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Activated Carbons from Shredded Waste Tire for Malachite Green Adsorption

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Abstract

This work aimed to evaluate the adsorptive properties of shredded waste tire-based activated carbons prepared through zinc chloride or potassium hydroxide activation. The activated carbons were characterised for specific surface and functional groups, and malachite green was used to probe the removal performance at different dye concentrations and contact times. Potassium hydroxide-activated carbon with a 319 m^2/g surface area displayed a higher adsorption capacity of 102 mg/g as compared to zinc chloride-activated carbons for the concentration range studied. The adsorption data obeyed pseudo-second-order model, indicating the chemically driven adsorption. The experimental results show the feasibility of shredded waste tire to be converted into activated carbon for dyes removal.

Keywords: Activated carbon, adsorption, chemical activation, malachite green, shredded waste tire

Introduction

A tire is discarded as waste due to its abrasion state unsafe for road traffic and transport. About 1000 million waste tires are produced annually worldwide. The disposal of waste tires is a challenging problem. Its durability is making the disposal and reprocessing difficult. Besides, the tire is generally immune to biological degradation due to the cross-linked rubber molecules [1]. The common disposal method is to stockpile in the landfill. However, there are always hazards associated with this practice to human health and the environment [2]. Stockpiling of a waste tire provides a breeding ground for flies and mosquitoes, causing diseases such as dengue fever. It is also a fire hazard which may result in a serious air pollution issue [3].

The waste tire is a mixture of different polymers such as natural rubber, butadiene rubber and styrene-butadiene rubber plus additives like carbon black, sulphur and zinc oxide. The carbon black constitutes approximately 32%, while the total carbon content can be as high as 70-75%. The carbonaceous nature of the waste tire resembles that of activated carbon, where the only apparent physical difference is that the former has a less-developed porous structure [4]. Therefore, the waste tire could be a promising feedstock of activated carbon, and this strategy would solve the problems revolving around the waste tire management and disposal, and the associated environmental issues.

The waste tire can be converted into activated carbon through pyrolysis at 400-700°C [5]. The process is typical to break the linkage of carbon atoms and eliminate volatile matters, whereby the pathways produced giving rise to the high specific surface. The characteristics and adsorption properties of activated carbon are greatly influenced by the degree of burn off, often is a function of temperature, time, particle size and heating rate [1]. Also, chemical activation is normally recommended to enhance the structural characteristics by generating additional micro- and mesopores within the carbon matrix [6].

Malachite green (MG) is a blueish cationic dye that has been widely used as colourant and biocide in the textile and manufacturing industries. It is soluble in water but resistant to light, rendering a problematic removal and degradation from industrial effluent [7]. Activated carbon adsorption is a preferred dye-containing wastewater treatment technique because it is cheap, easy to operate and practical. Therefore, the present work aimed to evaluate the feasibility of activated carbons-derived from the shredded waste tire in the MG's adsorption.

Materials and Methods

Preparation and characterisation of activated carbons

The waste tire supplied by a thread compounds company in Selangor. Potassium hydroxide (> 85%), zinc chloride (> 98%) and MG dye (C.I. No. 42000, λ_{max} = 650 nm, 95%) were purchased from R&M Chemicals, Essex, United Kingdom. Figure 1 shows the molecular structure of MG. All chemicals are of analytical-grade reagent.

Activated carbons were prepared from waste tire by chemical activation. The shredded tire was mixed with $ZnCl_2$ at weight ratios (chemical:tire) of 1:1 and 2:1, and KOH at a weight ratio of 1:1. These samples are designated as Z1, Z2 and K1, respectively. The solid-liquid mixture was stirred at 100 rpm and 70°C for 2 hours to homogenise the mixture. Upon oven-drying at 110°C for 24 hours, the impregnated tire was subjected to carbonisation in a furnace under an anoxic environment at 600°C for 2 hours. After that, the resultant materials were soaked in 0.1 M HCl overnight

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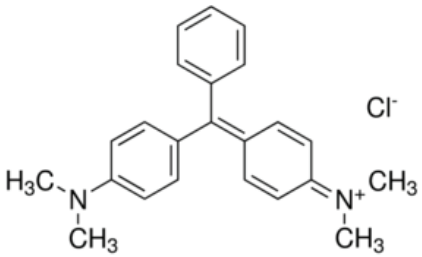

Figure 1 Molecular structure of malachite green ($C_{23}H_{25}N_2$, MW = 365 g/mol)

and washed with hot distilled water to remove excess minerals to a solution pH of 4. Then, the samples were oven-dried and ready to use for characterisation and adsorption. Activated carbons were characterised for surface area and functional groups using a Pulse Chemi Sorb 2705 with liquid N_2 at 77°C and a Shimadzu IR Tracer-100, respectively.

