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# Zinc Chloride-activated Waste Carbon Powder for Decolourization of Methylene Blue

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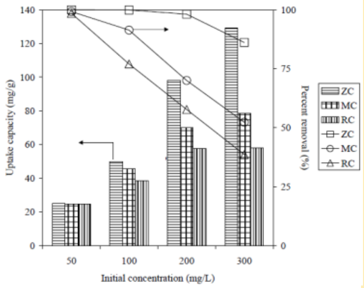
**Graphical abstract**



**Abstract**

Waste carbon powder from pyrolysis of discarded tyre was converted into activated carbon for decolourization of metylene blue (MB). The precursor was activated using $ZnCl_2$ (ZC), recycled $ZnCl_2$ solution from the earlier activation (RC), and irradiated water (MC). Activated carbons were characterized according to surface area and morphology. The values of surface area were recorded as 288, 104 and 113 $m^2/g$ for ZC, RC and MC, respectively. The decolourization of MB was observed to have the following order: ZC>MC>RC. The maximum adsorption capacity of MB by ZC was found to be 154 mg/g. Adsorption data for all activated carbons studied obeyed Redlich-Peterson isotherm for which the process could be described as mixed features of Langmuir and Freundlich models. The kinetics data were well-fitted to pseudo-second-order model, suggesting the chemisorption process.

*Keywords*: Activated carbon; irradiated water activation; methylene blue; waste carbon powder; zinc chloride activation

## 1.0 INTRODUCTION

The release of dyes from textile industries into receiving water affects the aquatic creatures because some dyes are highly toxic and carcinogenic [1-3]. Dyes block the passage of sunlight into the stream, thus destroy the life cycle and food chain in water, and disrupt the biodiversity within. Deteriorating quality of water will also bring bad implications to public health and daily life.

Methylene blue (MB) is commonly used in dying textile and medicinal treatments [2-5]. It is not strongly hazardous but can cause some harmful effects such as eye injury, difficult breathing, nausea, vomiting, profuse sweating, Heinz body formation, diarrhea, gastritis, mental confusion, cyanosis, jaundice, tissue necrosis in humans and methemoglobinemia [1-5]. These health effects have triggered strong measure for MB removal as one of the major environmental concerns.

Methods for dye removal include adsorption, chemical coagulation, ion exchange, biological treatment and electrolysis [2,3,6]. Of these, adsorption by activated carbon is highly effective to remove dye because of the large surface area and unique textural properties of activated carbon [7-8]. However, activated carbon precursors like coal and petroleum pitch are not renewable, while regeneration of the spent activated carbon is relatively expensive. This scenario has resulted in the searches for alternative carbonaceous precursors that are abundantly available and low cost. One of the promising candidates under this category is waste carbon powder, a pyrolysis by-product of bulk waste tyre.

Activated carbon can be prepared through two common routes, namely physical activation and chemical activation. Activating agents for physical activation are $CO_2$ and steam, while chemical agents such as KOH, $ZnCl_2$, $H_3PO_4$, $K_2CO_3$, etc. are commonly used in chemical activation. Chemical activation is usually being carried out at a lower temperature without carbonization, and usually results in a higher yield compared to physical activation [9-12].

The aim of this work was to investigate the potential of $ZnCl_2$-activated waste carbon powder for MB removal from aqueous solution. Attempts were also made to activate the carbon by using recovered zinc chloride solution and irradiated water environment. The effects of initial dye concentration and agitation time were examined and discussed.

## 2.0 EXPERIMENTAL

### 2.1 Materials

All chemicals were of analytical-reagent grade. Waste carbon powder was obtained from Bukit Batu Brickmills (M) Sdn. Bhd. Methylene blue (MB) was used as the dye to be treated. Figure 1 shows the molecular structure of MB, and its general properties are listed in Table 1. MB is a basic dye which carries a positive charge (cationic dye).

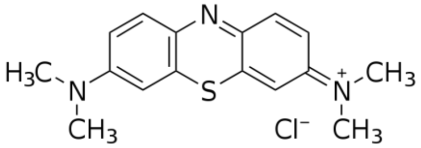


**Figure 1** Molecular structure of methylene blue

**Table 1** Characteristics of methylene blue

| | |
|---|---|
| Chemical formula | $C_{16}H_{18}N_3SCl$ |
| IUPAC name | 3,7-bis(Dimethylamino)-phenothiazin-5-ium chloride |
| Molar mass | 319.85 g/mol |
| Colour index number | 52015 |
| Wavelength, λ | 663 nm |
| Solubility in water | 1 g/25 ml |

## 2.2 Preparation of Activated Carbon

The waste carbon powder was pre-treated at 250˚C in furnace for about 1.5h to remove oil covering its surface.

