

Adsorption of basic dyes from aqueous solution onto activated carbons

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Received 22 May 2006; received in revised form 21 February 2007; accepted 26 February 2007

Abstract

The aim of this research is to compare the adsorption capacity of different types of activated carbons produced by steam activation in small laboratory scale and large industrial scale processes. Equilibrium behaviour of the activated carbons was investigated by performing batch adsorption experiments using bottle-point method. Basic dyes (methylene blue (MB), basic red (BR) and basic yellow (BY)) were used as adsorbates and the maximum adsorptive capacity was determined. Adsorption isotherm models, Langmuir, Freundlich and Redlich–Peterson were used to simulate the equilibrium data at different experimental parameters (pH and adsorbent particle size). It was found that PAC2 (activated carbon produced from New Zealand coal using steam activation) has the highest adsorptive capacity towards MB dye (588 mg/g) followed by F400 (476 mg/g) and PAC1 (380 mg/g). BR and BY showed higher adsorptive affinity towards PAC2 and F400 than MB. Under comparable conditions, adsorption capacity of basic dyes, MB, BR and BY onto PAC1, PAC2 and F400 increased in the order: MB < BR < BY. Redlich–Peterson model was found to describe the experimental data over the entire range of concentration under investigation. All the systems show favourable adsorption of the basic dyes with $0 < R_L < 1$.

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Keywords: Adsorption; Equilibrium isotherm; Basic dye; Activated carbon

1. Introduction

Today, rapidly changing technologies, industrial products and practices generate waste that if improperly managed, could threaten public health and the environment [1]. Among all industrial sectors, textile industries are rated as high polluters, taking into consideration the volume of discharge and effluent composition [2]. In general, several difficulties are encountered in removal of dyes from wastewaters. By design, dyes are highly stable molecules, made to resist degradation by light, chemical, biological and other exposures. Commercial dyes are usually a mixture of large complex and have often unreported molecular structure and properties. Dyes also vary widely in chemical composition. Furthermore, dyeing wastewater compositions are not simple solutions of dye in water, but include many other materials such as particulates, processing assistants, salts, surfactants, acids and alkalis [3]. Basic dyes are considered as one of the more problematic classes of dye. Generally, basic dyes are cationic dyes with cationic properties originating from the positive charge that is generally delocalized throughout the chro-

mophoric system, although it is probably more localized on the nitrogen atoms. Basic dyes are so called because of their affinity to basic textile materials with net negative charge [4]. Basic dyes have been classified according to their chemical constitution as well as dyeing properties. In chemical classification, the term “cationic dyes” is usually preferred [5]. This class of dye can be applied to wool, silk and leather and also to tannin-mordanted cotton [6]. According to Anliker et al. [7], basic dyes have been classified as toxic colorants. As a result, improved or cost effective technologies are required to remove them from textile effluents.

Considerable attention has been paid to adsorption technologies as efficient and versatile methods of removing dyes from textile wastewater effluents. Adsorption is a separation process by which certain components of a fluid phase are attracted to the surface of a solid adsorbent and form attachments via physical or chemical bonds, thus removing the component from the fluid phase [8,9]. More precisely, adsorption processes usually occur in interfacial layers which are regarded as two regions: the surface layer of the adsorbent (often simply called the adsorbent surface) and the adsorption space, in which the enrichment of the adsorptive can occur [10,11].

In general, adsorption processes may be classified as physical or chemical depending on the nature of forces involved. Many

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physico-chemical factors influence the adsorption process and these include; adsorbate/adsorbent interaction, adsorbent surface area and pore structure, chemistry of the surface, nature of the adsorbate, effect of other ions, particle size, pH, temperature, contact time, etc. [3,12]. The low cost, simple design, easy handling and sludge free cleaning operations have established the adsorption technique as more effective and convenient in comparison to other techniques such as: coagulation, flocculation, precipitation and activated sludge [13,14].

A significant body of research on textile wastewater decolorization using adsorption has been conducted. Al-Qaisieh [15] studied the ability of the untreated date seeds to remove basic dyes using an agitated batch adsorber. It was found that palm seeds have moderate adsorption capacity for methylene blue and no tendency to adsorb phenol and *p*-nitrophenol. Al-Degs [16] studied the tendency of commercial activated carbons to adsorb problematic reactive dyes from aqueous solution. The results showed that activated carbon was effective and its capacity was from 20 to 100 g dye/g carbon. Chern and Huang [17] used the granular activated carbon for the removal of yellow and red acid dyes from aqueous solution. The results showed that the activated carbon was very effective in removing the dyes from aqueous solution.

Adsorption processes provide a feasible treatment especially if the adsorbent is inexpensive and readily available [18]. Among commercial adsorbents, activated carbon is the most commonly used adsorbent [19,20]. The use of activated carbon has been highlighted as an effective technique for dye removal. Due to its unique molecular structure, activated carbon has an extremely high affinity for many classes of dyes including basic dyes [21].

The present work is focussed on the comparison of the adsorption capacity of three activated carbons (PAC1 and PAC2 developed at QUB for this work, and commercially available Filtrasorb 400). Basic dyes were chosen to be the model adsorbates, due to: (i) toxicity of basic dyes; (ii) the tinctorial value of basic dyes is very high, less than 1 ppm of dye is visible in solution [22]; (iii) basic dyes ionise in solution and form cations which will have high affinity for negatively charged adsorbent surfaces and facilitate adsorption processes [23].

