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Adsorption of Methylene Blue onto activated carbon produced from steam activated bituminous coal: A study of equilibrium adsorption isotherm

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Abstract

Equilibrium adsorption isotherm for the removal of basic dye (Methylene Blue) from aqueous solution using bituminous coal-based activated carbon has been investigated. Liquid phase adsorption experiments were conducted and the maximum adsorptive capacity was determined. The effect of experimental parameters, namely, pH and adsorbent particle size were studied. Equilibrium data were mathematically modelled using the Langmuir, Freundlich and Redlich–Peterson adsorption models to describe the equilibrium isotherms at different solution pH values and particle sizes, and isotherm constants were determined. The results indicate the potential use of the adsorbent for the removal of Methylene Blue (MB) from aqueous solution. Maximum adsorption capacity of 580 mg/g at equilibrium was achieved. It was found that pH plays a major role in the adsorption process. The optimum pH for the removal of MB from aqueous solution under the experimental conditions used in this work was 11. The Redlich–Peterson isotherm was found to best fit the experimental data over the whole concentration range as indicating from the high values of the correlation coefficients ($r^2 > 0.99$).

Keywords: Activated carbon; Bituminous coal; Steam activation; Methylene Blue; Adsorption; Equilibrium isotherm

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1. Introduction

Textile industry use dyes and pigments to colour their product. There are more than 100,000 commercially available dyes with over 7×10^5 tonnes of dyestuff are produced annually. Many types of dye are used in textile industries such as direct, reactive, acid and basic dyes. Most of these dyes represent acute problems to the ecological system as they considered toxic and have carcinogenic properties, which make the water inhibitory to aquatic life [1,2]. Due to their chemical structure, dyes possess a high potential to resist fading on exposure to light and water. The main sources of wastewater generated by the textile industry originate from the washing and bleaching of natural fibers and from the dyeing and finishing steps. Given the great variety of fibers, dyes and process aids, these processes generate wastewater of great chemical complexity and diversity, which are not adequately treated in conventional wastewater treatment plant [3].

Numerous studies have been conducted to assess the harm impacts of colorants on the ecosystem. It was found that colorants may cause problems in water in several ways: (i) dyes can have acute and/or chronic effects on exposed organisms with this depending on the dye concentration and on the exposure time; (ii) dyes are inherently highly visible, minor release of effluent may cause abnormal coloration of surface waters which captures the attention of both the public and the authorities; (iii) the ability of dyes to absorb/reflect sunlight entering the water, this has drastic effects on the growth of bacteria and upsets their biological activity [4,5]; (iv) dyes have many different and complicated molecular structures and therefore, are difficult to treat and interfere with municipal waste treatment operations [6,7]; (v) dyes in wastewater undergo chemical and biological changes, consume dissolved oxygen from the stream and destroy aquatic life [8]; (vi) dyes have a tendency to sequester metal ions producing microtoxicity to fish and other organisms [9].

Regarding the aforementioned problems, government legislation concerning the quality of textile industrial wastewater effluents is becoming increasingly strict, especially in developed countries. This forces textile industries to treat their waste effluent to an increasingly high standard. For example, environmental policy in UK, since September 1997, has stated that no

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synthetic chemical should be released into the marine environment [2]. This challenge has prompted intensive research in new and advanced treatment technologies, some of which are currently making their way to full-scale installation [3]. This is paralleled with increased demand currently being placed on water supply and waste disposal, and thus have necessitated broader concepts in the application of wastewater treatment.

Basic dyes were known from the past as synthetic dyes. Historically, basic dyes are important because the first synthetic dye, Mauvein (CI 50245), which was discovered in 1856 by William Perkin, belongs to this class of dye [10].

By definition, basic dyes are cationic dyes with cationic properties originating from positively charged nitrogen or sulfur atoms. The charge is generally delocalized throughout the chromophoric system, although it is probably more localized on the nitrogen atoms. In fact, basic dyes are so named because of their affinity to basic textile materials with net negative charge [11]. Most basic dyes are beautiful, shiny, crystalline compounds and their most outstanding property is brilliance. Their tinctorial value is very high; less than 1 ppm of the dye produces an obvious coloration [12,13]. According to Anliker et al. [14], basic dyes have been classified as toxic colorants.