***Chemical activation***: the precursor was impregnated with $ZnCl_2$ at impregnation ratio (chemical agent over precursor) of 1. Activation was performed at 550°C for 1.5h in furnace. The activated carbon was washed using distilled water in a soxhlet unit to recover $ZnCl_2$. The activation procedures were repeated using the recycled $ZnCl_2$ solution to produce another activated carbon. Activated carbons were designated as ZC and RC for activation using fresh and recycled $ZnCl_2$ solution, respectively.

***Irradiated water activation***: the precursor was soaked in distilled water and activated under microwave at half magnitude of power intensity for 20 minutes. The resultant activated carbon was designated as MC.

The activated carbons were dried in an oven prior to characterization and adsorption studies.

## 2.3 Characterization of Activated Carbon

Thermal profile of the precursor was determined under $N_2$ flow at a heating rate of 10°C/min by thermogravimetric analysis (TGA7, PerkinElmer). The surface area of activated carbon was measured using surface area analyzer (Micromeritics PulseChemiSorb 2705, USA), while the surface morphology was determined using SEM instrument (Philips XL 40, Netherlands).

## 2.4 Adsorption Studies

***Equilibrium isotherms***: Methylene blue (MB) was employed as the pollutant probe in adsorption. In batch adsorption, 0.1g of activated carbon was added into conical flasks containing 50mL of MB of varying concentrations (50 to 300ppm). The solution pH was not adjusted, and measured as 5.5±0.3 for all initial concentrations studied. The flasks were sealed, and the mixtures were allowed to equilibrate on orbital shaker at 28±1°C and 90rpm for 72 hours. Thereafter, the solutions were filtered and the residual concentrations were determined using Visible Spectrophotometer (Biochrome Libra S6, UK) at a wavelength of 690 nm. The amount of methylene blue adsorbed at equilibrium, $q_e$ (mg/g), was calculated by simple mass balance,

$$q_e = \frac{(C_0 - C_e)}{m} V \qquad (1)$$

where $C_0$ and $C_e$ (mg/L) are initial and equilibrium concentrations, respectively, $V$ (mL) is the volume of the solution and $m$ (g) is the mass of dry adsorbent. Equilibrium data were analyzed using the commonly used isotherm models, namely Langmuir, Freundlich and Redlich-Peterson models.

***Adsorption kinetics***: Activated carbon that demonstrated the highest MB removal in equilibrium studies was selected for kinetics evaluation. A fixed amount of 0.1 g of activated carbon was added to different batches of 50 ml MB solution having concentrations of 50 and 300 mg/L. The residual concentration was measured at preset time intervals for 72 hours. Kinetics data were fitted to pseudo-first order, pseudo-second order and intraparticle diffusion models, and the respective constants were determined.

# 3.0 RESULTS AND DISCUSSION

## 3.1 Characteristics of Activated Carbon

Figure 2 represents the thermogravimetric profile of waste carbon powder before activation.

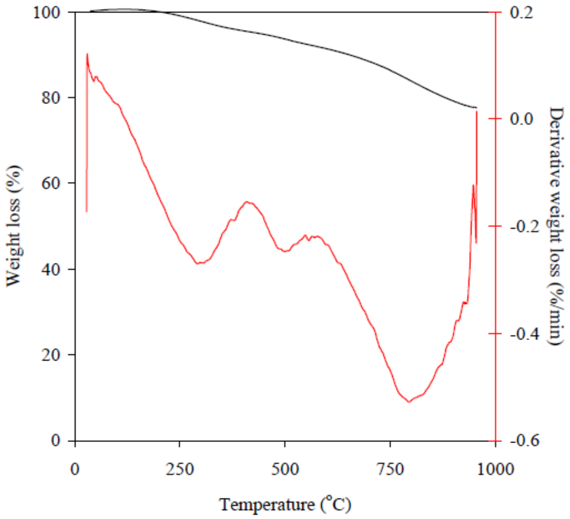


**Figure 2** Thermogravimetric analysis of waste carbon powder before activation

The profile shows three main regions of considerable weight loss, i.e., at temperatures 300, 500 and 800°C. The first region indicates the removal of oil that covers the surface of carbon powder. It should be noted that the raw material contains almost negligible amount of moisture, and it does not mix with water in its as-received condition. For the carbon powder to be homogeneously impregnated in $ZnCl_2$ solution, the layer of oil must first be removed. The second and third regions signify the release of volatile and further decomposition of material. The precursor originally contains high carbon content; 90.9% combustible material and 9.1% ash. Due to its fine powder form that presumably consists of dense aromatic or graphitic structure, longer duration was required to burn the precursor into ash. This explains why the weight loss was only 25% although the temperature was close to 1000°C.