2. Experimental

2.1. Materials

Three basic dyes, which pose significant problems for removal by conventional technologies, were chosen as the model adsorbates. These include; methylene blue C. I. 52015 (MB) (ACROS Organics, USA); basic red C. I. 22 (BR); basic yellow C. I. 21 (Dyestar, GmbH & Co., Frankfurt). All dyes were commercial samples and were used without further purification. Table 1 lists the physical characteristics of the adsorbates used in this work and Fig. 1 depicts the chemical structure.

Three activated carbons were used in this work. PAC2 was produced, in conjunction with QUB, by the steam activation of New Zealand bituminous coal on a pilot scale using rotary kiln. This carbon was produced at a temperature of 1050 °C and steam concentration of 120 kg steam/kg carbon. The kiln

Table 1
Physical characteristics of the adsorbates

Dye	Molecular volume ^a (cm ³ /mol)	Molecular diameter ^a (nm)
Methylene blue	241.9	0.8 ^b
Basic red 22	337.6	1.13
Basic yellow 21	419.3	1.24

^a James and Lord [48].

^b Calvo et al. [49].

had a mean residence time of 7 h. Filtrasorb 400 supplied by Chemviron Carbon (UK). F400 is one of the most widely used grades of activated carbon in the wastewater treatment industry. It is produced by the gas activation of bituminous coal and it has high surface area (1050–1200 m²/g) and good mechanical hardness [24]. PAC1 refers to the activated carbon produced from Venezuelan bituminous coal in a laboratory scale processes using physical activation (detailed description of the production process is found elsewhere [25]).

The adsorbents were 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. Surface area, total pore volume and pore size distribution of the activated carbons were determined from N₂ adsorption/desorption isotherms using an adsorption apparatus (Nova 4200, Quantachrome Instruments, UK). The measured relative pressure and adsorbed volume of nitrogen gas were used in multi-point BET method to calculate the monolayer coverage of nitrogen

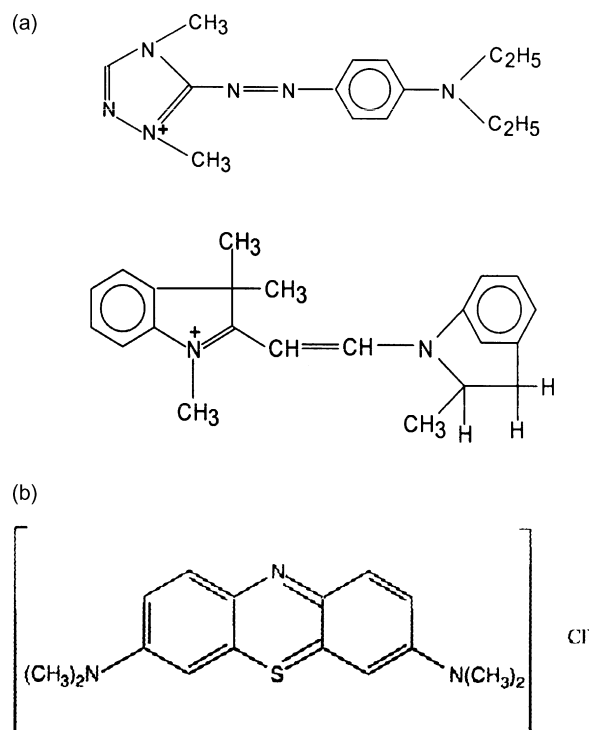


Fig. 1. Chemical structure of adsorbates: (a) basic red 22; (b) basic yellow 21; (c) methylene blue.

Table 2
Physical and chemical characteristics of activated carbons

	F400	PAC1	PAC2
Ultimate analysis			
C (%)	62.10	78.22	81.78
H (%)	0.51	0.4	0.35
N (%)	0.3	0.67	0.38
O (%)	35.67	19.18	16.77
S (%)	1.42	1.53	0.72
Proximate analysis			
Ash (%) ^a	6	26.10	3.66
Moisture (%)	2	2.044	5.717
Volatile (%) ^a	–	2.833	2.232
Fixed carbon	–	69.023	88.39
Total surface area (BET) (m ² g ⁻¹)	1216.4	863.50	857.14
Micropore surface area (m ² g ⁻¹)	918.70	783.58	801.83
Total pore volume (cm ³ g ⁻¹) × 10 ¹	8.211	4.695	4.467
Micropore volume (cm ³ g ⁻¹)	0.456	0.380	0.389
Average pore radius (nm)	1.124	1.233	1.210
Surface acidity ^b (mequiv. g ⁻¹)	0.408	0.389	0.462
Surface basicity ^b (mequiv. g ⁻¹)	0.610	0.482	0.560
pH _{solution} (10 wt%)	8.30	7.95	8.20
pH _{ZPC} ^c	7.80	8.30	6.30

^a Calculations were done on dry basis.

^b Both the surface acidity and basicity of the activated carbons were determined by using titration methods as reported by Al-Degs et al. [50].

^c Alkalimetric titration technique recommended by Al-Ghouti et al. [51] was adopted to measure surface charge density of activated carbons and to determine pH_{ZPC}.

adsorbed on the adsorbent surface from which total surface area was then calculated. The characteristics of pore structure and pore size distribution of mesopores was identified using *t*-plot and BJH methods. Pore size distributions were evaluated by applying the BJH method whereas the *t*-plot method was used to estimate V_{micro} . Table 2 shows the physical and chemical characteristics of the adsorbents used in this work.