The most important basic dye is Methylene Blue, discovered by Caro in 1878. Methylene Blue is a dark green powder or crystalline solid. It is widely used as a stain and has a number of biological uses. It dissociates in aqueous solution like electrolytes into Methylene Blue cation and the chloride ion. The coloured cation is adsorbed by several adsorbents preferentially to a very great extent [15]. For that reason, Methylene Blue was selected to be the adsorbate in this research. It has various harmful effects on the human beings, so it is of utmost importance to be removed from wastewater. In addition, it is used as a convenient indicator in the evaluation of active carbons [16].

Recently adsorption technology is rapidly gaining prominence as a technique for removing organic and inorganic micropollutants from aqueous effluents [17]. Adsorption processes may be classified as physical or chemical depending on the nature of forces involved. When adsorption occurs without any chemical reaction, it is generally termed as physical adsorption "physisorption". It is brought about as a result of Van der Waals forces [18,19]. These forces are electrostatic in origin, and are termed dispersion forces. Dispersion forces exist in all type of matter and are always present regardless of the nature of other interactions and often account for the major part of the adsorbate–adsorbent potential [20]. Many parameters can affect the quality of physical adsorption; these include properties of the adsorbed material (molecular size, boiling point, molecular mass and polarity) and properties of the surface of the adsorbent (polarity, pore size and spacing) [19]. If the adsorbate undergoes chemical interaction with the adsorbent, the phenomenon is referred to as chemical adsorption or "chemisorption". It involves a sharing of electrons between the adsorbate molecules and the surface of the adsorbent. It is restricted to just one layer of molecules on the surface, although it may be followed by additional layers of physically adsorbed molecules [21]. Under favourable conditions, both processes can occur simultaneously or alternatively.

Adsorption technology has been used extensively in industrial processes for many purposes of separation and purification. The removal of coloured and colourless organic pollutants from industrial wastewater is considered as an important application of adsorption process using suitable adsorbents [22]. Highly functional porous materials with high surface areas are generally used for such applications as they show excellent efficiency [23].

This work investigates the adsorption of Methylene Blue onto activated carbon produced from bituminous coal using equilibrium isotherms. A further aim is to describe equilibrium data using equilibrium isotherm models.

2. Experimental

2.1. Materials

Adsorption technique for the treatment of dye containing aqueous solution using low cost activated carbon has been investigated. The activated carbon (PAC2) was produced by the steam activation of New Zealand bituminous coal on an industrial scale. The adsorbent was washed and sieved into the desired particle size before coming in contact with dye aqueous solution. The ultimate and proximate analysis of the adsorbent was determined using the Perkin-Elmer 2400 Series 2 CHNC Elemental Analyzer and the Mettler Toledo TGA/SDTA 851e, respectively. Table 1 shows the physical and chemical characteristics of the adsorbent (PAC2) used in this work.

Methylene Blue C.I. 52015 (MB), supplied by ACROS Organics, USA, was used as an adsorbate in this work. It has molecular volume of 241.9 ($cm^3 mol^{-1}$) and molecular diameter of 0.8 (nm). The chemical structure of Methylene Blue is shown in Fig. 1. Deionised water (18.2 $\mu\Omega$) was used as a solvent in this work to prepare stock dye solutions.

2.2. Method

2.2.1. Production of activated carbon

The production process pass through different stages which include preparation of the raw material and this included drying,

Table 1
The physical and chemical characteristics of PAC2 determined in this study

Total surface area (BET) ($m^2 g^{-1}$)	857.1
Micropore surface area ($m^2 g^{-1}$)	801.8
Total pore volume ($cm^3 g^{-1}$)	4.5×10^{-1}
Micropore volume ($cm^3 g^{-1}$)	3.9×10^{-1}
Carbon content (%)	81.8
Hydrogen content (%)	0.35
Nitrogen content (%)	0.38
Oxygen content (%)	16.8
Moisture content (%)	5.7
Ash content (%)	3.7
Volatile content (%)	2.2
Fixed carbon	88.4
Surface acidity (meq g^{-1})	0.46
Surface basicity (meq g^{-1})	0.56
$pH_{solution}$ (10 mass%)	8.2
pH_{zpc}	6.3

