PREPARATION OF ACTIVATED CHARCOAL ADSORBENT FROM WASTE TIRE

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Abstract: Activated carbons were prepared from waste tire in two different routes. Some physical properties of thus prepared activated carbons were measured and the characterization of their phases was done by XRD measurement. The adsorption isotherms of methylene blue were simulated by the Langmuir and Freundlich isotherms. The Langmuir isotherms were found to have better fitting with Q_{max} values 0.227, 0.255 and 0.256 mmol/g for the activated carbons prepared in air, nitrogen, nitrogen and steam respectively while it was 0.275 mmol/g for activated carbon impregnated with H_3PO_4. The overall reaction was found to be pseudo-second order with the rate constant of 8.314×10^{-4} Lg/(mmolmin). The surface area of the best prepared activated carbon was 334.2 m^2/g.

Keywords: Waste tire; Activated carbon; Methylene blue; Adsorption isotherms; Kinetics of adsorption

INTRODUCTION

Waste tires have been a disposal problem in the past and are continuing to accumulate throughout the world today. Europe, the USA and Japan together generate more than 5×10^6 tonnes of scrap tires a year [1]. Other world communities like South East Asia have also recorded a rapid growth in automobile ownership and, as a consequence, have increased scrap tire generation. Such a rapidly increasing trend and the fact that the majority of these tires are stockpiled in landfills present one of our most potentially hazardous material disposal problems of today. The disposal of tires represents a major environmental issue throughout the world, since the same properties that make them desirable as tires, most notably durability, also make their disposal and reprocessing difficult, they are almost immune to biological degradation [2]. Moreover, waste tire stockpiles constitute environmental and health hazards by producing air pollution from tire stockpile fires and breeding grounds for potential disease carrying mosquitoes and vermin.

Once the used tires are not in condition for further use they are difficult to cut up, hard to store or transport and of little value to anyone. To reduce the negative environmental impacts, such as those caused by disposal of scrap tires (a non-biodegradable waste) in landfills or by incineration, constituent chemicals and energy content can be recovered by a number of available technologies. One of the established process method is pyrolysis which involves the decomposition of organic wastes at high temperatures in an inert atmosphere or under vacuum. This process presents an alternative to scrap tire disposal in landfill sites and can result in the recovery of useful products in an environmentally friendly manner. The products recovered by a typical pyrolysis process are usually, 33–38 wt. % pyrolytic char, 38–55 wt. % oil and 10–30 wt. % gas fraction [3]. The pyrolytic oil contains many valuable hydrocarbons and, therefore, can be used as a source of chemical feedstock such as limonene, benzene, toluene, xylene, etc [4]. Pyrolysis gases consist primarily of hydrogen, carbon dioxide, carbon monoxide, ethane, butadiene and other hydrocarbon gases such as propane, propene, butane, etc. The pyrolytic char can be utilised for synthesis of activated carbon and thereby adsorption of phenols, basic dyes and metals[5, 6]; phenols and p-chlorophenols[7]; butane[8] and natural gas[9].

The most successful attempts to produce high quality adsorbent carbons from waste tires use a two-step process consisting of pyrolysis and activation. Two types of activation, thermal/physical and chemical activation are in practise for activation of waste tires. The basic differences between physical and chemical activation is the number of stages required for activation and the activation temperature. Chemical activation occurs in one step while physical activation employs two steps, carbonization and activation. Moreover, chemical activation temperatures (200-800°C) are lower than those of physical activation (800-1000°C). The purpose of this study was to prepare activated carbons from waste tire by using physical as well as chemical activation

techniques for application in adsorption of methylene blue.

EXPERIMENTAL METHODS

Sample Preparation and Characterisation

Pieces of waste automobile tire were collected from a workshop in Kirtipur, Kathmandu, Nepal. These pieces were washed, dried, divided into small chunks, then crushed to fine dustand sieved. The fine tire dust was then subjected to pyrolysis in four different atmospheres: (1) Pyrolysis in open air (**Type I**), (2) Pyrolysis in inert atmosphere (passage of Nitrogen gas) under constant bubbling of nitrogen gas (**Type II**), (3) Pyrolysis in inert atmosphere along with steam (Nitrogen gas through water-steam generated at 60°C)(**Type III**), (4) Chemical impregnation with H_3PO_4 prior to pyrolysis in inert atmosphere along with N_2-water-steam (**Type IV**). Thus prepared activated carbon were then weighed and kept in tight impermeable plastic bags separately. As for the characterization, the densities of the sample were determined with the help of mass to volume ratio. The phase analysis of the samples was done by analysing respective diffractograms obtained from X- Ray Diffractometer (Bruker axs Company, Germany).