2.2. Methods

Equilibrium relationships between adsorbent and adsorbate can be described by adsorption isotherms. Batch adsorption experiments were undertaken in 100 ml flasks. Stock of dye solution was prepared (1000 ppm) and diluted accordingly to obtain concentrations within the range 100–1000 ppm. 0.05 g of a pre-determined size of adsorbent was brought into contact with 50 ml of dye aqueous solution of a desired concentration and pH in the flask. The pH of the solution 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, due to the acid–base characteristic of the dyes. Preliminary samples of the dye solution and potassium phosphate were scanned between 300 and 700 cm⁻¹ to check if there is chemical interaction between the dyes and potassium phosphate. Results indicated that there were no such interactions. Each bottle was kept in a state of agitation (100 rpm) using Gerhardt Laboshaker for the pre-determined period to reach equilibrium (preliminary experiments had shown that the adsorption studied was completed

after 21 days). Upon equilibrium, samples of (4–5) ± 0.5 ml were withdrawn and filtered through 0.45 μm cellulose nitrate membrane, 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. Analysis was made at the wavelength corresponding to the maximum absorbance of 663, 533 and 416 for MB, BR and BY, respectively. The amount of dye adsorbed onto the activated carbon was calculated by a mass balance. 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. Duplicate samples were measured and the standard deviation was found to be less than 2%. The equilibrium solid phase concentration, q (mg/g) was then calculated according to the following equation:

$$q = \frac{V}{m}(C_i - C_e) \quad (1)$$

where C_i and C_e are the initial and equilibrium dye concentrations, respectively (mg/l), V the volume of solution (l) and m is the mass of adsorbent (g).

3. Results and discussion

3.1. Effect of solution pH

The adsorption behaviour of methylene blue (MB) using activated carbons in both acidic and alkaline solutions was studied. Fig. 2 illustrates the effect of the pH of the solution on the amount of MB adsorbed per unit mass of activated carbon (PAC2). From the data, it is evident that increasing solution pH serves to increase the adsorption capacity, with a significant enhancement in the adsorption process occurring as the pH increased from 9 to 11. The maximum adsorption capacity 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 [26]. Thus, as pH was increased, the surface functional groups on the carbon were deprotonated, which

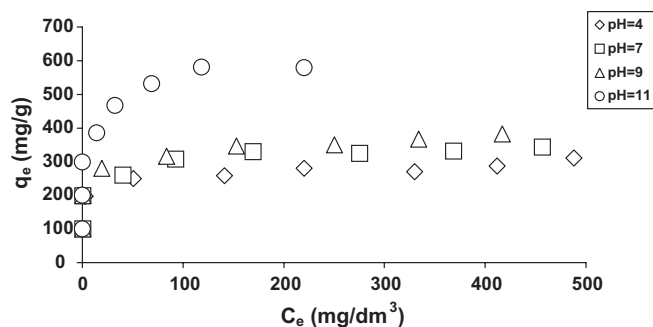


Fig. 2. Effect of the solution pH on the adsorption of methylene blue onto PAC2. Mass of adsorbent = 0.05 g, volume of dye solution = 50 ml, concentration = 100–800 mg/dm³, particle size < 106 μm, temperature = 20 °C.

results in a decrease in surface charge density. This implies that the adsorption of cationic dye could be enhanced at higher pH [27].

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 means 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 [28] reported that alkalinity enhanced the adsorption of electropositive substances, such as methylene blue. Sastri [28] 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 leading to the decrease in the repulsion between the adsorbent surface and dye and thus, improving the adsorption capacity. Al-Degs [16] reported that activated carbon adsorbents generally carried a net negative surface charge in solution which has significance for adsorption processes in which cationic dyes are involved.

It is also obvious that as loading increases, the driving forces for adsorption decrease, leading to an ultimate saturation value beyond which further adsorption is not feasible. Similar effect of solution pH on the adsorption of methylene blue onto F400 and PAC1 were observed with maximum adsorption capacity, $q_{emax} = 372$ and 492 mg/g for PAC1 and F400, respectively (data summarised in Table 3). Figs. 3 and 4 show the adsorption isotherms of PAC1 and F400 as a function of pH, respectively. These variations in the capacity for the three activated carbons can also be explained in terms of pH_{ZPC} . Adsorptive capacity of PAC1 is lower than that of F400 and PAC2 due to the fact that this adsorbent has pH_{ZPC} 8.2 and the equilibrium values of the solution pH were less than pH_{ZPC} even in the case of initial value of solution pH 11.

Surface acidity and basicity can provide another explanation for the higher adsorptive capacity of PAC2. The data in Table 2 indicate that PAC2 has higher surface acidity than that of F400. However, the acidic sites on adsorbent surface are usually responsible for MB adsorption, as a result, it is reasonable that PAC2 has higher adsorptive capacity toward MB than F400.

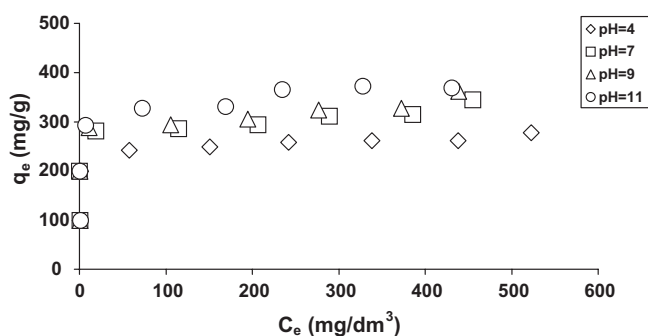


Fig. 3. Effect of the solution pH on the adsorption of methylene blue onto PAC1. Mass of adsorbent = 0.05 g, volume of dye solution = 50 ml, concentration = 100–800 mg/dm³, particle size < 106 μ m, temperature = 20 °C.