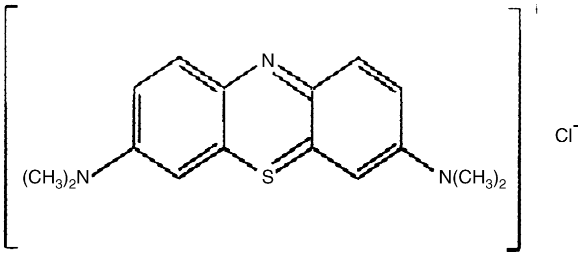

Fig. 1. Chemical structure of Methylene Blue.

crushing and sieving into the desired size. New Zealand bituminous coal was used as a precursor material for the production of activated carbon using steam activation at temperature 1000 °C for 6 h in a rotary kiln. It can produce up to 50 kg of activated carbon per hour. The kiln is approximately 10 m in length, has an internal diameter of 87 cm and is capable of reaching temperatures up to 1000 °C. It has 4 burners, a fan system and an exhaust pipe into the plant scrubber. Fig. 2 shows simplified schematic diagram of the kiln. The following paragraph gives some details on the different parts of the kiln and how the coal being used is converted into activated carbon by steam activation.

The weigh belt feeder WBF feeds coal at a controlled rate into the kiln. Fan F_1 feeds air to burners B_1-B_4, which indirectly heat the rotating kiln tube from the outside. The exhaust gases from the end of the tube, which will contain combustible volatiles from the coal and/or product hydrogen and carbon monoxide from reaction of steam with the coal, pass via a recycle loop (poorly drawn) back into the burner cavity of B_1 where they will be burned. The exhaust gases from burners B_1-B_4 pass into the exhaust pipe going down the side of the kiln, and out into the exhaust fan.

A thermocouple is attached to the end of the steam pipe so that a temperature inside the tube can be obtained, together with temperatures T_1–T_4 in the heating cavities outside the tube, T_{rec} measured in the recycle loop, and T_{ex} in the exhaust before the exhaust fan, which then pumps the exhaust gases into the scrubber. The temperatures can then be read from data acquisition software on the adjacent portable P.C. Not shown in the diagram is that, the outlet end of the kiln is fitted with wheels, the large exhaust pipe down the side with bellows, and expansion joints have had to be put in before the fan to cope with the expansion of the system when heated to 1000 °C. The Kiln tube is expands by over 20 cm when heated to 1000 °C.

The kiln is presently elevated by between 8 and 9 cm at the inlet end, giving an elevation of approximately 0.5°. The kiln can turn at speeds varying from 2 rpm down to around 0.15 rpm giving residence times from just under 2 h up to 12 h. Steam is fed into the system from the boiler via a central pipe, fitted with a valve and a Spirax Sarco DIVA steam flow meter system to measure the flow rate in kg/h.

The outlet end is fitted with a flexible joint to be able to facilitate the expansion of the system, and then attached to a water-cooled vibrating exit feeder, which empties the product into a bucket, which this is then bagged. Presently, there is no oxygen meter fitted to the system, there are sample points and pressure measurement points fitted before the exhaust fan, but these are very hot, typically around 600–700 °C, making gas measurement by Drager tube difficult/impossible.

2.2.2. Equilibrium sorption test

The isotherm studies have been undertaken to assess the efficiency of the adsorbent to remove Methylene Blue dye from aqueous solution. Batch adsorption experiments were carried out by shaking constant mass (0.05 g) of a pre-determined size of adsorbent with constant volume (50 ml) of Methylene Blue solutions of increasing initial dye concentration (100–1000 ppm) to maintain constant mass to volume ratio. The pH of the solutions was adjusted to the required value by adding either 1.0N HCl or 1.0N NaOH. Buffer solution of potassium phosphate (1 mM) was added to the dye solution to enable better control of the pH because the dye has acid–base characteristics. Each jar was sealed using parafilm and kept in a state of agitation (100 rpm) using Gerhardl Laboshaker for the pre-determined period to reach equilibrium (3 weeks). Upon equilibrium, the samples were filtered and analysed using Perkin-Elmer UV/vis spectrometer (Lambda 12 model, Germany). The first part of the filtrate was discharged to avoid the effects of dye adsorption on the filter paper. All the measurements were made at a wavelength corresponding to the maximum absorbance of 663. Dilution were undertaken when absorbance exceed 1.0. The amount of dye adsorbed onto the activated carbon was measured by subtracting the remaining concentrations of the dye solution from the initial concentration. The effects of pH and adsorbent particle size on the adsorption process were studied. Blank samples were prepared to account for any colour leached from adsorbent.

