervals (0–300 min) from the adsorbent by centrifugation at 5000 rpm for 5 min. An Agilent 1100 series high performance liquid chromatography system comprising of a quaternary pump, auto sampler was employed for the analysis of the m-LR. The volume of sample injected was 10 μ L at a flow rate of 1.0 mL/min. The mobile phase consisted of 0.1% formic acid (solvent A) and methanol (solvent B) (Sathishkumar *et al.* 2010).

Isotherm studies were conducted at various initial concentrations of m-LR (50–200 μ g/L). Adsorption studies were carried out at different temperatures (303, 313, 323 and 333 K) to obtain the equilibrium isotherms. The equilibrium adsorption capacity was calculated using Equation (1), where q_e (μ g/mg) is the equilibrium adsorption capacity. C_0 and C_e are the initial and equilibrium concentration (μ g/L) of m-LR in solution. V (L) is the volume and M (mg) is the weight of adsorbent.

RESULT AND DISCUSSION

Adsorption of methylene blue

The extent of methylene blue adsorption (a cationic dye) has long been used for the evaluation of adsorption properties of mesoporous AC (Paneth & Radu 1924). The adsorption isotherms for methylene blue onto different percentage burn-off ACs are shown in Figure 2. RWAC93 showed high adsorption capacity of methylene blue which was 620 mg/g.

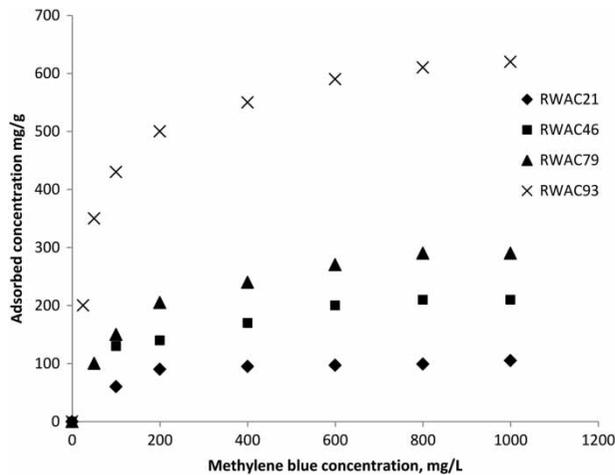


Figure 2 | Adsorption isotherms for methylene blue onto different activated carbon from waste rubber wood at 298 K.

RWAC93 was selected for batch adsorption studies of m-LR because it exhibited the highest surface area which was important for adsorption of large molecules like microcystins. The higher percentage burn-off AC showed higher adsorption of methylene blue, because of removing more volatile compounds from the rubber wood at higher percentage burn-off treatment, which caused the carbon structure to open up giving rise to more surface area. Table 1 summarizes the adsorption capacity of methylene blue onto RWAC93 which was compared with other adsorbents. Warhurst *et al.* (1997) mentioned that the extent of methylene blue adsorption was related to the mesopore volume of a carbon; which revealed the possibility that methylene blue adsorption might have some use in predicting m-LR adsorption, and so could provide a simple method of screening carbons in situations where N_2 adsorption isotherms are unobtainable due to cost or lack of facilities. It was evident that the adsorption capacity for the RWAC93 percentage burn-off AC prepared in this work was better than that of many commercial carbons. Hence RWAC93 percentage burn-off AC can be considered as adsorbent for the removal of microcystins from water sources.

