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Investigation of adsorption performance of activated carbon prepared from waste tire for the removal of methylene blue dye from wastewater

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ABSTRACT

Disposal of exhausted waste rubber tires discarded from vehicles is a serious environmental problem. Their storage requires large amount of space and can cause fire hazard. Burning of these tires produces toxic gases, which impose severe health hazards. In this study, tire activated carbon, obtained by the pyrolysis of waste tire, is used for the removal of Methylene blue dye from its aqueous solutions through adsorption process. The morphology and other characteristics of the tire activated carbon have been analyzed using scanning electron microscope, energy dispersive X-ray analyzer and Brunauer–Emmett–Teller surface area analyzer. The results show that at ambient temperature, the maximum adsorption of dye onto tire activated carbon has been achieved at pH 3, 4 g of adsorbent and contact time of 90 min. The adsorption isotherms and kinetics of dye with tire activated carbon were also investigated. Pseudo-second-order kinetic model and Langmuir isotherm have been found suitable for the adsorption of Methylene blue dye over tire activated carbon. The obtained results demonstrate that waste tires can work as potential adsorbent for the removal of Methylene blue dye from wastewater.

Keywords: Activated carbon; Adsorption; Tire; Methylene blue; Kinetics; Isotherm

1. Introduction

Dyes are extensively used in textile, paper and printing industries etc., and are one of the major hazardous chemical constituents of the effluents discharged from these industries. These colored effluents not only obstacle light permeation and disturb the aquatic ecosystem but also exhibit toxicity towards living organisms.

Methylene blue (MB) is a cationic dye that has wide range of uses in chemistry, biology, medical, laboratory and industries [1]. Recent studies have established that long-term exposure of MB creates risk factors on the humans, which include vomiting, nausea, anemia and hypertension [2]. In recent years, various techniques have been developed for the removal of MB from water and wastewater. These techniques include adsorption, biosorption, coagulation/flocculation, advanced oxidation, ozonation, membrane filtration, etc. [3,4]. However, it is now well established that among all these techniques adsorption is the most efficient, economic and versatile technique for the removal of dyes from water and wastewater. Activated carbon (AC) is used in adsorption of pollutants in water or wastewater treatment but one of the disadvantages of AC is relatively high capital cost. In the past one decade, the global research in this area is focused to invent new and financially viable adsorbents, and in this hunt various waste materials have been prepared to replace AC [5], which is expensive and requires skilful reactivation and modification processes. Some interesting waste materials, which have been investigated as adsorbents are hen feather [6], banana pith [7], rice husk [8], wood [9], etc.

Also, waste rubber tire has been used for the removal of organic compounds [10], heavy metals [11] and pesticides [12] from wastewater.

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Studies showed that worldwide annual production of scrap tires is about 1,000 million [13,14]. It is now well known that tires are mixture of polymers such as natural rubber, butadiene rubber and styrene butadiene rubber, carbon black, sulphur and zinc oxide [15]. Majority of the tires consist of carbon black [13] and this carbonaceous adsorbent acts similar to AC. The waste tires pose considerable risk to public health and environment and along with fire hazards, they provide good living conditions for mosquitoes, insects, rats, etc. Moreover, storage of waste tires requires large amount of space and disposal of these tires is a costly affair [12]. Therefore, use of waste tire as potential adsorbent for the removal of MB from aqueous solution is a thoughtful attempt. Then, the objective of this study was to use waste tire as sorbent for removing MB and for recycling a waste material.

2. Materials and methods

Present study explores the competence of adsorbent tire activated carbon (TAC) obtained from scrap tires of cars to remove a water soluble dye MB. The dye in work was of analytical grade and its stock solutions were prepared by dissolving 1 g of dye in 1 L. Solutions of different concentrations, required in the analysis, were set by diluting dye stock solution using double distilled water.

To prepare the TAC, tires were crushed into small pieces (about 1 cm^2). These tire pieces were first washed by tap water and then rinsed several times in double distilled water. Washed tire pieces were now dried at 100°C for 2 h. For carbonization, the dried tires were pyrolyzed at 800°C for 3 h and at a pressure of 1 atm. Then for the activation of sample, carbon–zinc chloride mixture in the ratio, 20 g of carbon and 40 mL of $ZnCl_2$, was added and obtained material was dried in an oven at 100°C for 12 h. In the next step, sample was heated in an electric furnace under a nitrogen flow of 200 mL/min and a heating rate of 450°C/min. Finally, adsorbent (TAC) thus formed was sieved to 20 BSS mesh size and stored in a desiccator until used [12,13].