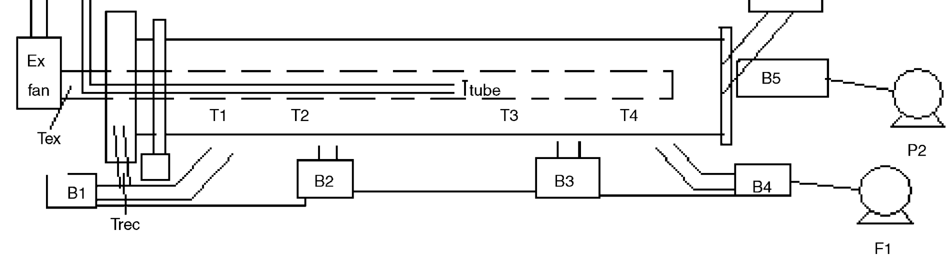

Fig. 2. Simplified schematic diagram of the kiln.

3. Mathematical modelling

The study of the adsorption equilibrium isotherm is helpful in determining the maximum adsorption capacity of adsorbate for the given adsorbent [24]. Adsorption equilibrium is a dynamic concept achieved when the rate at which molecules adsorb on to a surface is equal to the rate at which they desorb [21]. At equilibrium, no change can be observed in the concentration of the solute on the solid surface or in the bulk solution. The position of equilibrium is characteristic of the entire system; the solute, adsorbent, solvent, temperature, pH and so on [20]. An empirical expression of equilibrium adsorption is frequently used. The distribution coefficient between the solid phase and aqueous phase, K_d is defined as the ratio of the concentration of the adsorbate bound to solids to the total dissolved concentration at equilibrium.

$$K_d = \frac{[S-M]}{[M_T]} \tag{1}$$

where S represents the solid surface, M represents the adsorbate, $[M_T]$ is the total dissolved aqueous concentration (mg/dm^3), $[S-M]$ the adsorbed concentration (mg/g) and K_d is the distribution coefficient (dm^3/g). K_d is an equilibrium constant that is too empirical for some purposes, but it can be quite useful for comparisons of adsorption in complex adsorption systems [25].

Generally, the capacity of an adsorbent for a particular adsorbate involves the interaction of three properties: the concentration, C_e, of the adsorbate in the fluid phase, the concentration, q_e, of the adsorbate in the solid phase and the temperature, T, of the system. If T is kept constant, C_e and q_e can be graphed to represent the equilibrium. Such a plot gives an adsorption isotherm [21]. An adsorption isotherm shows the equilibrium relationship at constant temperature, of concentration in the fluid and the adsorbed quantity. The equilibrium adsorption isotherm is fundamentally important in the design of adsorption systems. Such adsorption isotherms may be used for scaling-up batch type processes with moderate success [26,27]. The shape of the equilibrium adsorption isotherm provides information about the homogeneity and heterogeneity of the adsorbent surface [28].

Three adsorption isotherm models were used in this work, Langmuir, Freundlich and Redlich–Peterson Isotherms. They differ in the basic assumptions, shape of the isotherm and nature of the adsorbent surface [28].

3.1. Langmuir isotherm model

This model can be described by the following form:

$$q_e = \frac{QK_LC_e}{1+(a_LC_e)} \tag{2}$$

where q_e is the solid phase equilibrium concentration (mg/g), C_e the liquid phase equilibrium concentration (mg/dm^3), Q an energy term and in most cases equal to unity and K_L (dm^3/g) and a_L (dm^3/mg) are the Langmuir constants.

The model assumes that adsorption occurs on a homogenous adsorbent surface of identical sites that are equally available and energetically equivalent with each site carry equal numbers of molecules and no interaction between adsorbate molecules [28–30].

Table 2
Values of separation factor R_L

Value of R_L	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favourable

Eq. (3) below represents the linearized form of Langmuir equation.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L}C_e \tag{3}$$

Thus, a linear plot of C_e/q_e versus C_e confirms the validity of the Langmuir model. For Langmuir type adsorption process, the influence of the isotherm shape on whether adsorption is “favourable” or “unfavourable” can be classified by a term “R_L” a dimensionless constant separation factor [31].

$$R_L = \frac{1}{1+K_LC_o} \tag{4}$$

where R_L is a dimensionless constant separation factor, C_o the initial concentration of dye solution (mg/dm^3) and K_L is the Langmuir constant (dm^3/g). The parameter R_L indicates the shape of the isotherm accordingly. Table 2 depicts the values of R_L.