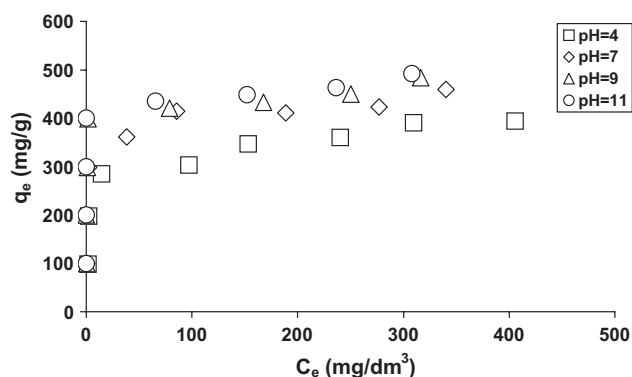
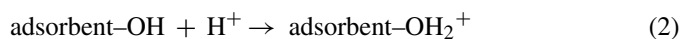
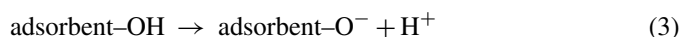


Fig. 4. Effect of the solution pH on the adsorption of methylene blue onto F400. Mass of adsorbent = 0.05 g, volume of dye solution = 50 ml, concentration = 100–800 mg/dm³, particle size < 106 μ m, temperature = 20 °C.

Ko et al. [29] proposed two expressions for the adsorbent surface acidity and basicity according to the following equations:



and



where Eq. (2) expresses surface basicity and Eq. (3) expresses surface acidity.

Although relating carbon performances to their surface area and pore structure is an accepted strategy, since higher surface areas often offer more interaction probabilities in solution and can accommodate more molecules [16], however this concept is not valid for certain systems. For example, at pH 11, PAC2 shows higher adsorptive capacity toward MB than F400, although F400 has higher surface area and microporosity. According to Allen et al. [30] and Giles et al. [31], the solute adsorbs onto the surface due to the affinity of the surface for the solutes. The adsorbate molecules can be linked to molecular wedges creating access to new surfaces and effectively clearing blocked pores. This process will tend to further increase the adsorptive capacity of the adsorbent [30,31].

F400 shows higher adsorptive capacities in the range of pH 4–9 than PAC2 and PAC1, although the equilibrium values of the solution pH $< pH_{ZPC}$. The adsorptive capacity was attributed to the large surface area and well-developed porosity. This behaviour confirms that physical characteristics and surface chemistry can affect the adsorption process. The differences in the adsorptive capacities of F400 and PAC2, for pH 11 can be attributed to the surface charge density determination. Data indicated that PAC2 has higher negative charge than F400, as a result, the electrostatic attraction between adsorbent surface and MB will be stronger in the case of PAC2.

Although PAC1 and PAC2 have comparable physical characteristics (i.e., surface area and total pore volume), there were significant differences in the adsorptive capacities of these two activated carbons particularly at solution pH 11. This variation in the adsorption capacity showed low correlation between adsorptive capacities and physical properties of the carbons. Similar behaviour was obtained by Al-Degs et al. [32] when anionic

Table 3
Langmuir, Freundlich and Redlich–Peterson isotherm constants for adsorbents and MB dye systems at different pH values

pH	Langmuir				Freundlich		
	K_L (dm ³ /g)	a_L (dm ³ /mg)	q_m (mg/g)	r^2	K_F (mg/g)/(dm ³ /g) ⁿ	n	r^2
PAC2							
4	27.770	0.0916	298	0.9924	182.55	13.04	0.9396
7	51.810	0.1502	345	0.9986	185.18	9.740	0.8611
9	47.610	0.1238	385	0.9970	209.15	10.33	0.9762
11	172.41	0.2930	588	0.9930	265.95	6.430	0.9281
pH	Redlich–Peterson			R_L			
	β	a_r (dm ³ /mg)	r^2				
PAC2							
4	0.9923	0.0984	0.9961	0.043			
7	0.9446	0.2087	0.9989	0.023			
9	1.0150	0.1185	0.9950	0.025			
11	0.9003	0.4808	0.9990	0.007			
pH	Langmuir				Freundlich		
	K_L (dm ³ /g)	a_L (dm ³ /mg)	q_m (mg/g)	r^2	K_F (mg/g)/(dm ³ /g) ⁿ	n	r^2
PAC1							
4	38.91	0.1439	270	0.9979	197.74	20.4	0.9772
7	36.76	0.1199	307	0.9933	234.69	19.72	0.6220
9	38.75	0.1124	345	0.9925	248.31	20.79	0.6150
11	72.99	0.1920	380	0.9982	257.57	16.92	0.9006
pH	Redlich–Peterson			R_L			
	β	a_r (dm ³ /mg)	r^2				
PAC1							
4	0.9922	0.1511	0.9990	0.031			
7	1.1100	0.0602	0.9930	0.033			
9	0.9107	0.1897	0.9951	0.031			
11	0.9490	0.2646	0.9937	0.016			
pH	Langmuir				Freundlich		
	K_L (dm ³ /g)	a_L (dm ³ /mg)	q_m (mg/g)	r^2	K_F (mg/g)/(dm ³ /g) ⁿ	n	r^2
F400							
4	28.810	0.0670	430	0.9938	185.31	8.03	0.9468
7	88.490	0.1946	455	0.9960	278.16	12.5	0.9520
9	138.88	0.2916	476	0.9965	335.50	18.05	0.6945
11	196.07	0.4117	476	0.9973	373.25	24.39	0.9459
pH	Redlich–Peterson			R_L			
	β	a_r (dm ³ /mg)	r^2				
F400							
4	0.8782	0.1344	0.9979	0.044			
7	0.9585	0.2516	0.9982	0.014			
9	0.9319	0.4343	0.9973	0.008			
11	0.9459	0.5531	0.9987	0.006			

dyes were removed from aqueous solution using different types of activated carbons with comparable physical properties. The authors correlated the differences in the adsorptive capacities to the surface chemistry of the carbons. Juang and Swei [4] explained the adsorption process of basic dye onto the adsorbent surface and considered that many conjugate π -bonds exist on the carbon surface, which are non-localized and highly active. After activation, a number of oxygen-containing functional groups exist in the crystal lattice of the surface, mainly the electron acceptor (e.g., carbonyl and carboxyl). It is thus probable that

electrostatic interaction occurs between the electron-acceptor groups on the activated carbon surface and the positive charge on basic dye compound.