Adsorption Study

Commercial methylene blue (obtained from BDH, England) was used to prepare 500 mg/L stock solution by dissolving accurately weighed dye in distilled water. The various concentration range of methylene blue solutions were obtained by diluting the dye stock solution in accurate proportions to initial concentration. The maximum absorption at wavelength and calibration curve of absorbance as a function of initial concentration of aqueous methylene blue solutions were obtained using spectrophotometer (WPA Linton Cambridge UK Spectrophotometer, Type S104 No. 385).

10 mg of activated carbon was added to 25 mL of varying concentrations of methylene blue solution (15- 100 mg/L). The solutions were kept in shaker for four continuous hours. After shaking the mixture, the supernatant solution was separated and washed. The absorption was measured by spectrophotometer at l_{max} and then the concentrations were calculated with the help of calibration curve. The uptake amount (mmol/g) was calculated using the following formula:

$$\text{Uptake (mmol/g)} = \frac{(C_i - C_{eq})}{W} \times V \qquad \text{... (i)}$$

Where, C_i and C_{eq} are initial and equilibrium concentrations (mmol/L), respectively. V and W are volume of the solution (L) and mass of the sample (g), respectively.

RESULTS AND DISCUSSIONS

Characterisation of the Activated Charcoal

All the char obtained were smelly and dark black in appearance. In going from type I to type IV, the mass loss percentage during the carbonisation process was found increasing from 20.93% to 42.50% while the density was found decreased from 1.13 to 1.02 g/ml. This decrease in density is attributed to the increase in the surface area of the sample as density is inversely proportional to the specific volume. The increase in surface area from type I to type IV is attributed to the gradual increase in the number of pores. The specific surface area was calculated by the following equation:

$$S_{MB} = \frac{N_g \times a_{MB} \times N \times 10^{-20}}{M} \qquad \cdots \text{(ii)}$$

Where, S_{MB} is the specific surface area in 10^{-3} km^2 kg^{-1}, N_g is the number of molecules of methylene blue adsorbed at the monolayer of AC in kg kg^{-1} (or $N_g = Nm*M$), a_{MB} is the occupied surface area of one molecule of methylene blue[10] =197.2 Å^2, N is Avogadro's number (6.023 x 10^{23}), M is the molecular weight of methylene blue, (373.9 g mol^{-1} which corresponds to methylene blue hydrochloride with three groups of water[11]) and N_g/M gives mmol/g which is equivalent to the Q_{max} of Langmuir equation[11]. The specific surface area was increased from 284 to 334 m^2/g during the process of obtaining activated carbon from type I to IV.

Phase Analysis

X-ray diffraction weak peaks were observed at 2q = 26.6° and 47.46 for silica (SiO_2) and activated carbon. The presence of silica is expected to be due to the addition as filler in tire manufacturing process and the activated carbon appeared after pyrolysis process. The broad hump appeared in the range of 2q = 20-30° indicated that all the samples are almost amorphous in nature with having relatively high specific surface area in comparison to the previous work [11]. The XRD patterns of all the four types of activated charcoal are shown in the Fig. 1.

Adsorption Isotherms

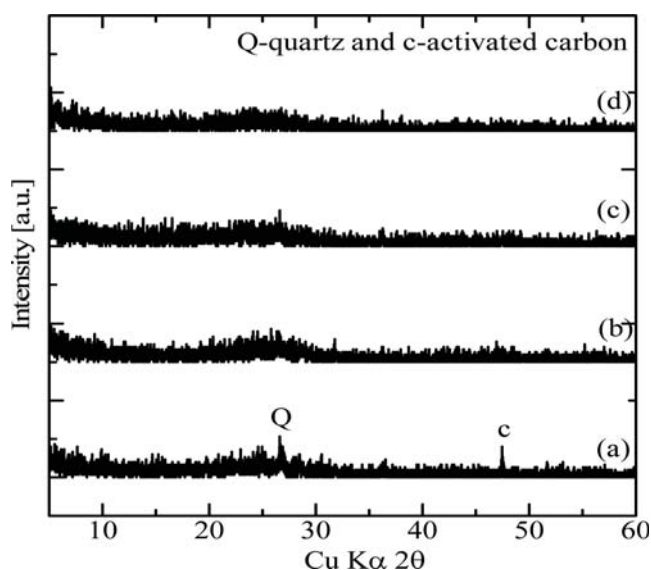The wavelength corresponding to maximum absorbance was observed at 660 nm in all concentrations which is also in