Malachite Green Adsorption

A 0.05 g of activated carbon (AC) was added into 50 mL of MG solution of varying concentrations (2 to 100 mg/L). The mixture was allowed to equilibrate on the shaker at 30°C for 72 hours. The residual concentration was measured by UV-Vis spectrophotometer (Drawell DU-8200) at a wavelength of 650 nm. The correlation is a.u. = 0.0289 × concentration, R^2 = 0.993 for concentrations between 2 mg/L and 15 mg/L. The adsorption capacity, Q_e (mg/g) was calculated as,

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

where, C_o (mg/L) is the initial concentration of dye, C_e (mg/L) is the equilibrium concentration of dye, m (g) is the mass of activated carbon and V (L) is the volume of dye solution.

A 0.05 g of AC was added into 50 mL of MG solution. A small volume of solution was withdrawn from the mixture at varying time intervals to study the effect of time on MG adsorption [8]. The adsorption capacity at time t, Q_t (mg/g) was computed as,

$$Q_t = \frac{(C_o - C_t)}{m} V \quad (2)$$

where C_t (mg/L) is the dye concentration at time t. Figure 2 shows the images of activated carbons and MG adsorption by bottle-point technique.

Kinetic models, namely pseudo-first-order, pseudo-second-order and intraparticle diffusion, were employed to describe the adsorption controlling mechanism. The pseudo-first-order model describes the adsorption reaction based on adsorption capacity, where particle diffusion is a significant step. The interaction between adsorbate molecules and the surface of adsorbent could be due to the van der Waals force [9]. It is given as,

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (3)$$

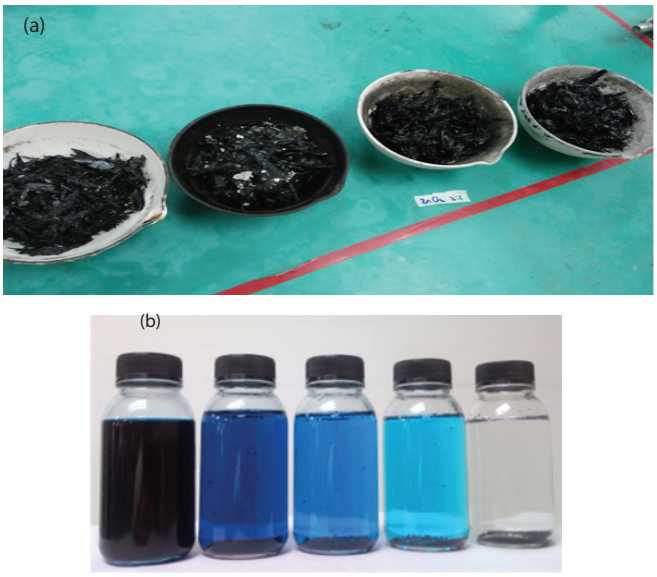

Figure 2 (a) Shredded waste tire-based activated carbons, (b) MG adsorption by bottle-point technique

where, Q_e and Q_t (mg/g) are the amount of dye adsorbed at equilibrium and at time t, respectively, and k_1 (h^{-1}) is the rate constant of the pseudo-first-order model. This equation is generally valid only for low concentration or initial adsorption period. The pseudo-second-order model describes the adsorption reaction, where the driving force of the process is the fraction of available adsorption sites. It can be expressed as,

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (4)$$

where, k_2 (g/mg.h) is the rate constant of pseudo-second-order adsorption. The intraparticle diffusion model describes the diffusion-controlled kinetics, where the pore diffusion is the rate-limiting step if the plots q_t vs $t^{0.5}$ is linear and passes through the origin. The model is given as,

$$q_t = k_d t^{0.5} + c \quad (5)$$

where, k_d (g/mg.hr) is the rate constant for intraparticle diffusion and c is the intercept at origin. The kinetic models were solved by non-linear regression using Solver of MS Excel by minimising the sum of squared errors (SSE) to yield the optimum regression coefficient, R^2.

Results and Discussion

Characteristics of activated carbons

The surface area of activated carbons was recorded as 131, 151 and 319 m^2/g for Z1, Z2 and K1, respectively. Increasing the weight ratio for zinc chloride activation slightly increases the surface area of activated carbon from 131 to 151 m^2/g. KOH is a better activator for waste tire as it resulted in increasing carbon burn-off, leading

to a high specific surface of 319 m^2/g. The devolatilisation of char develops the rudimentary pore structure, while the presence of KOH-carbon reaction enhances the porosities by widening the existing pores and creating new pores [6].