3.2. Freundlich isotherm model

The Freundlich isotherm assumes that the adsorption occurs on heterogeneous surface at sites with different energy of adsorption and with non-identical adsorption sites that are not always available [32,33]. Mathematically it is characterised by the heterogeneity factor ‘$1/n$’ [28].

$$q_e = K_FC_e^{1/n} \tag{5}$$

where K_F is the Freundlich constant (mg/g)/(dm^3/mg)^n and n is the heterogeneity factor. The K_F value is related to the adsorption capacity; while $1/n$ value is related to the adsorption intensity. Freundlich model can be represented by the linear form as follows:

$$\ln q_e - \ln K_F = \frac{1}{n}\ln C_e \tag{6}$$

A plot of $\ln q_e$ versus $\ln C_e$, gives a straight line with K_F and $1/n$ determined from the intercept and the slope, respectively.

3.3. Redlich–Peterson isotherm model

The formula of Redlich–Peterson isotherm model can be represented by Eq. (7):

$$q_e = \frac{K_rC_e}{(1+a_rC_e^{\beta})} \tag{7}$$

where K_r is the modified Langmuir constant (dm^3/g), a_r (dm^3/mg) and β are the constants. For simplicity, $K_r = K_L$. This model can describe the adsorption process over a wide range of concentrations. It has a linear dependence on concentration in the numerator and an exponential function in the denominator [26].

a_r and β can be estimated from the slope and the intercept of the linearised form of Redlich–Peterson equation, respectively.

$$\log\left(\frac{K_r C_e}{q_e}-1\right)=\beta\log C_e+\log a_r \qquad (8)$$

4. Results and discussions

Equilibrium relationships between adsorbent and adsorbate can be described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium. The distribution of dye between the adsorbent and dye solution, when the system is in a state of equilibrium, is important in establishing the capacity of the adsorbent for the dye [30]. The capacity of activated carbon for a given pollutant is usually determined by carrying out an adsorption isotherm. In order to characterise the adsorption power of adsorbent, the application of adsorption technique for the treatment of basic dye (MB) solutions using low cost material has been investigated. The effect of the solution pH and adsorbent particle size on the removal of Methylene Blue from aqueous solution has been studied.

4.1. *Effect of solution pH*

The pH of solution from which adsorption occurs may influence the extent of adsorption. pH affects adsorption in that it governs the degree of ionization of the acidic and basic compounds [34]. In general, initial pH value may enhance or depress the uptake. This is attributed to the change of the charge of the adsorbent surface with the change in pH value. The effect of pH can be described on the basis of the influence of pH on the zero point of charge (pH$_{ZPC}$), which is the point at which the net charge of the adsorbent is zero.

Fig. 3 shows the relationships between the amount of MB adsorbed per unit mass of activated carbon (PAC2) and their final concentrations in the aqueous solution at different pH values. It can be seen from the figure that as the solution pH increases, the adsorption capacity increases with a significant enhancement in the adsorption process occurring as the pH increased from 9 to 11 (alkaline range). The maximum adsorption capacity defined as the amount at the isotherm plateau, was increased from 312 (mg/g) at pH 4 to 580 (mg/g) at pH 11. This can be attributed to the electrostatic attraction between the positively charged dye and the negatively charged surface of PAC2 (pH > pH$_{ZPC}$). Increasing solution pH increases the number of hydroxyl groups thus, increases the number of negatively charge sites and enlarges the attraction between dye and adsorbent surface [35]. According to Al-Degs et al. [36], pH$_{ZPC}$ can be used as index of the ability of the surface to become either positively or negatively charged. This ability is controlled by the pH of the surrounding solution. When pH of solution <pH$_{ZPC}$, the activated carbon adsorbent will react as a positive surface and as a negative surface when pH of solution >pH$_{ZPC}$. Thus, as pH was increased, the surface functional groups on the carbon were deprotonated, which results in a decrease in surface charge density. This implies that adsorption of cationic dye could be enhanced at higher pH [37].