Table 2 shows the yield and surface area of activated carbons.

**Table 2** Yield and surface area of activated carbons

| **Activated carbon** | **Yield (%)** | **Surface area ($m^2/g$)** |
|---|---|---|
| ZC | 91.2 | 288 |
| MC | 76.0 | 113 |
| RC | 85.8 | 104 |

The yield of activated carbon was determined from the weight of resultant product over the weight of waste carbon powder after the pre-treatment. In general, the activation of waste tyre powder gives a better yield compared to other carbonaceous material because the precursor was readily rich in carbon content [11]. The values reported in this work were somewhat greater compared to previous related works [13]. A decrease in yield indicates that there was burn-off of carbon material during the activation. Results show that the yield of ZC is slightly higher compared to that of RC and MC. A higher $ZnCl_2$ ratio is expected to inhibit the release of volatile matter from the precursor [14]. The ratio of recovered $ZnCl_2$ used to prepare RC is presumably lesser than 1 due to some amount that has already been used up and/or evaporated from the first activation, thus resulting in a lower yield of RZ. From Table 2, the values of surface area were recorded as 288 and 104 $m^2/g$ for ZC and RC, respectively. A higher surface area of ZC over RC proved that $ZnCl_2$ impregnation ratio plays an important role during the activation, wherein its amount determines the surface area of activated carbon. Notwithstanding that, the utilization of recovered $ZnCl_2$ for subsequent activation was still feasible to produce activated carbon with high surface area. MC showed a lower yield because microwave heating could reach high temperature in a shorter period, thus speeding up the release of tar or volatile matter [15]. The surface area of MC was as good as that of RC, suggesting the potential of using irradiated water in activated carbon preparation.

Figure 3 shows the SEM images of activated carbons. The formation of melt, vesicles, precipitates of inorganic salts and surface etching were observed on the surface of activated carbons. Under the same magnification, ZC showed a larger particle size compared to MC and RC due to the dominance of activating agent. Comparable morphology between MC and RC signifies a much lower amount of $ZnCl_2$ used to activate RC. All activated carbons displayed irregular structures with cracks and crevices which confirmed the amorphous and heterogeneous structures. However, the pore textures are not clearly observed from these SEM images probably due to the fine powder form.

## 3.2 Equilibrium Isotherms

In this work, the pH of the solution was not adjusted prior to adsorption. At the end of the process, the values of equilibrium pH were found to be consistent for all activated carbons studied, and were measured as 6.1±0.2. The consistent values of equilibrium pH suggested that the amount of protons adsorbed for each activated carbon is uniform although the surface area of activated carbon is different; ca. about 0.005 mmol/g proton was adsorbed. Therefore, it is adequate to utilize single component isotherm models to represent the adsorption data.

Figure 4 displays the removal of MB by activated carbons at different initial concentrations.