The pH of each testing solution was measured using microprocessor based pH meter, and absorbance data was collected by employing UV/Vis Spectrophotometer DR5000 over the wavelength range 400–600 nm. Quartz cuvettes of path length 10 mm were used for testing solutions. The characterization of the adsorbents was carried out using standard procedures by employing scanning electron microscope (SEM), energy dispersive X-ray (EDX) analyzer, surface area analyzer and mercury porosimeter. Elemental analyzer was employed to detect key elements of the TAC.

All adsorption studies were carried out in batches using adsorbent TAC. Stock solution of MB was prepared by dissolving 1 g of dye in 1 L double distilled water and dye solutions in the concentration range of 50–100 mg/L were prepared by dissolving the stock solution in distilled water. A series of 100 mL graduated volumetric flasks containing 25 mL of dye solution at different concentrations were employed at desired pH. Adjustment of pHs of the solution was made by NaOH and HCl. A predetermined amount of adsorbent of a particular particle size was added into each flask separately and was mechanically agitated. After shaking and keeping the solutions for most favorable time, the solutions were filtered and the uptake of the dye was monitored spectrophotometrically by measuring absorbance at λ_{max} 665 nm. The difference in the absorbance before and after addition of adsorbents suggests the amount of dye uptaken. For examining the adsorption kinetics, a series of 25 mL solution of dye of predetermined concentration and a known amount of adsorbent were taken in a stoppered 100 mL conical flask. The mixture flasks were kept in a water bath, at a desired temperature and were agitated mechanically followed by procedure described above. Studies were also conducted for various time intervals to determine the time at which the adsorption equilibrium was reached and the maximum removal of dye was attained. The amount of dye adsorbed at equilibrium, q_e, was calculated from the mass balance equation given by [16,17]:

$$q_e = \frac{V(C_o - C_e)}{m} \quad (1)$$

where C_o is the initial dye concentration in liquid phase (mol L^{-1}); C_e is the liquid phase dye concentration at equilibrium (mol L^{-1}); V is the volume of dye solution (L) and m is the mass of adsorbent (g).

3. Results and discussion

3.1. Characterization of adsorbent material

Since adsorption process is a surface phenomenon, recognition of morphology, composition and surface characteristics of the adsorbent is highly desirable. Through SEM micrographs, morphology and porous surface of the TAC were observed. Fig. 1 presents surface images of the TAC at different magnification levels. It can be easily

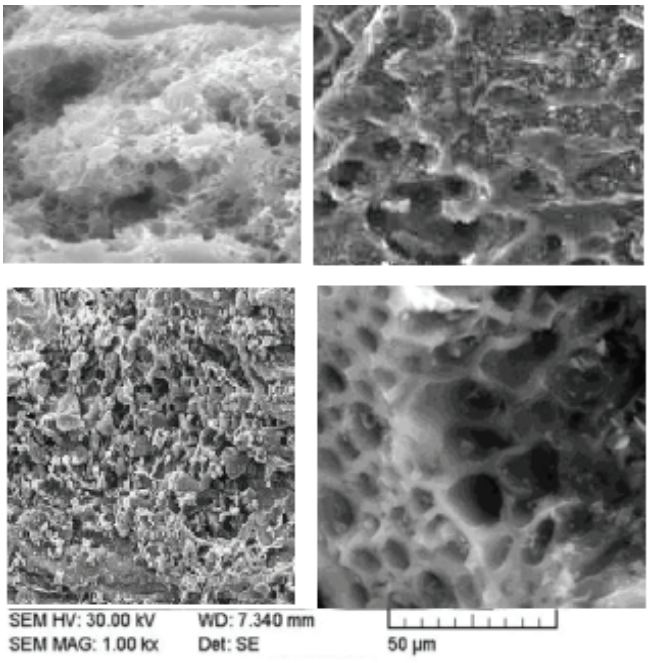

Fig. 1. SEM micrographs of the tire activated carbon.

observed that in all the images TAC texture is quite porous and homogeneous. The pores of TAC observed in these images are having diameter in micrometer range. On the basis of this fact, it can be inferred that TAC possesses adequate morphology and has a compact structure [5,18]. The specific surface area of TAC was found up to 396 m^2/g and the total pore and micropore volume were 0.59 and 0.28 cm^3/g, respectively.