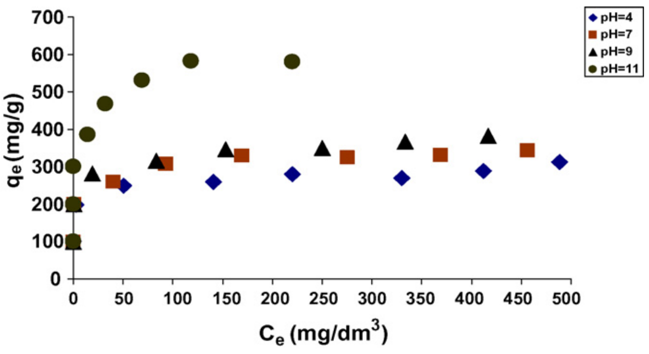

Fig. 3. Effect of the solution pH on the adsorption of Methylene Blue onto PAC2. Mass of adsorbent, 0.05 g; volume of dye solution, 50 ml; concentration, 100–800 mg/dm^3; particle size, <106 μm; temperature, 20 °C.

The experimental determination of pH$_{ZPC}$ of PAC2 revealed that this activated carbon has pH$_{ZPC}$ 6.3. The equilibrium values of pH of solution were in the range of 8.2–9.0 in the case of initial value of pH solution = 11. This mean that the pH of the solution >pH$_{ZPC}$. Thus, in this case the activated carbon adsorbent acts as a negative surface and attracts the positively charged dye (MB). Sastri [15] reported that alkalinity enhanced the adsorption of electropositive substances, such as Methylene Blue. The author also referred to the existence of a characteristic region of pH for each carbon in which maximum variations of adsorption are noticeable and suggested that the change in adsorption in this region is due to a sharp variation in the sign and magnitude of the charge carried by the adsorbent. Generally, the net positive charge decreases with increasing pH value lead in the decrease in the repulsion between the adsorbent surface and dye and thus, improving the adsorption capacity. It is also obvious from the figure that as loading increases, the driving forces for adsorption decrease, leading to an ultimate saturation value beyond which further adsorption is not feasible.

4.2. *Effect of adsorbent particle size*

Adsorption is a surface phenomenon; as such, the extent of adsorption is proportional to specific surface area, i.e., to that portion of the total surface area that is available for adsorption [38]. The effect of particle size was determined by conducting the adsorption process with activated carbons of different particle size, namely, <106, 106–180, 180–250 and 250–500 μm. Fig. 4 illustrates a plot of solid phase concentration versus liquid phase concentration for Methylene Blue adsorption onto PAC2 at different particle sizes. The results show the role played by the adsorbent particle size on the adsorptive properties of activated carbons. As the particle size decreases, the adsorption capacity of PAC2 increased. For example, the adsorption capacity from a solution with a concentration of 600 (mg/dm^3) was increased

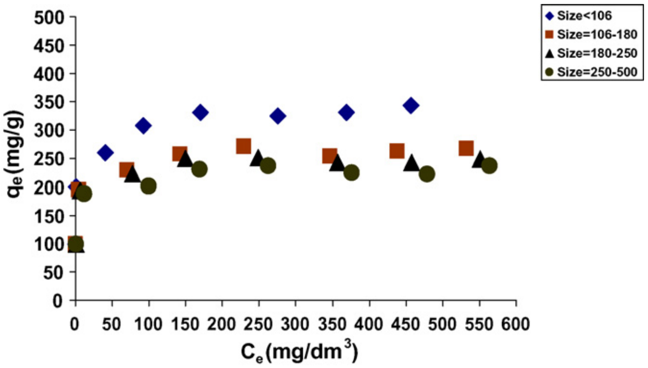

Fig. 4. Effect of adsorbent particle size on the adsorption of Methylene Blue onto PAC2. Mass of adsorbent, 0.05 g; volume of dye solution, 50 ml; concentration, 100–800 mg/dm^3; pH, 7; temperature, 20 °C; size in μm.

from 253 to 325 (mg/g) as the particle size decreases from 106 to 180 μm to size <106 μm.

An increase in capacity with decreasing particle size mainly suggests that the dye molecules do not completely penetrate the particle or partly that the dye molecules preferentially adsorb near the outer surface of the particle [39]. The effect of adsorbent particle size on the adsorption process can be explained as follow, as the particle size decreases, more surface area are available for the adsorption process. Matthews [40] ascribed the increases in adsorption capacity with decreasing the particle size to that adsorption is limited to the external surface area of the adsorbent as the smaller particles have a larger external surface area for adsorption process. A similar trend was observed by Poots et al. [41] when peat was used to remove acid dyes from aqueous solution. The authors attributed this trend to the inclusion of the surface area associated with pores inside the particles, thus limiting the adsorption to the external surface area and a narrow layer just below the surface.