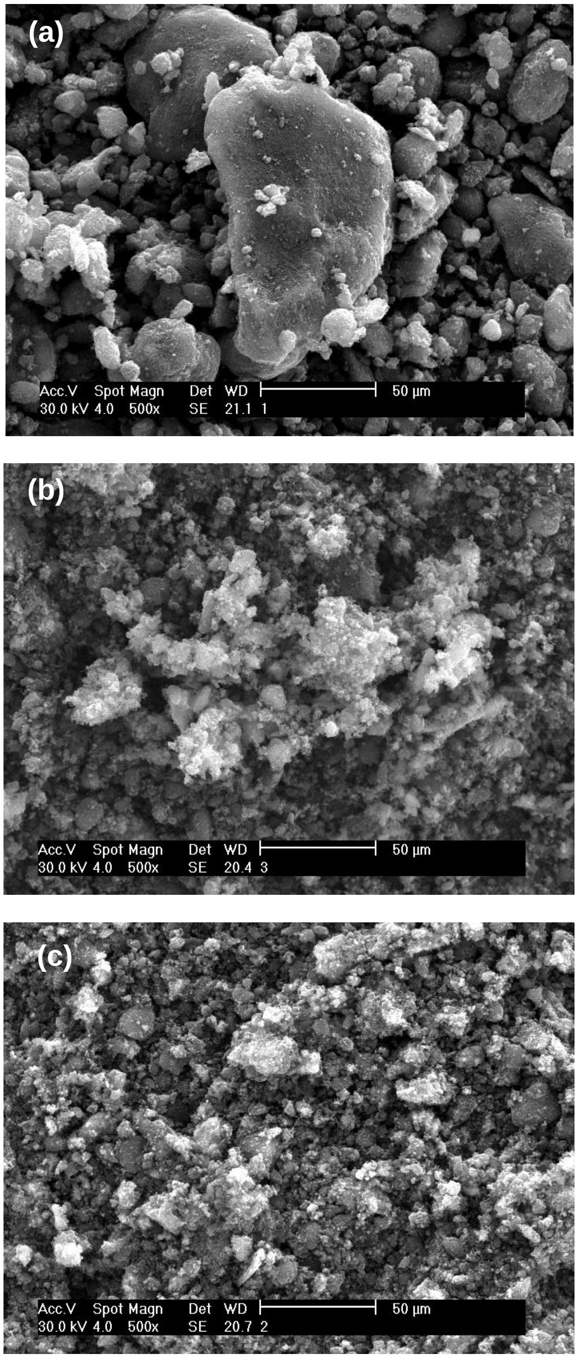


**Figure 3** SEM images of activated carbons (a) ZC, (b) MC and (c) RC

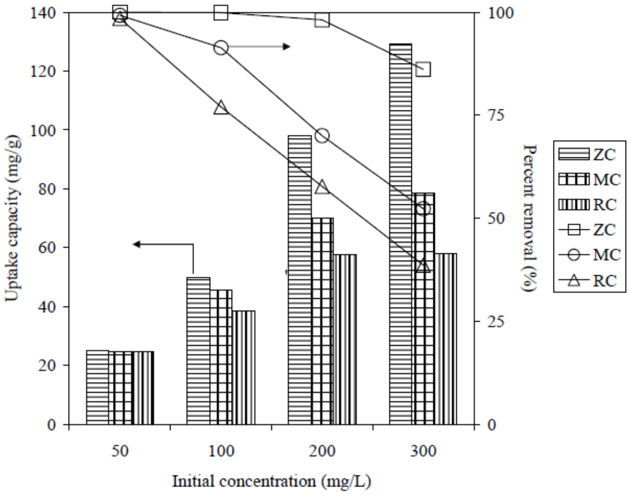


**Figure 4** Uptake of methylene blue at different initial concentrations after 72 hours

The removal of MB by all activated carbons was found to increase with increasing initial concentration. At initial concentration of 50 mg/L, all activated carbons demonstrated an identical removal of MB at 25 mg/g which was equivalent to 100% removal. It implies the feasibility of using irradiated water, and recovered $ZnCl_2$ for subsequent activated carbon preparation, that suits for adsorption at lower concentration. As initial concentration increases to 300 mg/L, the decolourization of MB was found to follow the order: ZC>MC>RC, which corresponds directly to their values of surface area. ZC was able to remove nearly 100% MB at concentration approaching 200 mg/L, while MC and RC displayed a decreasing trend of percent removal at concentrations above 50 mg/L. In general, the increase of initial concentration increases the driving force for adsorption. At higher concentrations, however, the presence of adsorbate molecules are higher than the surface sites can accommodate thus decreasing the percent removal. Adsorption is a process that is dependent on the initial concentration. Thus, if the surface of activated carbon is completely saturated, no change in uptake capacity could be observed even as the concentration increases. This can be visualized by the uptake of RC at concentrations of 200 and 300 mg/L.

Three commonly used isotherm models for single solute adsorption, namely Langmuir [16-17], Freundlich [18] and Redlich-Peterson [19] models were used to describe the adsorption data. The Langmuir isotherm indicates monolayer adsorption onto a completely homogeneous surface, and is given as,

$$q_e = \frac{Q_0 b C_e}{1 + bC_e} \qquad (2)$$

where $Q_0$ (mg/g) is the maximum uptake per unit mass of adsorbent to form a complete monolayer on the surface of adsorbent, and $b$ (L/mg) is a constant related to the affinity of the binding sites. The empirical Freundlich isotherm based on sorption on a heterogeneous surface is given by,