It is clear from Figs. 2–4 that the isotherms have similar shape which may indicate a similar adsorption mechanism. An enhancement in dye adsorption as the liquid phase concentration increases is evident.

PAC2 and F400 were used to investigate their ability to remove basic red 22 (BR) and basic yellow 21 (BY) dyes (data summarised in Table 4). Comparing the adsorptive capacities

Table 4
Langmuir, Freundlich and Redlich–Peterson isotherm constants for adsorbents and BR and BY dye systems at different pH values

pH	Langmuir				Freundlich			
	K_L (dm ³ /g)	a_L (dm ³ /mg)	q_m (mg/g)	r^2	K_F (mg/g)/(dm ³ /g) ⁿ	n	r^2	
PAC2 and BR								
4	104.16	0.3541	294	0.9847	271.02	77.519	0.0308	
7	78.740	0.1338	588	0.9927	328.32	10.694	0.7535	
11	666.66	0.6666	1001	0.9967	379.90	3.157	0.4104	
pH	Redlich–Peterson							
	β						a_r (dm ³ /mg)	r^2
PAC2 and BR								
4						1.0128	0.3263	0.9952
7						0.8622	0.2962	0.9886
11						1.1447	0.3959	0.9887
pH	K_L (dm ³ /g)	a_L (dm ³ /mg)	q_m (mg/g)	r^2	K_F (mg/g)/(dm ³ /g) ⁿ	n	r^2	
								AC2 and BY
7	526.31	0.842	625	0.9978	464.51	21.05	0.4945	
pH	Redlich–Peterson							
	β						a_r (dm ³ /mg)	r^2
PAC2 and BY								
7						0.9620	1.070	0.9976
pH	K_L (dm ³ /g)	a_L (dm ³ /mg)	q_m (mg/g)	r^2	K_F (mg/g)/(dm ³ /g) ⁿ	n	r^2	
								F400 and BR
4	59.880	0.1257	476	0.9892	277.14	11.38	0.4480	
7	59.520	0.1070	556	0.9886	227.56	6.925	0.6571	
11	312.51	0.3437	909	0.9969	480.5	17.56	0.866	
pH	Redlich–Peterson							
	β						a_r (dm ³ /mg)	r^2
F400 and BR								
4						0.9552	0.1641	0.9871
7						0.8967	0.2004	0.9848
11						0.9596	0.4224	0.9945
pH	K_L (dm ³ /g)	a_L (dm ³ /mg)	q_m (mg/g)	r^2	K_F (mg/g)/(dm ³ /g) ⁿ	n	r^2	
								F400 and BY
7	400	0.480	833	0.9994	547.01	12.46	0.6613	
pH	Redlich–Peterson							
	β						a_r (dm ³ /mg)	r^2
F400 and BY								
7						0.9739	0.5517	0.9977

of PAC2 at pH 7 for MB, BR and BY, it was found that PAC2 has higher adsorptive capacities for BY ($q_{\text{emax}} = 645$ mg/g) than for BR ($q_{\text{emax}} = 614$ mg/g) and MB ($q_{\text{emax}} = 343$ mg/g). This can be attributed to the molar volume of the basic dyes. Basic yellow dye has a molecular volume of 419.3 cm³/mol whereas MB and BR have a molecular volume of 241.9 and 337.6 cm³/mol, respectively. It is generally accepted that the capacity for activated carbon adsorption is higher when the adsorbate has a higher molar mass [4]. Allen et al. [30] illustrated that dyes usually associate in aqueous solution to form dimers and pos-

sibly larger micelles. Such large groups of molecules will be hindered in their progression through the porous structure of the adsorbent. The process will be assisted if both the dye and the adsorbent carry opposite charges, which is the case here. Thus, the dye cations will experience physical and electrical attraction forces, the extent of which depends on their structure, molecular size and functional groups.

The differences in the adsorptive capacities were more pronounced in the case of MB furthermore comparative capacities were obtained in the case of BR and BY due to the similar molec-

ular size of both dyes. El Geundi [33] suggests that when dye molecules are of similar size, the molecular mobility in solution and in the adsorbent will be similar and therefore molecular size should have no effect on adsorption capacity.

The effect of pH on the efficiency of F400 for removing BR and BY dyes from aqueous solution was also determined (data summarised in Table 4). It was found that F400 has higher capacity at pH 4 than PAC2. This can be ascribed to the pH_{ZPC} . The equilibrium solution pH for F400 was greater than pH_{ZPC} whereas in the case of PAC2 it was lower. Thus, the adsorptive capacity of F400 was higher than that of PAC2. On the contrary, PAC2 shows higher adsorptive capacity than F400 at pH 11. It is also clear from the data presented in Table 3 that F400 has higher adsorptive capacity for BY than PAC2 which can also be attributed to the effect of pH_{ZPC} , the equilibrium solution pH and the physical characteristics of both adsorbents. When the equilibrium solution pH exceeds the pH_{ZPC} , an enhancement in the adsorptive capacities was observed.