4.3. Adsorption equilibrium modelling

The capacity of activated carbon for various dyestuffs can be determined by measuring equilibrium isotherms. Basically, adsorption isotherm is important to describe how adsorbates interact with adsorbents. Thus, the correlation of the equilibrium data by either theoretical or empirical equations is essential to practical operation [41]. Adsorption isotherms were analysed according to Langmuir, Freundlich and Redlich–Peterson models. The constants in Langmuir and Freundlich are very useful parameters for predicting adsorption capacities and also for incorporating into mass transfer relationship to predict the design of contacting experiments [31].

Adsorption isotherms were analysed according to the linear form of Langmuir, Freundlich and Redlich–Peterson isotherms using Eqs. (3), (6) and (8), respectively, and the parameters, k_L, a_L of the Langmuir, the values of the ratios k_L/a_L which represents the maximum adsorption capacity (monolayer saturation capacity), Q (mg/g), of the adsorbent for a particular dyestuff, Freundlich constants, K_F, n and Redlich–Peterson constants, β, a_r were determined for Methylene Blue dye. Table 3 displays the results of the calculated isotherm constants at different pH values and different adsorbent particle sizes.

It is obvious that the monolayer capacity of Methylene Blue onto PAC2 was significantly the highest at pH 11. This is consistent with the earlier findings. The results in Table 3 also illustrates that the monolayer saturation capacity decreases with increasing particle size. This effect is probably due to the inability of the large molecules to penetrate all the internal pore structure of activated carbon particles.

In general, Langmuir equation is intended for a homogenous surface. A good fit of this equation reflects monolayer adsorption; on the other hand, a good representation of the Freundlich equation, which is suitable for a highly heterogeneous surface, probably indicates multilayer adsorption [11]. According to Redlich and Peterson [42], Freundlich adsorption isotherm is well known to give an excellent representation of many data for moderate partial pressures and concentrations. It is not a reasonable relation for dilute solutions.

Although the correlation coefficients for Freundlich isotherm are significantly less than that of Langmuir and Redlich–Peterson isotherms, Freundlich isotherm was able to describe the experimental data especially at concentration range of 300–700 (mg/dm^3). However, since the correlation coefficient, r^2, yields the best fit isotherm constants based on the

Table 3
Langmuir, Freundlich and Redlich–Peterson isotherm constants for PAC2 and MB dye systems at different pH values and different adsorbent particle sizes

pH	Langmuir				Freundlich			Redlich–Peterson			R_L
	k_L (dm^3/g)	a_L (dm^3/mg)	Q (mg/g)	r^2	k_F (mg/g)/(dm^3/g)^n	n	r^2	β	a_r (dm^3/mg)	r^2	
4	27.77	0.0916	298	0.9924	182.55	13.04	0.9396	0.9923	0.0984	0.9961	0.043
7	51.81	0.1502	345	0.9986	185.18	9.740	0.8611	0.9446	0.2087	0.9989	0.023
9	47.61	0.1238	385	0.9970	209.15	10.33	0.9762	1.0150	0.1185	0.9950	0.025
11	172.4	0.2930	588	0.9930	265.95	6.430	0.9281	0.9003	0.4808	0.9990	0.007

Size (μm)	Langmuir				Freundlich			Redlich–Peterson			R_L
	k_L (dm^3/g)	a_L (dm^3/mg)	Q (mg/g)	r^2	k_F (mg/g)/(dm^3/g)^n	n	r^2	β	a_r (dm^3/mg)	r^2	
<106	51.810	0.1502	345	0.9986	185.18	9.74	0.8611	0.9446	0.2087	0.9989	0.023
106–180	63.290	0.2405	263	0.9987	177.13	14.85	0.9003	0.9528	0.2962	0.9975	0.013
180–250	107.52	0.4300	250	0.9993	177.54	17.76	0.8627	1.0204	0.3886	0.9996	0.011
250–500	48.780	0.2097	233	0.9971	162.36	17.30	0.7456	1.0368	0.1716	0.9976	0.024