Effect of initial m-LR concentration and contact time

The amount of m-LR adsorbed for different initial concentrations onto RWAC93 is shown in Figure 3. Different initial m-LR concentrations showed a rapid initial uptake

Table 1 | Comparison of adsorption capacities of various ACs for methylene blue

Adsorbents	Adsorption capacity (mg/g)	References
Date pit AC	590	Abdulkarim <i>et al.</i> (2002)
Activated coir pith	294	Namasivayam & Kadirvelu (1999)
Bamboo-based AC	454.20	Hameed <i>et al.</i> (2007)
Straw AC	472.10	Kannan & Sundaram (2001)
Coconut shell AC	277.90	Kannan & Sundaram (2001)
Rice husk AC	343.50	Kannan & Sundaram (2001)
Jute fibre AC	225.64	Tsai <i>et al.</i> (2001)
Hazelnut shell-based	8.8	Aygun <i>et al.</i> (2003)
Oil palm wood-based	90.9	Ahmad <i>et al.</i> (2007)
Oil palm fiber-based	277.78	Tan <i>et al.</i> (2007)
Oil palm shell-based	243.9	Tan <i>et al.</i> (2008)
Cotton stalk AC	180.0	Girgis <i>et al.</i> (2009)
Olive seeds carbon	190–263	Stavropoulos & Zabaniotou (2005)
<i>Posidonia oceanica</i> (L.) dead leaves	270.3	Dural <i>et al.</i> (2011)
<i>Hevea Brasilinesis</i> AC	620.0	This work

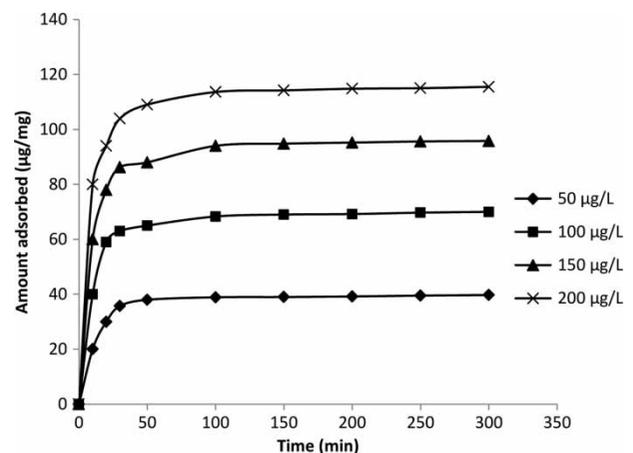


Figure 3 | Effect of initial concentration of m-LR and contact time.

of m-LR, with around 91% removal achieved within 30 min in all the concentrations studied. The adsorption of m-LR onto RWAC93 was found to increase with time and then attained equilibrium after about 300 min. On changing

the initial concentration from 50 to 200 $\mu\text{g/L}$, the amount adsorbed increased from 39.73 to 115.49 $\mu\text{g/mg}$ for a time period of 300 min, whereas the removal efficiency decreased from 94 to 79.8%. Certainly it is not unreasonable to expect that at low concentration, the ratio of available surface to the initial m-LR concentration is larger, so the removal becomes independent of initial concentrations. However, at higher concentrations the available surface area becomes less compared to the moles of adsorbate present. Hence the percentage removal was dependent upon the initial adsorbate concentration (Sathishkumar *et al.* 2008).

Effect of pH

The pH of the system determines the adsorption capacity due to its influence on the surface properties of AC and ionic form of m-LR. Experimental studies were conducted for the range of pH 1–9. Maximum adsorption of m-LR onto RWAC93 was found to occur at pH 2.5 as shown in Figure 4. Because of several scenarios, adsorption of m-LR onto RWAC93 decreases below pH 2.5:

- The pH_{zpc} of RWAC93 as measured in this study was 3.6. The maximum adsorption capacity was observed at pH 2.5. At pH 2.5, m-LR is essentially in anionic form (Maagd *et al.* 1999) and RWAC93 would be carrying cationic charges so there could be a possible ion pairing effect leading to higher adsorption at pH 2.5.
- At pH 2.5, the m-LR molecules may behave as a filament and become smaller in size due to their tendency to coil, which could lead to increased adsorption of m-LR. It is interesting to mention that until pH 7, the adsorption capacity of RWAC93 was high and thus it can be used