Equilibrium adsorption isotherm data for BR onto PAC2 and F400 at pH 11 (Table 3) indicate a high and extensive uptake of BR. Generally, lower dye uptake was observed as the adsorption process proceeded. This suggests that a decrease in the overall negative charge of the adsorbent surface occurred as the cationic dye is adsorbed due to decreasing attractive forces between the saturated adsorbent surface and unadsorbed dye molecules remaining in the solution.

Sixty to 99.8% of BY dye removal was achieved by PAC2 at pH 7 over the whole range of concentrations (100–1000 mg/l) and 94–99.6% in the case of BR and pH 11.

From these data the use of activated carbons, PAC1, PAC2 and F400 for removing basic dyes is technically feasible. The activated carbon capacities are significantly greater than those obtained previously using low cost adsorbents. Matthews [35] reported a value of $q_{\text{emax}} = 160 \text{ mg/g}$ for the adsorption of BR onto peanut hulls. Allen et al. [30] obtained a values of 235.3 and 390.0 mg/g for the adsorption of BR and BY onto lignite, respectively. A values of 210 and 160 (mg/g) for the adsorption of RB and BY onto Kudzu were recorded by Allen et al. [36]. McKay et al. [37] used bagasse pith to remove acidic and basic dyes from solution. It was found that adsorbent has grater affinities for basic dyes than that for acidic dyes and obtained a value of 76.6 mg/g for BR.

3.2. Effect of adsorbent particle size

Fig. 5 illustrates a plot of solid phase concentration versus liquid phase concentration for methylene blue adsorption onto PAC2 at different particle sizes. As the particle size decreases, the adsorption capacity of PAC2 increased, e.g., the adsorption capacity from a solution with a concentration of 600 mg/dm³ was increased from 253 to 325 mg/g as the particle size decreases from 106–180 μm to size <106 μm .

An increase in capacity with decreasing particle size indicates that the dye molecules do not completely penetrate the adsorbent particle [38]. Matthews [35] correlated increase in adsorption capacity to decrease the particle size and suggested that adsorption may be limited to the external surface area of the

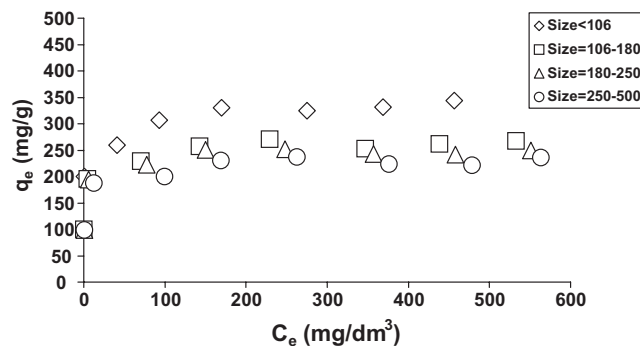


Fig. 5. Effect of adsorbent particle size on the adsorption of methylene blue onto PAC2. Mass of adsorbent = 0.05 g, volume of dye solution = 50 ml, concentration = 100–800 mg/dm³, pH 7, temperature = 20 °C, size in μm .

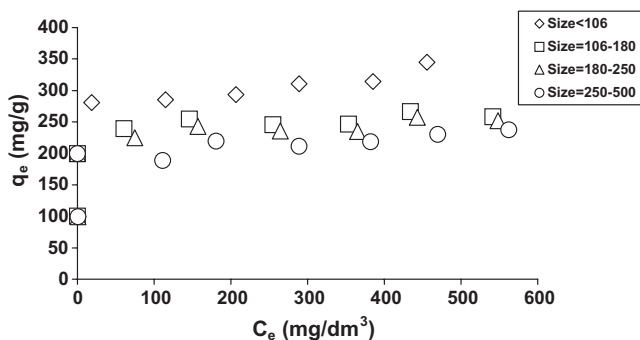


Fig. 6. Effect of adsorbent particle size on the adsorption of methylene blue onto PAC1. Mass of adsorbent = 0.05 g, volume of dye solution = 50 ml, concentration = 100–800 mg/dm³, pH 7 temperature = 20 °C, size in μm .

adsorbent as the smaller particles have a larger external surface area for adsorption process. A similar trend was observed by Poots et al. [39] when peat was used to remove acid dyes from aqueous solution. This is also agrees with the findings of Walker [40] that a substantial increase in the adsorption of acidic dyes onto GAC F400 was recognised with a decrease in adsorbent particle size. Similar effects were obtained for the adsorption of methylene blue onto F400 and PAC1. Figs. 6 and 7 depict the effect of adsorbent particle size on the adsorption process of methylene blue onto PAC1 and F400, respectively. Percentage of MB removal by PAC2 was decreased from 54 to 37% as the particle size increases from <106 to 250–500 μm for initial dye

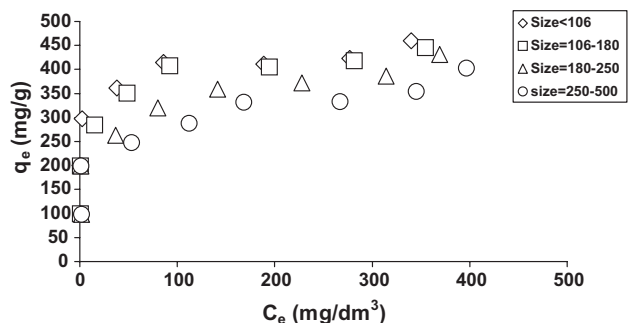


Fig. 7. Effect of adsorbent particle size on the adsorption of methylene blue onto F400. Mass of adsorbent = 0.05 g, volume of dye solution = 50 ml, concentration = 100–800 mg/dm³, pH 7, temperature = 20 °C, size in μm .

concentration = 600 mg/dm³. Decreases of 10% and 15% in the percentage of MB removal was obtained in the case of F400 and PAC1 as the particle size increases from <106 to 250–500 μm, respectively. A similar decrease in BR dye adsorption onto PAC2 and F400 was found when increasing the adsorbent particle size.