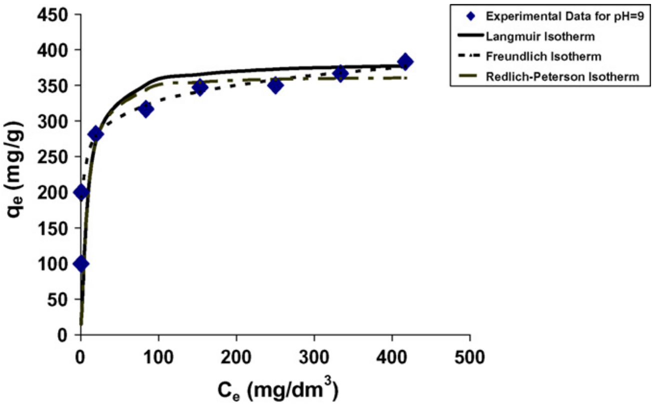

Fig. 5. Model fit of adsorption isotherm of Methylene Blue adsorption onto PAC2.

linearised isotherm plots, it may not provide the best isotherm constants to correlate the original isotherm equation with the experimental data [43]. Langmuir model fit the adsorption data quite well at high dye concentration and Redlich–Peterson isotherm shows the best fit of the experimental data over the whole concentration range and this is clear from the correlation coefficient in Table 3. According to the values of R_L, all the systems show favourable adsorption of Methylene Blue, i.e., $0 < R_L < 1$. The low values of R_L indicate high and favourable adsorption of Methylene Blue onto PAC2.

The values of the heterogeneity factor ($1/n$) in Table 3 indicate that the activated carbon has a heterogeneous structure. The results show that the value of n is greater than unity indicating that the dye is favourably adsorbed by the activated carbon. This is in great agreement with the findings regarding to R_L values. The magnitude of Freundlich constant indicates easy uptake of Methylene Blue from aqueous solution. In order to assess the different isotherms and their ability to correlate the experimental results, the theoretical plots for each isotherm have been shown with the experimental data for the adsorption of Methylene Blue onto PAC2. Fig. 5 shows the fit of the isotherm models to the experimental data for the adsorption of Methylene Blue onto PAC2 at pH 9 and Fig. 6 shows the fit of the isotherm models to the experimental data for Methylene Blue and PAC2 at particle size 180–250 μm.

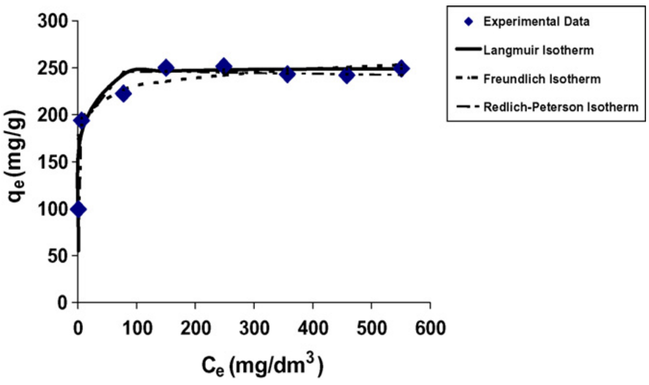

Fig. 6. Model fit of adsorption isotherm of Methylene Blue adsorption onto PAC2 at particle size, 180–250 μm.

5. Conclusions

Liquid phase adsorption processes were employed and adsorption isotherms were constructed to investigate adsorption capacity and ability of the adsorbent to remove Methylene Blue dye from aqueous solution. Effects of the experimental conditions on the performance of the adsorbent in the equilibrium study were investigated. Experimental data were mathematically modelled using different useful mathematical models.

pH plays a major role in the adsorption process. The optimum pH for the removal of MB from aqueous solution under the experimental conditions used in this work was 11. This exhibits the role of pH in imparting adsorbent surface charge. As the particle size decreases, the adsorption capacity of PAC2 increased. The increase in capacity with decreasing particle size mainly suggests that the dye molecules do not completely penetrate the particle or partly that the dye molecules preferentially adsorb near the outer surface of the particle. Therefore, it can be concluded that smaller activated carbon particles are recommended for such adsorption processes. Of the three isotherm models applied, Langmuir, Freundlich and Redlich–Peterson, the Redlich–Peterson isotherm was found to best fit the experimental data over the whole concentration range as indicating from the high values of the correlation coefficients ($r^2 > 0.99$). The closeness of the correlation coefficient to unity would indicate a perfect fit. All the adsorption systems studied show favourable adsorption of the basic dyes as indicated from the low value of R_L ($0 < R_L < 1$).

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