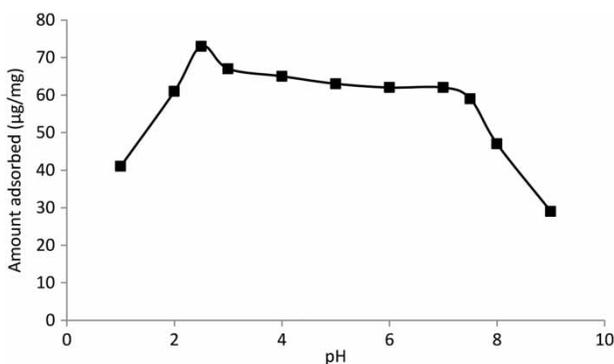


Figure 4 | Effect of pH on adsorption of m-LR.

for m-LR removal without compromising the quality of drinking water. While at high pH (>7), it was found that the structure may become an open net which offers larger dimensions or cross-sectional area.

- At lower pH, m-LR shows lower water solubility and subsequently an increase in m-LR affinity for the AC RWAC93 surface.

Effect of temperature

The adsorption capacity of m-LR onto RWAC93 increased with temperature. The adsorption capacity varies with temperature and initial concentration as shown in Figure 5. With increase in temperature from 293 to 323 K, the adsorption capacity increased from 30.82 to 84.51 $\mu\text{g/mg}$ for the initial concentration of 200 $\mu\text{g/L}$ at pH 2.5. Similar trends were observed for all the other concentrations. Generally, adsorption is an exothermic process. Indeed it is not illogical to anticipate that the adsorption of a relatively hydrophobic m-LR by a hydrophobic RWAC93 from an aqueous solution will be exothermic, but in the present study it was observed that the adsorption process was endothermic in nature. The enhancement in the adsorption capacity with increase of temperature may be due to the following reasons:

- The chemical interaction between adsorbate and adsorbent, created some new adsorption sites.

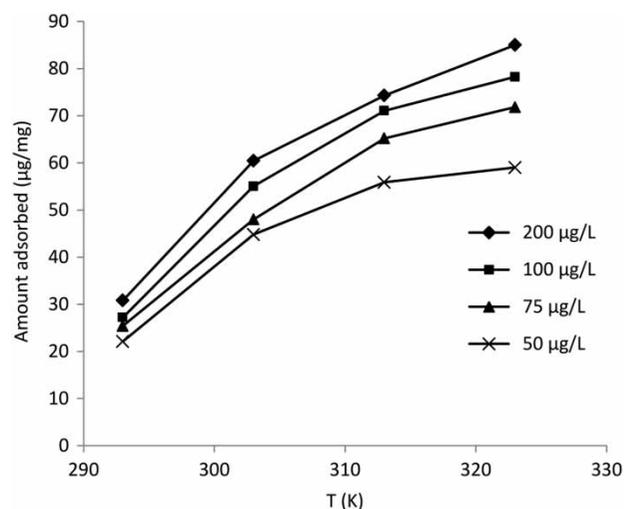


Figure 5 | Effect of temperature on adsorption of m-LR at pH 2.5.

- (b) The rate of intraparticle diffusion of m-LR into the pores of adsorbent increased at higher temperature (Karthikeyan et al. 2005).
- (c) The heat liberated during adsorption of m-LR was insufficient to compensate for the heat required to displace the solvent (aqueous) (Pendleton et al. 2001).

The standard Gibb's energy was evaluated by Equation (2):

$$\Delta G = -RT \ln K_C \quad (2)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature and K_C is the equilibrium constant. The thermodynamic parameters, such as change in standard enthalpy (ΔH°) and standard entropy (ΔS°) from 303 to 333 K were determined using Equation (3):

$$\ln K_C = \Delta S^\circ / R - \Delta H^\circ / RT \quad (3)$$

ΔH° and ΔS° were obtained from the slope and intercept of the plot of $\ln K_C$ versus $1/T$ as shown in Figure 6. The positive value of ΔH° indicates that the adsorption process was endothermic. The negative values of ΔG° reflect the feasibility of the process and spontaneous nature of the adsorption; moreover the values of ΔG° become more negative with increase in temperature. Table 2 summarizes the results.