3.3. Equilibrium isotherm modelling

Equilibrium adsorption isotherm data were analysed according to Langmuir, Freundlich and Redlich–Peterson models. The general formula of the equation correlating adsorption equilibria can be expressed as

$$q_e = \frac{QKC_e}{\delta + (hC_e^\beta)} \quad (4)$$

Setting δ and β equal to unity, Eq. (4) is reduced to

$$q_e = \frac{QK_L C_e}{1 + (a_L C_e)} \quad (5)$$

where q_e is the solid phase equilibrium concentration (mg/g), C_e the liquid phase equilibrium concentration (mg/dm³), Q an energy term and in most cases equal to unity and K_L (dm³/g) and a_L (dm³/mg) are Langmuir constants [42,43].

Eq. (6) represents the linearized form of Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (6)$$

Thus a linear plot of C_e/q_e versus C_e confirms the validity of the Langmuir model. According to Redlich and Peterson [44], for low concentrations Langmuir equation is sound and well confirmed. The Langmuir adsorption isotherm has been successfully applied to many pollutants adsorption process and has been the most widely used adsorption isotherm for the adsorption of solute from a liquid solution [45].

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 [37]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

where R_L is a dimensionless constant separation factor, C_0 the initial concentration of dye solution (mg/dm³) and K_L is the Langmuir constant (dm³/g). The parameter R_L indicates the shape of the isotherm accordingly.

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

The Freundlich isotherm endorses the heterogeneity of the surface and assumes that the adsorption occurs at sites with different energy of adsorption. The energy of adsorption varies as a function of surface coverage [46]. Eq. (8) represents Freundlich

isotherm:

$$q_e = K_F C_e^{1/n} \quad (8)$$

where K_F is Freundlich constant (mg/g (mg/dm³)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:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (9)$$

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. Freundlich adsorption model is used when more than monolayer coverage of the surface is expected and the site is heterogeneous with different binding energy. An unlimited supply of unreacted sites is assumed to be available. The exponent $1/n$ is usually less than 1.0 because sites with the highest binding energies are utilized first, followed by weaker sites, and so on [47].

Redlich and Peterson have developed an empirical formula that incorporates the features of Langmuir and Freundlich isotherms as given in the following equation:

$$q_e = \frac{K_r C_e}{1 + a_r C_e^\beta} \quad (10)$$

where K_r is the modified Langmuir constant (dm³/g), a_r (dm³/mg) and β are constants. For simplicity, $K_r = K_L$. This formula reduces to Freundlich isotherm at low surface coverage and to Langmuir isotherm at high adsorbate concentration. 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 [45].

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

$$\log \left(\frac{K_r C_e}{q_e} - 1 \right) = \beta \log C_e + \log a_r \quad (11)$$

Adsorption isotherms were analysed according to the linear form of Langmuir, Freundlich and Redlich–Peterson isotherms 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_m (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. Tables 3 and 4 display the results of the calculated isotherm constants at different pH values.

It is evident that the monolayer capacity of methylene blue onto F400 was significantly higher than that onto PAC2 and PAC1 except at pH 11 where PAC2 has the highest monolayer saturation capacity (588 mg/g). It is also clear that the pH has less effect on the monolayer capacity for F400 where as it has great effect in the case of PAC2 especially as the pH increase from 9 to 11. On this basis, it is to be expected that methylene blue will have a strong adsorption affinity for PAC2 at pH 11 and for F400 at other pH values. In the pH range of 4–9, PAC1 and

PAC2 would appear to have similar adsorption capacity and F400 has much greater affinity for dye, see Table 3. Langmuir model fits 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 as evident from the correlation coefficients in Table 3.

The low values of R_L indicate high and favourable adsorption of methylene blue on the three activated carbons: PAC1, PAC2 and F400. The values of the heterogeneity factor ($1/n$) in Table 3 would indicate that all the activated carbon have 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.

Table 5 shows the results of the calculated isotherm constants at different particle size for MB systems and 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. Since the constant K_F (Freundlich constant) gives an indication of adsorption capacity of the adsor-

Table 5
Langmuir, Freundlich and Redlich–Peterson isotherm constants for adsorbents and MB dye systems at different particle size