The mechanisms of KOH activation can be described as follows: firstly, the etching of carbon by a redox reaction with various K compounds via 6 KOH + 2 C → 2 K + 3 H_2 + 2 K_2CO_3 which results in the development of porous network; secondly, further generation of porosity by gasification of carbon; thirdly, metallic K intercalated in the carbon matrix can be removed by repeated washing, generating a large number of micropores [6].

Figure 3 shows the FTIR spectra of waste tire-based activated carbons. All activated carbons exhibit similar peaks at different intensity. The spectra are more simplified when compared with that of waste tire [10]. The peaks at 3800-3700 cm^{-1} are generally attributed to O–H stretching of physisorbed moisture in the porous matrix of activated carbons. The peak at 2360 cm^{-1} could be assigned to N=C=O stretching of isocyanate that has been shifted from 2150-1990 cm^{-1} (–NCS, isothiocyanate) in the waste tire [10]. The peaks at 1530 cm^{-1} and 1020 cm^{-1} represent the rubber common characteristics i.e., C=C–C aromatic ring stretching and cyclohexane ring stretching, respectively.

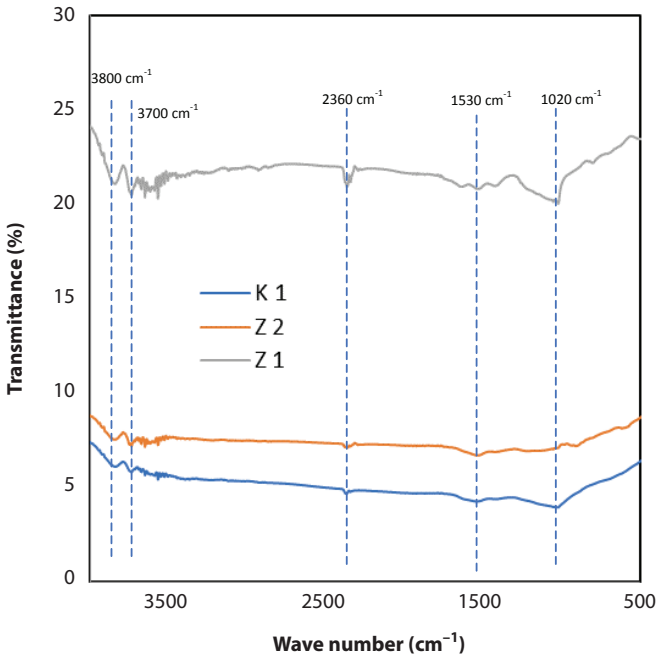

Figure 3 FTIR spectra of shredded waste tire-based activated carbons

Adsorption Studies

Figure 4 illustrates the removal of MG by waste tire activated carbons. All activated carbons clearly demonstrate an increasing trend in adsorption as dye concentration increases. This is typically true until a saturation point or maximum capacity is attained. At lower concentrations, there are plenty of available sites for

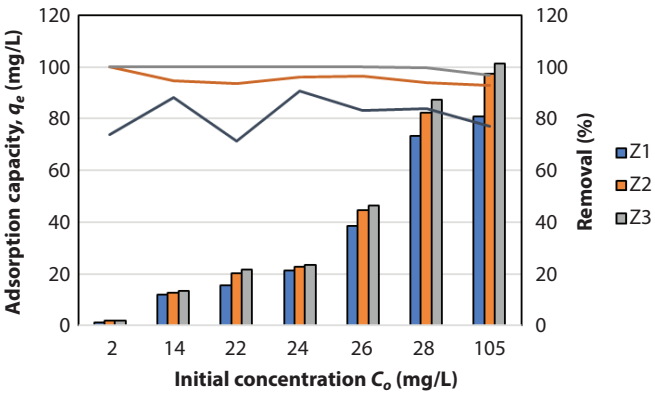

Figure 4 MG adsorption by waste tire-based activated carbons

adsorption, at which the adsorption is concentration-independent. As concentration increases, the concentration gradient offers a driving force for MG molecules to overcome solid mass transfer resistance for diffusion to increase the adsorption capacity. Z2 shows a greater dye capacity than Z1 due to a higher specific surface that encourages the interaction probabilities between dye molecules and adsorbent surface. Likewise, K1 exhibits a better removal performance than $ZnCl_2$-activated carbons. It shows a MG capacity of 102 mg/g at C_o = 105 mg/L, and sustains a 100% removal performance up to C_o = 88 mg/L. This could be linked to its higher surface area as compared to the other two counterparts. A higher specific surface provides more active sites to accommodate MG molecules for a better removal performance. Also, the performance of K1 exhibits an equivalent standing with other MG adsorbents reported in the literature [11].