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (3)$$

where $K_F$ and $1/n$, are the Freundlich constants which correspond to the maximum adsorption capacity and intensity, respectively. The $1/n$ value ranging from 0 to 1 is considered to represent surface heterogeneity. It is also suggested that the $n$ values ranging between 2 and 10 represent favourable adsorption process. The Redlich-Peterson isotherm which combines the features of the Langmuir and Freundlich equations can be described as,

$$q_e = \frac{AC_e}{1 + BC_e^g} \qquad (4)$$

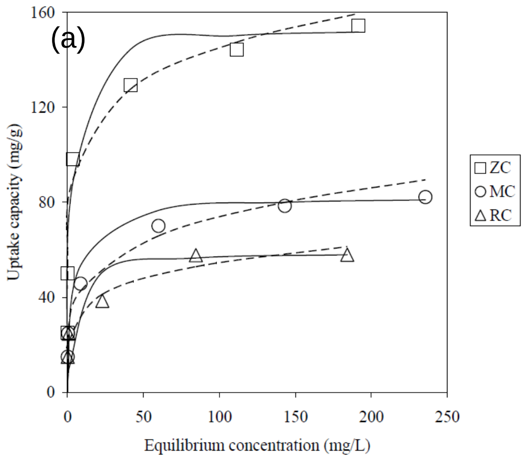
where $A$, $B$ and $g$ are all the Redlich-Peterson constants, and $0<g<1$. The Redlich-Peterson equation becomes Henry's law when $g$ equals 0, while it becomes Langmuir model when $g$ is unity. The non-linear models were solved using *Solver* add-in of Microsoft Excel, and their applicability was deduced based on coefficient of determination ($R^2$). Figure 5 shows the equilibrium adsorption of MB onto activated carbons, and the respective constants of the isotherm models are tabulated in Table 3.

All activated carbons studied displayed a concave shape uptake capacity against equilibrium concentration which indicates favourable and rapid adsorption in dilute solution. The values of maximum removal were recorded as 154, 83 and 59 mg/g for ZC, MC and RC respectively. All three models were found to correlate the adsorption data well. However, the Freundlich and Redlich-Peterson models were more fitted to linear approximation; the $R^2$ values are close to unity. The Freundlich model suggests that the uptake of MB by activated carbons is a normal adsorption onto heterogeneous surface. This could be supported by the surface morphology of activated carbons (Figure 3). The applicability of Redlich-Peterson model indicates the adsorption process as joint features between Langmuir (monolayer adsorption) and Freundlich (adsorption on heterogeneous surface) models. As can be seen from Figure 5(a), the removal of MB obeyed Freundlich isotherm at lower equilibrium concentration, and switched to Langmuir isotherm as the uptake began to level-off.

Among the activated carbons studied, ZC demonstrated a greater adsorption affinity for MB. It is likely due to its high surface area, which allows for greater interaction probabilities between the surface sites and adsorbate molecules especially at lower concentration.

**Table 3** Constants of isotherm models

| **Isotherm model** | **Activated carbon** | | |
|---|---|---|---|
| | **ZC** | **MC** | **RC** |
| Langmuir | | | |
| $Q_0$ (mg/g) | 154 | 82.6 | 59.2 |
| $b$ (L/mg) | 0.369 | 0.211 | 0.254 |
| $R^2$ | 0.969 | 0.957 | 0.892 |
| Freundlich | | | |
| $K_F$ (mg/g)(L/mg)$^{1/n}$ | 74.1 | 26.3 | 22.7 |
| $1/n$ | 0.146 | 0.224 | 0.191 |
| $R^2$ | 0.983 | 0.979 | 0.964 |
| Redlich-Peterson | | | |
| $A$ (L/g) | 2260 | 240 | 451 |
| $B$ | 26.4 | 6.86 | 17.6 |
| $g$ | 0.888 | 0.840 | 0.837 |
| $R^2$ | 0.985 | 0.993 | 0.967 |