Fig-1: **XRD patterns of activated carbons obtained from activation of waste tire.**
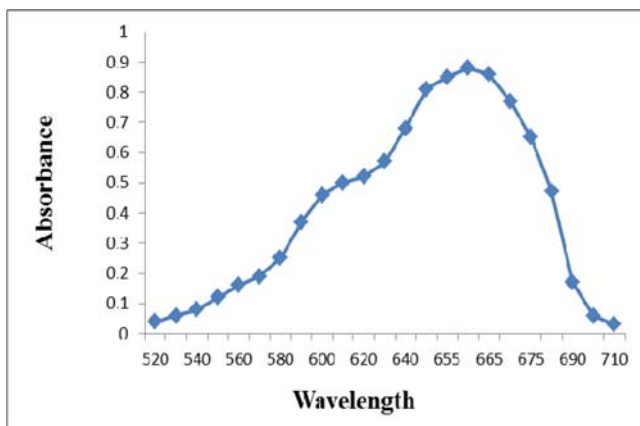
Fig-2: The plot for the determination of the l_{max} of methylene blue.

Fig-3: Calibration curve for methylene blue.

trend with previous report[13]. Hence, this wavelength was used to obtain the calibration curve of absorbance as a function of methylene blue concentration. The straight line passing through origin of the calibration curve indicated the validity of Beer Lambert's law in the concentration range of 2 mg/L to 12 mg/L. The data for the adsorption isotherms and kinetics of methylene blue adsorption on activated charcoal prepared from the waste tires were obtained from the calibration curve.

The adsorption isotherms of methylene blue were simulated by the mathematical equations of Langmuir [13] and Freundlich [14]. The Langmuir model assumes the adsorption to occur on homogeneous surface by a monolayer adsorption and predicts a linear relation between $\frac{C_e}{Q_e}$ and C_e which can be mathematically rearranged as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}} C_e + \frac{1}{Q_{max} b} \qquad \cdots \quad (iii)$$

Where, Q_e (mmol/g) is adsorption capacity at equilibrium; C_e is equilibrium concentration (mmol/L); Q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage (mmol/g) and b is Langmuir constant (L /mmol).

The Freundlich model assumes surface heterogeneity which provides an empirical relationship between the adsorption capacity and equilibrium constant of the adsorbent.

$$\log Q_e = \frac{1}{n} \log C_e + \log k_f \qquad \cdots \quad (iv)$$

where, k_f [(mmol/g) (L/mmol) $^{1/n}$ and n (g/L) are Freundlich constants related to adsorption capacity and adsorption affinity of the adsorbent respectively.

The resulting adsorption isotherms are shown in Fig 2. The overall parameters calculated from the Langmuir and Freundlich equations using the experimental data are listed in Table 1. The adsorption values increase initially at an exponential rate and after reaching a certain critical value no such sharp rise was observed and adsorption attains equilibrium. The correlation coefficient values indicate the overall adsorption isotherms were better fit to Langmuir
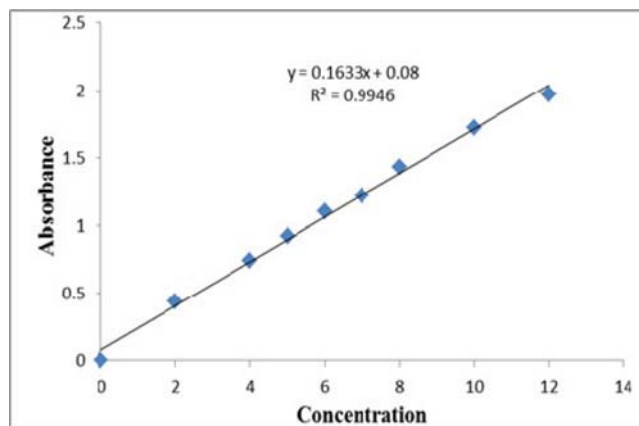
model in comparision to Freundlich model. These behaviours are expected to be due to the surface homogenity.

According to the Langmuir data, the maximum adsorption capacities (Q_{max}) of methylene blue for type I, type II, type III and type IV are 0.227, 0.255, 0.256 and 0.275 mmol/g respectively. The variation in the adsorption capacities is attributed to the difference in the relative number of pores in the adsorbent and hence to the active surface area of the adsorbent. The Langmuir constant 'b' is related to the free energy change of adsorption (DG) according to the following formula [15]:

$$\Delta G = -RT \ln(1000b) \qquad \cdots \quad (v)$$

Where, R is gas constant, 8.314J/ (mol K) and T is temperature in Kelvin scale. The Gibbs free energy indicates the degree of spontaneity of the adsorption process. The negative values reflect feasibility of all the adsorbents and the spontaneity of the adsorption process.
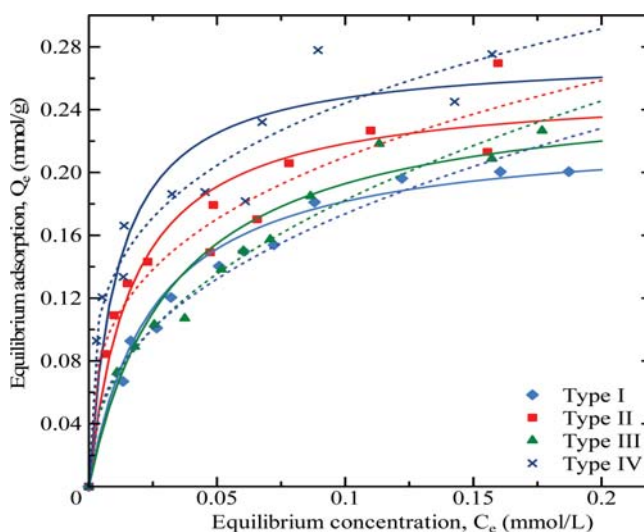
3.4. Kinetics of Methylene Blue Adsorption

Fig-4: The adsorption isotherms for the adsorption of methylene blue on various types of activated carbon obtained from waste tire.

For the investigation of the rate law describing the adsorption capacity, kinetic data obtained from batch experiments were analysed using first order [16] and the psuedo-second order [13] equations. The equations were rearranged to obtain the linear form as follows:

$$\frac{t}{Q_t} = \frac{1}{k_2}Q_e^2 + \frac{1}{Q_e}t \qquad \cdots \ (vii)$$

Table 1: The calculated Langmuir and Freundlich constants are tabulated below:

Type	Langmuir constants				Freundlich constants		
	Q_{max}	b	R^2	ΔG	K_f	n	R^2
I	0.227	40.031	0.9762	-26	0.43	2.54	0.9479
II	0.255	59.677	0.9526	-27	0.42	3.32	0.9364
III	0.256	30.586	0.9436	-26	0.49	2.33	0.9735
IV	0.275	90.174	0.9685	-28	0.44	3.91	0.9207

The calculated data from the plots of $Log_{10}(Q_e-Q_t)$ and t/Q_t as a function of reaction time are shown in **Table 2**. The value of correlation coefficient (R^2) for first order rate equation and a pseudo second order equation was found to be 0.9076 and 0.9999 respectively while the Q_e values obtained from the above two equations were 0.019 and 0.135 mmol/g respectively. The correlation coefficient data indicated that the pseudo-second order reaction model is the better fitting for methylene blue by type (IV) adsorbent.

$$Log_{10}(Q_e - Q_t) = Log_{10}Q_e - \frac{k_1}{2.303}t \qquad \cdots \ (vi)$$

A plot of methylene blue adsorption as a function of reaction time is shown in Fig. 5. As shown in Fig. 5, the rate of adsorption goes on increasing initially and reaches to an equilibrium value at around 200 minutes. There was no any appreciable change in the adsorption value after this reaction time. The rapid adsorption of methylene blue by activated charcoal is due to the abundant availability of active sites on the sorbent material, and as these sites become occupied, the adsorption slows down and attains equilibrium.

4. CONCLUSION

The overall study showed that the waste tire can be a promising material for the preparation of activated carbon. The specific surface area increased under the atmosphere of Nitrogen and steam and the increase amount of methylene blue adsorption from 0.227 to 0.275 mmol/g by thus prepared activated carbon is a praiseworthy achievement. The kinetics

Table 2: Kinetic data for the adsorption of methylene blue on type (IV) activated charcoal

Reaction Order	Rate constant [L. g/ (mmol/min)]		Qe value (mmol/g)	R^2
	K_1	K_2		
First Order	1.7×10^{-2}		0.019	0.9076
Pseudo-second Order		8.313×10^{-4}	0.135	0.9999
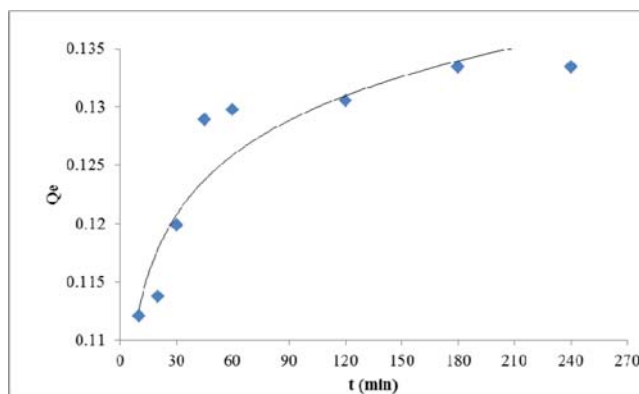
Fig-5: **The methylene blue adsorption (Q_e) of type IV activated carbon as a function of time.**

followed by this type (IV) activated carbon was a psuedo second order equation. The rate constant and equilibrium adsorption values obtained from pseudo second order equation were found to 8.313×10^{-4} L g/(mmol min) and 0.135 mmol/g respectively.

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