The elemental analysis was carried out by using EDX and its results are presented in Table 1. The analysis using EDX analyzer clearly shows that TAC consists of carbon, oxygen, hydrogen, nitrogen and sulphur, out of which carbon is the most dominant element.

3.2. Effect of pH

The effect of pH in the removal of the MB was studied over a pH range of 1–11 (Fig. 2). The results show that the amount of dye removed by TAC increased as the pH increases from 1 to 3 and afterwards it decreases till pH 11. Therefore, optimum pH of 3 was selected for further studies.

This higher adsorption at acidic pH is due to pH effect on the surface charge of the dye and its greater accessibility to the active surface areas of TAC. In the lower pH range, the higher adsorption may be due to increased protonation by neutralization of the negative charge at the surface of the adsorbents. The preference of the dye for active sites facilitates the diffusion process in the working solution [6,13]. While, with increase in alkaline conditions or pH, protonation reduces and electrostatic repulsive force becomes operative, which thereby retards diffusion and adsorption [19].

3.3. Effect of contact time and concentration

The rate of dye removal in different contact time and with different dye concentrations was also studied and presented in Fig. 3. Results explain that initially in the first 60 min the adsorption process is rapid and after this time until about 90 min, only an imperceptible increase of dye uptake is observed, which continues till 120 min. Thus it can be interpreted that under these conditions the adsorption has attained equilibrium. The high dye removal efficiency is due to increase in number of active sites and surface functional groups. As the time passes, these activated groups on the TAC surface are filled up with dye ions and therefore adsorption attains saturation.

Fig. 3 also exhibits that with the increase in initial dye concentration from 50 to 100 ppm dye uptake increases. Increase in concentration of the dye decreases the resistance towards the dye uptake, which increases the mass driving force among adsorbent and adsorbate thereby enhancing the percentage adsorption of the dye [20,21].

3.4. Effect of adsorbent dose

The effect of dosage of adsorbent on the MB removal was studied at different concentrations of the dye. It is found that with the increase in the adsorbent amount (0.5–6 g) efficiency of the dye removal increases significantly (Fig. 4). The results show that already 4 g of TAC leads to 90% dye removal. It is also interesting to note that the time required to reach equilibrium decreased at higher dosages of TAC. This initial rise in removal with adsorbent amount is probably due to a stronger driving force and increase in the available surface sites [20,22,23].

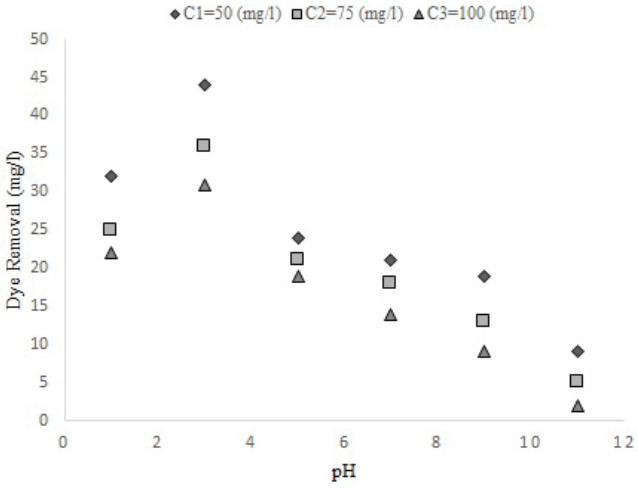

Fig. 2. Effect of pH on the removal of dye by TAC at 20°C.

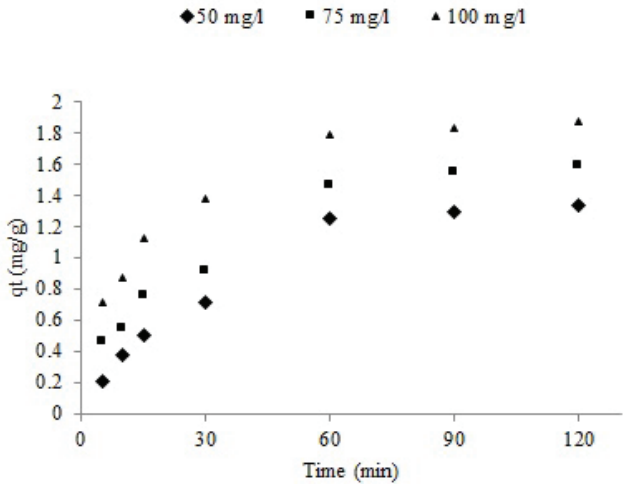

Fig. 3. Adsorbed concentration vs. adsorption time for dye removal by TAC.