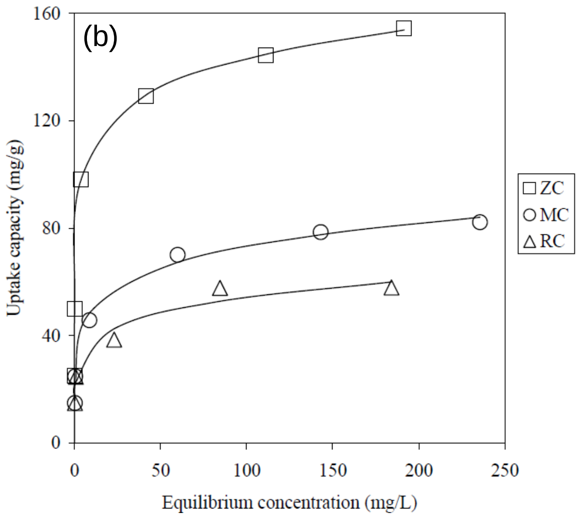


**Figure 5** Equilibrium adsorption of methylene blue. (a) Lines were predicted from Langmuir (solid) and Freundlich (dashed) models; (b) Lines were predicted from Redlich-Peterson model

### 3.3 Adsorption Kinetics

A better understanding of the mechanism and rate of adsorption is important to design the adsorption process. This part describes the kinetics evaluation of ZC at two concentrations, i.e., 50 and 300 mg/L. ZC was selected because it performs better than the other two activated carbons, while the two concentrations were chosen to evaluate the kinetics in diluted solution and at the point approaching surface saturation.

The kinetics data was evaluated by using three kinetics models, namely pseudo-first order [20], Ho's pseudo-second order [21] and intraparticle diffusion models [22]. Pseudo-first order model is given by,

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \qquad (5)$$

where $q_t$ (mg/g) is the amount of MB adsorbed at time $t$ (h), and $k_1$ (h$^{-1}$) is the rate constant of first order adsorption. Ho's pseudo-second-order equation based on chemical related adsorption is expressed as,

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \qquad (6)$$

where $k_2$ (g/mg.h) is the rate constant of pseudo-second-order adsorption. The initial adsorption rate, $h$, of pseudo-second-order as $t$ approaching zero is defined as,

$$h = k_2 q_e^2 \qquad (7)$$

Half-adsorption time, $t_{1/2}$, is defined as the time required for the adsorption to take up half as much MB as its equilibrium value. It is often used as a measure of the adsorption rate, and is expressed as,

$$t_{1/2} = \frac{1}{k_2 q_e} \qquad (8)$$

The diffusion mechanism and rate-controlling steps in the adsorption process could be explained by the Weber and Morris intraparticle diffusion model [22],

$$q_t = k_P t^{0.5} + C \qquad (9)$$

where $k_P$ (mg/g.h$^{0.5}$) is the intraparticle diffusion rate constant, and C is the intercept that gives an idea about the boundary layer thickness, i.e., the larger the intercept, the greater the boundary layer effect. All kinetics constants were solved using *Solver* add-in, given the condition where the sum of squared error is the least thus yield the optimum value of correlation of determination ($R^2$).

Figure 6 illustrates the kinetics profiles of ZC at two different concentrations, and the respective constants are tabulated in Table 4. The convex upward kinetics curves generally indicate strong and favourable MB adsorption, and the equilibrium uptake over the studied period was reasonably tallied with Figure 4. From Figure 6, the uptake of MB was found to increase with increasing time upon reaching a plateau at about 30 min and 48 h for initial concentrations of 50 and 300 mg/L, respectively. ZC displayed a rapid increase in adsorption in diluted solution during the first few minutes, after which the uptake starts to increase gradually. Nearly 100% MB removal (24.8 mg/g) was attained after 30 min the solution was in contact with the adsorbent. However, a much slower removal was observed for MB concentration of 300 mg/L. The kinetics data were fitted to the commonly used kinetics models to elucidate the mechanisms of MB removal onto activated carbon.

**Table 4** Constants of kinetics model

| | **Initial methylene blue concentration (mg/L)** | |
|---|---|---|
| | 50 | **300** |
| $q_{e,\text{ Exp}}$ (mg/g) | 25 | 129 |
| Pseudo-first-order | | |
| $k_1$ | 0.883 min$^{-1}$ | 49.3 h$^{-1}$ |
| $q_{e,\text{ Model}}$ (mg/g) | 23.7 | 115 |
| $R^2$ | 0.967 | 0.928 |
| Pseudo-second-order | | |
| $k_2$ | 0.0707 g/mg.min | 0.0082 g/mg.h |
| $h$ | 42.4 g/mg.min | 124 g/mg.h |
| $t_{1/2}$ | 0.577 min | 0.991 h |
| $q_{e,\text{ Model}}$ (mg/g) | 24.5 | 123 |
| $R^2$ | 0.988 | 0.980 |
| Intraparticle diffusion model | | |
| $k_P$ | 0.295 min$^{-0.5}$ | 4.73 h$^{-0.5}$ |
| $C$ | 21.2 | 89.1 |
| $R^2$ | 0.575 | 0.909 |