Adsorption kinetics

The kinetics of adsorption described the rate of uptake of m-LR onto the RWAC93 and this rate controlled the

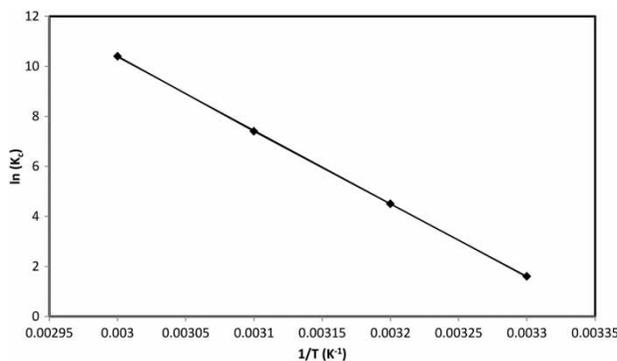


Figure 6 | Plot of $\ln K_C$ vs $1/T$ for m-LR adsorption onto RWAC93.

Table 2 | Values of thermodynamic parameters for m-LR adsorption onto RAC93

Temperature (K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹)	R^2
303	-4.030	29.333	110.10	0.998
313	-11.710			
323	-19.456			
333	-28.516			

equilibrium time. The mechanisms of adsorption depend on the physical and chemical characteristics of the adsorbent RWAC93. This study revealed that 85–90% of the adsorption takes place within the first 30 min of contact. The amount of m-LR removed in the first 30 min of contact increased with the concentration of the m-LR. To analyze the adsorption rate of m-LR onto RWAC93, the pseudo first order Equation (4) (Ho & McKay 1999) and pseudo second order models Equation (5) (Ho et al. 2000) were evaluated based on the experimental data.

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (4)$$

where q_e ($\mu\text{g}/\text{mg}$) is the equilibrium concentration of m-LR in solution, q_t ($\mu\text{g}/\text{mg}$) represents residual concentration and k_1 (min^{-1}) is the first order rate constant. In Table 3 the R^2 values show that the adsorption of m-LR onto RWAC93 did not follow first order kinetics. The kinetic data were further analyzed using the pseudo second order model, which can be expressed as

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (5)$$

where k_2 ($\text{mg}/\mu\text{g min}$) is the second order rate constant. The calculated q_e values agree very well with experimental values and a regression coefficient of above 0.99 confirms that the adsorption phenomena followed second order kinetics.

Generally, the intraparticle diffusion model is of major concern because it is a rate-determining step in the liquid adsorption systems, which control the adsorption kinetics (Guibal et al. 2003). The intraparticle diffusion varies with square root of time given by Weber & Morris (1963) as Equation (6):