Figure 5 shows the rate of MG adsorption by K1. MG's adsorption is rapid at the initial contact time, and the equilibrium is attained in less than 5 hours for C_o = 2.2 mg/L. As the concentration rises, a longer time is required to reach the equilibrium state. Many surface sites are available for adsorption at the beginning of contact, and the remaining surface sites after a lapse of time are still unoccupied due to repulsion between the readily adsorbed MG molecules on K1 and the bulk solution, rendering a slower adsorption rate [12]. The rapid diffusion of molecules happens at the outer surface, followed

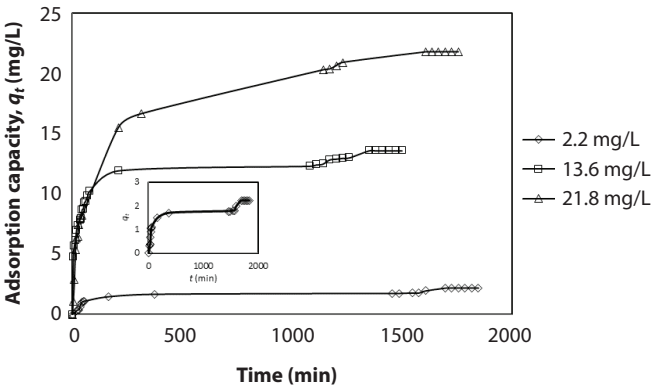

Figure 5 Effect of time on MG adsorption by K1 (inset: MG adsorption at C_o = 2.2 mg/L)

Table 1 Kinetics constants for MG adsorption by K1

C_o (mg/L)	$Q_{e\ exp}$ (mg/g)	Pseudo-first-order				Pseudo-second-order				Intraparticle diffusion			
		k_1 (hr^{-1})	Q_e (mg/g)	R^2	SSE	k_2 (g/mg.hr)	Q_e (mg/g)	R^2	SSE	k_d (mg/g.hr)	c	R^2	SSE
2.2	2.21	0.727	2.00	0.914	0.796	0.415	2.12	0.926	0.685	0.285	0.569	0.858	1.30
13.6	13.6	1.70	12.8	0.899	34.0	0.230	13.2	0.950	12.3	1.37	6.92	0.874	26.8
21.8	21.8	0.768	20.7	0.964	43.8	0.042	22.0	0.990	11.2	3.45	4.45	0.874	77.7

by slower adsorption inside the pores. The adsorption gradually increases with time, suggesting the formation of monolayer coverage on the surface of K1 [13]. Furthermore, a slight jump in adsorption was observed for MG adsorption at concentrations of 2.2 mg/L and 13.6 mg/L. This could have resulted from the cooperative adsorption and electrostatic attraction between the adsorbed molecules and the free molecules in solution, forming stacking multilayers of adsorbate on K1 surface [14]. However, this is less noticeable at higher concentrations because of the higher driving force for molecules to lodge onto pores.

The kinetic constants are summarised in Table 1. The pseudo-second-order model fits the kinetics data well with R^2 close to unity and smaller SSE values for all concentrations studied, signifying the model's applicability to describe the rate of MG adsorption onto K1. The reaction is dependent on the amount of MG adsorbed at equilibrium, where the molecule forms chemical bonding with the carbon surface [9]. According to the Arrhenius equation, a high rate constant indicates spontaneous reaction due to lower activation energy [15]. From Table 1, the k_2 value is higher at lower C_o because of rapid adsorption due to less repulsion between MG molecules.

Four sequential steps govern the mechanism of adsorption: (1) bulk diffusion describes the diffusion of dye molecules from the bulk solution to the surface of adsorbent; (2) film diffusion is the diffusion of dye molecules through the boundary layer; (3) pore diffusion or intraparticle diffusion where the dye molecules diffused from the surface into the adsorbent pores; (4) adsorption is the binding of dye molecules to the active sites on the adsorbent surface [8]. The intercept of the intraparticle diffusion plot, c indicates that the pore diffusion is not the sole rate-limiting step of MG adsorption by K1 [16].

Conclusion

The shredded waste tire was converted into activated carbons by $ZnCl_2$ or KOH activation. The performance of activated carbons was probed by malachite green adsorption. Activated carbon prepared using KOH activation exhibits a higher surface area of 319 m^2/g, and demonstrates a greater malachite green capacity of 102 mg/g. The kinetics data were best fitted into the pseudo-second-order model, indicating that the dye adsorption is a chemical process. To conclude, the waste tire can be exploited as the sustainable feedstock of activated carbon for environmental protection.

Acknowledgement

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