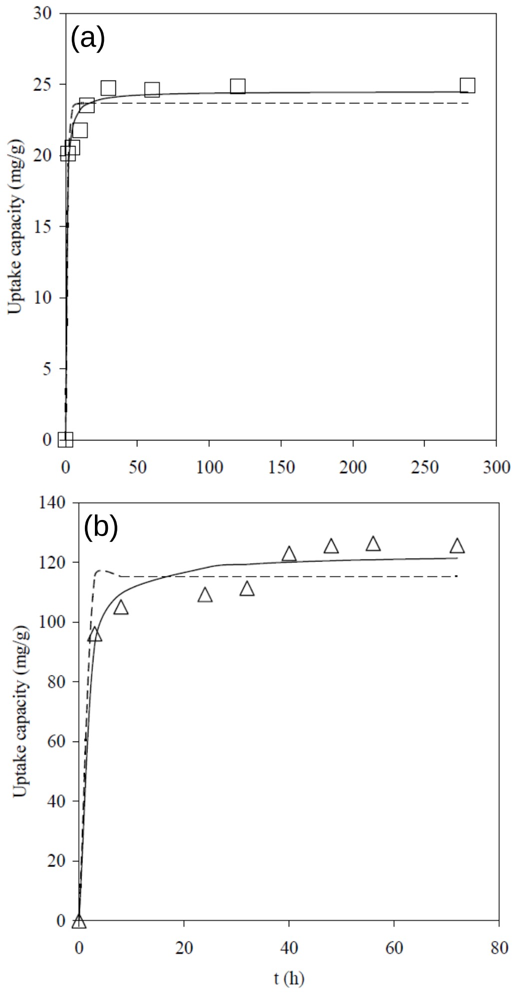
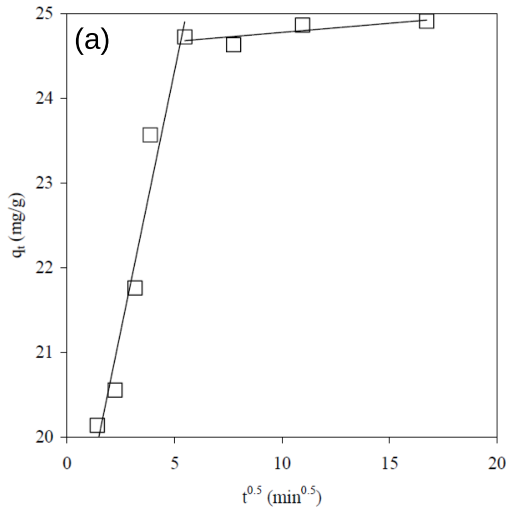


**Figure 6** Kinetics of methylene blue removal at initial concentrations of (a) 50 and (b) 300 mg/L. Lines were predicted from pseudo-first-order (dashed) and pseudo-second-order (solid) models



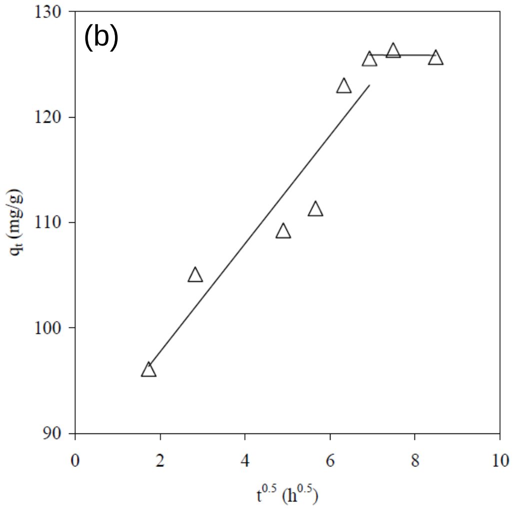


**Figure 7** Intraparticle diffusion model for methylene blue removal at concentrations of (a) 50 and (b) 300 mg/L

From Table 4, Ho's pseudo-second order kinetics model represents a reasonably better $R^2$ values compared to the other two kinetics models. The calculated values of MB uptake ($q_{e,\text{ Model}}$) were also in agreement with the experimental values ($q_{e,\text{ Exp}}$). MB removal onto ZC could therefore be sufficiently described as chemisoption or chemically driven adsorption [21].