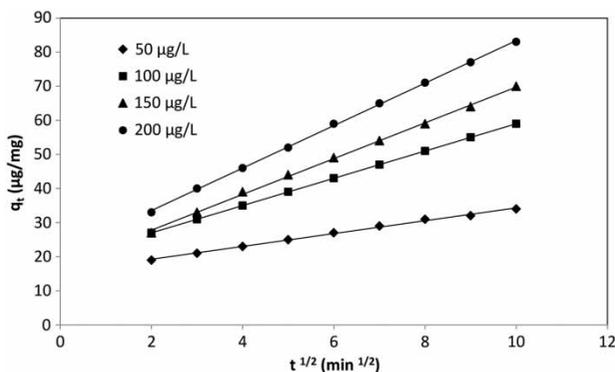
$$q_t = k_{id} t^{1/2} \quad (6)$$

Table 3 | Kinetic models for the adsorption of m-LR onto RAC93

Initial concentration C_0 ($\mu\text{g/L}$)	q_e (exp) ($\mu\text{g/mg}$)	Pseudo first order			Pseudo second order			Intraparticle diffusion	
		$k_1 \times 10^{-3}$ (min^{-1})	q_e (cal) ($\mu\text{g/mg}$)	R^2	$k_2 \times 10^{-3}$ ($\text{mg}/\mu\text{g min}$)	q_e (cal) ($\mu\text{g/mg}$)	R^2	k_{id}	R^2
50	34.85	16.18	19.47	0.863	9.684	34.61	0.9995	1.87	0.995
100	57.38	15.59	21.43	0.859	10.896	57.28	0.9993	4.00	0.998
150	69.85	12.32	28.73	0.924	11.945	68.01	0.9998	5.37	0.994
200	78.69	11.16	35.89	0.850	12.342	78.51	0.9996	6.25	0.989

where q_t is the amount adsorbed at a time ($\mu\text{g/mg}$), t is the time (min), k_{id} ($\mu\text{g/mg min}^{0.5}$) is the rate constant of intraparticle diffusion, which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$. If the regression of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. In our study although the regression was linear, the plot did not pass through the origin (Figure 7) thereby suggesting that intraparticle diffusion was related to the adsorption but not as a sole rate-controlling step. It was obvious from the figure that it can be distinguished into three stages for the adsorption of m-LR onto RWAC93:

- The first stage was an instantaneous adsorption which happened due to a strong electrostatic attraction between m-LR and the external surface of RWAC93.
- The second stage was a gradual adsorption stage, which can be attributed to intraparticle diffusion of m-LR molecules through the pores of the adsorbent RWAC93.

**Figure 7** | Intraparticle diffusion plot for different initial m-LR concentration.

- The final stage corresponds to the equilibrium adsorption when m-LR molecules occupy all active or possible sites of the adsorbent RWAC93.

The structure formula calculation of Lanaras et al. (1991) suggested that m-LR has dimensions ranging from 1.1 to 1.9 nm. Obviously such molecular dimensions cannot fit into micropores, during intraparticle diffusion, but it was concluded that the components of m-LR should (energetically) orient themselves to adsorb in the micropores (Pendleton et al. 2001).

Adsorption isotherms

Adsorption equilibrium data were fitted to the Langmuir and Freundlich isotherms at various temperatures, to quantify the adsorption capacity of RWAC93 for the removal of m-LR from aqueous solution. The Langmuir adsorption isotherm demonstrates surface homogeneity of the adsorbent and illustrates that the surface of the adsorbent possesses energetically equivalent small adsorption areas in terms of adsorption phenomenon. The Langmuir isotherm is based on the monolayer adsorption processes. The data of the equilibrium studies for adsorption of m-LR onto the surface of carbon sites of RWAC93 were expressed in the linear form as Equation (7) (Langmuir 1918):

$$C_e/q_e = 1/Q^0 b + C_e/Q^0 \quad (7)$$

where C_e is the equilibrium concentration ($\mu\text{g/L}$) and q_e the amount adsorbed at equilibrium ($\mu\text{g/mg}$). The Langmuir constant Q^0 ($\mu\text{g/mg}$) represents the monolayer adsorption capacity and b ($\text{L}/\mu\text{g}$) relates to the heat of adsorption.

The Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as Equation (8) (Freundlich 1907):

$$\ln q_e = \ln K_f + b_f \ln C_e \quad (8)$$

where K_f is the Freundlich adsorption capacity ($\mu\text{g}/\text{mg}$) and b_f is an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. The greater the values of b_f , the better is the favorability of adsorption.

From Table 4 it was observed that the Langmuir monolayer adsorption isotherm model yielded best fit as indicated by the highest regression coefficient values at all temperatures compared to the other model. The increase in the

Langmuir constant b with temperature confirms the endothermic nature of adsorption and the Freundlich constant b_f shows the favorability of adsorption at higher temperatures.