Table 1
Elemental analysis in tire activated carbon

Element Tyre	Ash	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen
Weight (%)	11.18	82.50	4.02	0.29	1.94	0.08

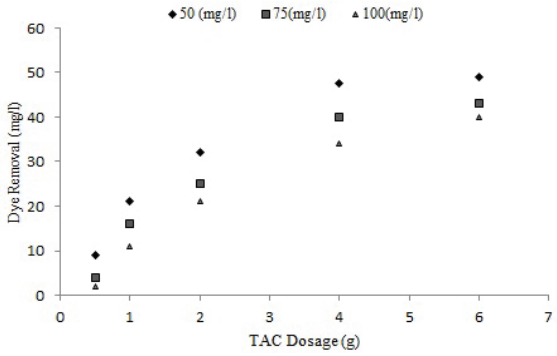

Fig. 4. Effect of sorbent mass on the dye removal by TAC.

3.5. Adsorption isotherms and kinetic studies

Adsorption isotherm experiments were conducted with different dye concentrations of dye at 25°C. In the present study, the following linear forms of Freundlich (Eq. (2)) and Langmuir (Eq. (3)) adsorption isotherms [17] are applied:

$$q_e = \log K_F + 1/n \log C_e \tag{2}$$

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bq_eQ_0} \tag{3}$$

where q_e is the amount of adsorbate in soil phase (mg/g), C_e is the equilibrium concentration of adsorbate in liquid phase (mg/L), K_F (mg/g)(L/mg)$^{1/n}$ and $1/n$ are the Freundlich constants. q_m is the maximum adsorption capacity (mg/g) and b (L/mg) is the Langmuir constant.

Data collected from the dye removal were analyzed through Langmuir and Freundlich adsorption isotherm models and presented in Figs. 5 and 6, respectively. It is clear from Fig. 5 that plot of C_e vs. C_e/q_e gives a straight line with regression coefficient (R^2) close to 1, indicating thereby verification of Langmuir adsorption isotherm for the adsorption of MB over TAC. Similarly plot of logC_e vs. logq_e also gives a straight line with regression coefficient (R^2) close to 1 (Fig. 6), verifying the involvement of Freundlich adsorption isotherm model in the ongoing adsorption process. These results suggest that the adsorption of MB on TAC involves monolayer coating of the dye on the surface of the synthesized adsorbent [24]. Calculated values of Freundlich and Langmuir constants are presented in Table 2.

In order to verify valid adsorption system, there are several kinetic models such as pseudo-first-order, pseudo-second-order, etc. [25]. These models are one of the important characteristics in explaining the rate of adsorption onto the adsorbent surface. The following linear forms of pseudo-first-order (Eq. (4)) and pseudo-second-order kinetic models (Eq. (5)) are used to investigate the mechanism and the rate of dye adsorption process:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

$$t/q = 1/k_2 q_e^2 + 1/q_e\, t \tag{5}$$

The values of q_e and q_t are the amount adsorbed at equilibrium and at any time t, respectively; the value of