The rate constant for adsorption in dilute solution (50 mg/L) is more than 500 times greater than that in 300 mg/L MB solution. Also, the initial adsorption rate, *h* for dilute solution is nearly 20 times higher. This phenomenon could be explained by the fact that there are plenty available sites to accommodate MB molecules at lower concentration which offers fast adsorption rate. As the concentration increases, more adsorbate molecules are competing for limited number of available sites thus decreasing the rate constant. Notwithstanding that, a greater concentration gradient in aqueous solution attracts more adsorbate molecules to lodge on the activated carbon surface thus increasing the uptake capacity; which is true until the surface saturation is reached.

Adsorption usually follows three consecutive steps, i.e., (i) film diffusion which transports the adsorbate from the bulk solution to the external surface of the adsorbent, (ii) particle diffusion which transports adsorbate from the liquid film to the solid surface, and (iii) Adsorbate-adsorbent interaction leading to the adsorption. The mechanism of adsorption could be described by the intraparticle diffusion model [22]. Figure 7 shows the intraparticle diffusion model for methylene blue removal onto ZC, and the respective constants are tabulated in Table 4. From the plots, there are two connecting lines of different slopes; the initial part (steep slope) indicates the initial stage of adsorption that reflects the thickness of boundary layer, and the second part represents the effect of intraparticle diffusion. Intraparticle diffusion is the rate-limiting step (the slowest step in MB adsorption that determines the rate constant) when the two lines yield a straight line through origin when combined. It happens when the resistance in the film is almost negligible because of thin boundary layer.

However, it was not the case for ZC because the adsorption data did not fit to the model. Thus, the intraparticle diffusion is not the only rate-limiting step that is controlling the adsorption of MB; it is expected that other cooperative steps are also involved including film diffusion and/or chemisorption.

**Table 5** Removal of methylene blue by various adsorbents

| **Adsorbent** | **Maximum uptake (mg/g)** | **pH** | **Surface area ($m^2/g$)** | **Reference** |
|---|---|---|---|---|
| $ZnCl_2$-activated tea waste carbon | 68.5 | - | - | [23] |
| Activated carbon fiber | 322 | - | 1035 | [24] |
| Multi-walled carbon nanotubes | 119 | - | 280 | [25] |
| $ZnCl_2$-activated corn husk carbon | 463 | 4.0 | - | [26] |
| Gypsum | 36 | 7.5 | 5.67 | [27] |
| Hyacinth root powder | 8.04 | 8.0 | - | [28] |
| Natural Jordanian Tripoli | 16.6 | 8.0 | 46.5 | [29] |
| MgO nanoparticle | 4.5 | 7.0 | - | [30] |
| $ZnCl_2$-activated pea shells carbon | 247 | 6.9 | - | [31] |
| Poplar leaves | 135 | 7.0 | - | [32] |
| Sugar extracted spent rice biomass | 8.13 | 5.2 | 0.407 | [33] |
| $ZnCl_2$-activated rice husk carbon | 9.73 | - | 181 | [34] |
| $ZnCl_2$-activated carbon powder | 154 | 5.5 | 288 | Present study |
| Irradiated water-activated carbon powder | 82.6 | 5.5 | 113 | Present study |

Table 5 summarizes some studies on the removal of MB by various adsorbents. A number of authors were silent on two important parameters that are usually reported to have influence on the removal of MB, i.e., surface area of adsorbent/activated carbon, and the solution pH at which the adsorption was carried out. MB is a cationic dye, and therefore a basic environment is favourable for adsorption because surface deprotonation would attract more MB molecules to the adsorbent. However, some studies [25-26] reported that solution pH greater than 4 would not give much difference in the uptake of MB. Compared to other adsorbents reported in literature, ZC and MC demonstrated comparable performance for MB removal at pH 5.5 (non-adjusted); which will be a merit for industrial applications.

## ■4.0 CONCLUSION

Activated carbons were prepared using $ZnCl_2$, recovered $ZnCl_2$ and irradiated-water environment for methylene blue removal from aqueous solution. $ZnCl_2$-activated carbon powder showed a greater removal of methylene blue because of its higher surface area than the other two activated carbons. Activated carbons prepared using recovered $ZnCl_2$ and irradiated water demonstrated feasible methylene blue adsorption in dilute solution. Decolourization of methylene blue onto activated carbons could be described by Redlich-Peterson model, while the kinetics data were better fitted to Ho's pseudo-second order model. Activated carbons prepared in this work could become a potential candidate for methylene blue removal.

## Acknowledgement

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