Size (μm)	Langmuir				Freundlich		
	K_L (dm^3/g)	a_L (dm^3/mg)	q_m (mg/g)	r^2	K_F ($\text{mg}/\text{g}/(\text{dm}^3/\text{g})^n$)	n	r^2
PAC2							
<106	51.810	0.1502	345	0.9986	185.18	9.74	0.8611
106–180	63.290	0.2405	263	0.9987	177.13	14.85	0.9003
180–250	107.52	0.4300	250	0.9993	177.54	17.76	0.8627
250–500	48.780	0.2097	233	0.9971	162.36	17.30	0.7456
Size	Redlich–Peterson			R_L			
	β	a_r (dm^3/mg)	r^2				
PAC2							
<106		0.9446	0.2087		0.9989		0.023
106–180		0.9528	0.2962		0.9975		0.013
180–250		1.0204	0.3886		0.9996		0.011
250–500		1.0368	0.1716		0.9976		0.024
Size	K_L (dm^3/g)	a_L (dm^3/mg)	q_m (mg/g)	r^2	K_F ($\text{mg}/\text{g}/(\text{dm}^3/\text{g})^n$)	n	r^2
PAC1							
<106	36.76	0.1199	307	0.9933	234.69	19.72	0.6220
106–180	64.51	0.2516	256	0.9980	209.26	29.85	0.4869
180–250	40.32	0.1613	250	0.9970	181.55	19.57	0.5872
250–500	18.12	0.0779	233	0.9950	112.33	8.60	0.7952
Size	Redlich–Peterson			R_L			
	β	a_r (dm^3/mg)	r^2				
PAC1							
<106		1.1108	0.0602		0.9930		0.033
106–180		0.9915	0.2627		0.9987		0.019
180–250		0.9817	0.1797		0.9979		0.030
250–500		0.9308	0.1117		0.9959		0.064
Size	K_L (dm^3/g)	a_L (dm^3/mg)	q_m (mg/g)	r^2	K_F ($\text{mg}/\text{g}/(\text{dm}^3/\text{g})^n$)	n	r^2
F400							
<106	88.49	0.1946	455	0.9960	278.16	12.5	0.9520
106–180	59.17	0.1360	435	0.9973	207.39	7.633	0.9202
180–250	26.54	0.0638	416	0.9897	177.46	7.256	0.9563
250–500	18.62	0.0484	385	0.9819	105.41	4.655	0.8982
Size	Redlich–Peterson			R_L			
	β	a_r (dm^3/mg)	r^2				
F400							
<106		0.9585	0.2516		0.9982		0.014
106–180		0.9758	0.1552		0.9991		0.020
180–250		0.9243	0.0979		0.9982		0.044
250–500		0.8982	0.0868		0.9992		0.062

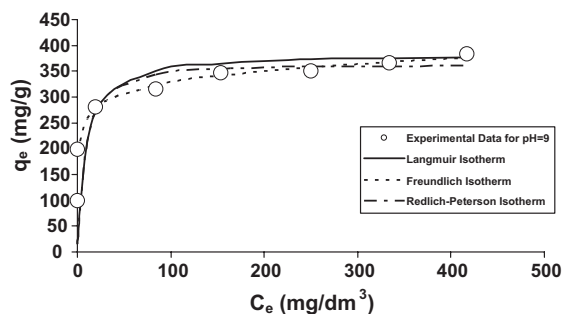


Fig. 8. Model fit of adsorption isotherm of methylene blue adsorption onto PAC2.

bent, it is clear that the affinity of the adsorbents decreases with increasing particle size. This confirms that dye uptake was a function of the specific surface area or external surface on the adsorbent.

Adsorption isotherm models were applied to the adsorption data of BR and BY onto F400 and PAC2. Table 4 lists the models constants. Results in Table 4 illustrates that as the solution pH was increased, the monolayer capacity increased with maximum value of approximately 1000 mg/g for PAC2 and BR dye at pH 11. The monolayer capacity for PAC2 is higher than that of F400 at pH 11 and this may ascribed to the relationship between equilibrium solution pH and pH_{ZPC} . An increase in K_F values was observed which indicates that adsorption affinity increases with increasing solution pH. Saturation monolayer capacity value, q_m , of BY dye is higher than that of BR dye and this can be explained in terms of molecular volume of each dye. In order to illustrate the correlation of the equilibrium isotherm models to the experimental data, a typical model prediction for each isotherm have been shown with the experimental data for the adsorption of basic dyes onto PAC1, PAC2 and F400, is shown in Fig. 8.

4. Conclusions

This work investigates liquid phase adsorption process for three activated carbons, PAC1, PAC2 and F400 at different pH and adsorbent particle sizes. Basic dyes (methylene blue, basic red 22 and basic yellow 21) were used as potential pollutants. Langmuir, Freundlich and Redlich–Peterson isotherm models were used to simulate experimental data. The main conclusions which can be drawn on the basis of present study are:

- Adsorbent surface chemistry, surface area and pore structure proved to be important factors in governing the adsorption process. Net surface charge and physical properties of adsorbents play a significant role in explaining the differences in adsorptive capacities of the activated carbons used in this investigation.
- Solution pH plays a major role in the adsorption process. The optimum pH for the removal of MB and BR from aqueous solution under the experimental conditions employed, was pH 11. The effect of pH can be described on the basis of the influence of pH on the zero point of charge (pH_{ZPC}). Adsorbent acts as a positively charged surface in the solution when the

pH is lower than pH_{ZPC} and as a negatively charged surface when the pH is greater than pH_{ZPC} .

Experimental data also indicated that adsorbent particle size has an influence on the adsorption capacities of activated carbons. As the particle size decreases, the adsorption capacity of PAC2 increased. The increase in capacity with decreasing particle size indicates that the dyes do not completely penetrate the particle or possibly that the dyes preferentially adsorb near the outer surface of the particle.

PAC2 and F400 proved potentially good carbon adsorbents for removing basic dyes from aqueous solution. Under comparable conditions, adsorption capacity of basic dyes, MB, BR and BY onto PAC1, PAC2 and F400 increase in the order: MB < BR < BY.

Of the three equilibrium isotherm models applied, the Redlich–Peterson isotherm was found to best describe the experimental data over the whole concentration range as indicated from the high values of the correlation coefficients ($r^2 > 0.99$). 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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