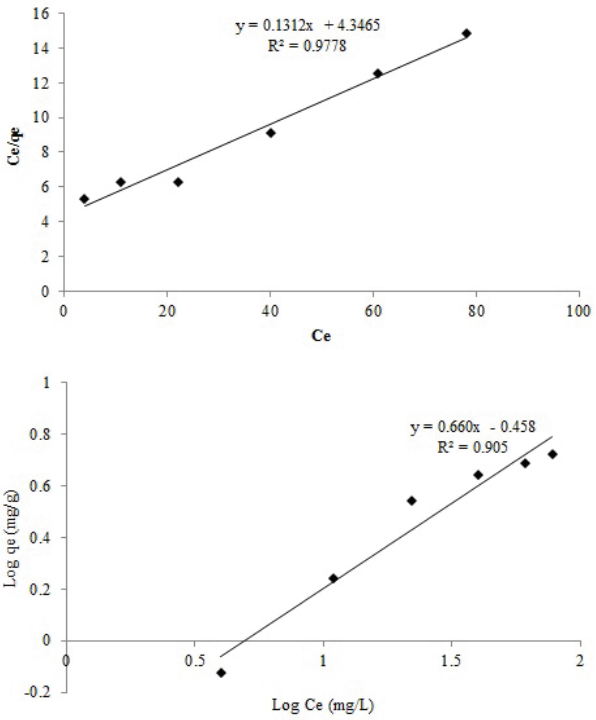

Fig. 5. Freundlich and Langmuir adsorption isotherms for the dye removal.

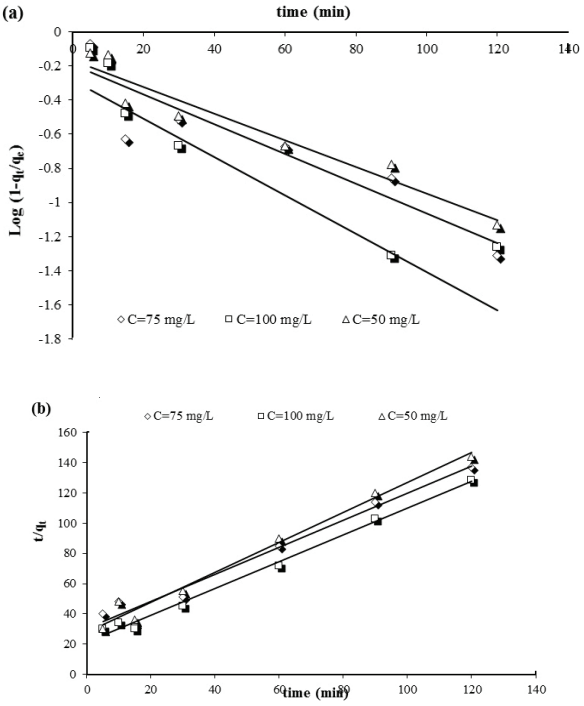

Fig. 6. Plots for kinetic models for the adsorption of Methylene blue onto TAC.

k_1 shows the pseudo-first-order rate constant. The value of constants q_e and k_2 can be described from the slope and intercept of the plot t/q_e and t, respectively [25].

Table 2
Calculated values of Freundlich and Langmuir constants for dye adsorption over TAC

Langmuir isotherm constant			Freundlich isotherm constant		
R^2	q_m (mg/g)	b (L/mg)	R^2	K_F (mg/g)	n (mg/L)
0.977	1.05	0. 2	0.905	2.568	1.278

Table 3
Values of R^2, rate constants and equilibrium concentrations obtained for pseudo-first-order and pseudo-second-order kinetic models at different concentrations of dye

Initial dye concentration	Pseudo-first-order			Pseudo-second-order		
	R^2	q_e	k_1	R^2	q_e	k_2
50 (mg/L)	0.92	0.52	0.02	0.99	0.58	0.1
75 (mg/L)	0.85	0.675	0.05	0.98	0.58	0.02
100 (mg/L)	0.65	0.85	0.02	0.99	0.65	0.05

To ascertain the adsorption mechanism, kinetic models were tested using the pseudo-first-order and pseudo-second-order equations. The parameters of kinetic models and the regression coefficients (R^2) for all of the concentrations are listed in Table 3. The R^2 value for the pseudo-second-order model is higher (>0.98) than pseudo-first-order (<0.93). Thus, this model is suitable for description of dye sorption for TAC and confirms the applicability of pseudo-second-order kinetics in the present case [26].

4. Conclusion

In this research, waste tires were used as initial compound in procurement of an adsorbent using pyrolysis method at 800°C. The synthesized adsorbent characteristics were investigated by using SEM, EDX analyzer and BET surface area analyzer. The experiments were carried out in batch conditions. The results indicate that removal of MB by TAC is dependent on the pH and dosage, and maximum dye removal efficiency can be achieved at pH 3, and 4 g TAC. Results of batch experiments indicate that TAC can more effectively remove MB from its aqueous solutions. Because of the relatively quick absorption, low cost and convenience to obtain, waste tyres can be used for the removal of MB from wastewater.

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