Desorption studies

For performing desorption studies, the exhausted 0.1 g of RWAC93 was treated with 2.0 M NaOH solution for regeneration. It was found that ~97.8% of the sorbed m-LR was recovered. Table 5 reveals that the introduced adsorbent can be used frequently, two to three times, without any significant reduction in sorption capacity.

Comparison of RWAC93 with other adsorbents for m-LR

The adsorption capacity of m-LR onto RWAC93 was compared with other adsorbents reported in literature and is given in Table 5. It was observed that m-LR can be removed with a wide range of pH (2.5–8.5). Further it can also be seen that the AC produced from waste rubber wood sawdust exhibited the highest adsorption capacity of 296.57 ($\mu\text{g}/\text{mg}$) and that could be due to the fact that more volatile compounds were released from the rubber wood sawdust at higher burn-off

Table 4 | Adsorption isotherms of RAC93 at different temperatures

T (K)	Langmuir adsorption isotherm constants			Freundlich adsorption isotherm constants		
	Q^0 ($\mu\text{g}/\text{mg}$)	b (L/ μg)	R^2	K_f ($\mu\text{g}/\text{mg}$)	b_f	R^2
303	296.57	0.231	0.9998	18.24	0.117	0.9750
313	302.81	0.258	0.9991	23.51	0.138	0.9586
323	317.78	0.281	0.9997	25.72	0.166	0.9234

Table 5 | Comparison of adsorption capacities of m-LR with other ACs

Adsorbents	Adsorption capacity	Contact time	pH	Model	Reference
Darco, G-60, wood PAC	1,259 $\mu\text{g}/\text{g}$	7 days	8.5	Freundlich	Mohamed et al. (1999)
Pine Wood AC	200 $\mu\text{g}/\text{mg}$	10 min	6–8.5	Langmuir	Júnior et al. (2008)
Sugar cane bagasse AC	161 $\mu\text{g}/\text{mg}$	10 min	6–8.5	Langmuir	Júnior et al. (2008)
Wood-based AC	196 $\mu\text{g}/\text{mg}$	72 h	2.5	Langmuir	Pendleton et al. (2001)
Coconut shell AC G1	16.1 mg/g	24 h	7.5	Langmuir	Huang et al. (2007)
Wood-based AC G3	83.3 mg/g	24 h	7.5	Langmuir	Huang et al. (2007)
Wood AC	220 $\mu\text{g}/\text{mg}$	–	–	Langmuir	Donati et al. (1994)
Peat	255.7 $\mu\text{g}/\text{g}$	30 min	3.0	Langmuir	Sathishkumar et al. (2010)
Pumice	21.5 $\mu\text{g}/\text{g}$	–	4.0	–	Gurbuz & Codd (2008)
Waste rubber wood AC first adsorption	296.57 $\mu\text{g}/\text{mg}$	300 min	2.5	Langmuir	Present study
Waste rubber wood activated carbon second adsorption	262.71 $\mu\text{g}/\text{mg}$				
Waste rubber wood activated carbon third adsorption	220.56 $\mu\text{g}/\text{mg}$				

treatment, which leads in turn to opening up the carbon structure. Hence, RWAC93 can be considered to be a viable adsorbent for the removal of m-LR from aqueous media.

CONCLUSION

It was found that rubber wood sawdust, an agricultural waste byproduct, converted into an activated carbonaceous adsorbent can be effectively employed for removal of m-LR from aqueous solutions. Adsorption of m-LR was found to be effective in the lower pH range and at higher temperatures and subsequent desorption was readily achieved upon alkaline treatment of the adsorbent. An increase in adsorption capacity with rise in temperature revealed that the adsorption was endothermic, which was confirmed by the evaluated thermodynamic parameters. The Langmuir isotherm fits the data better than the Freundlich isotherms.

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