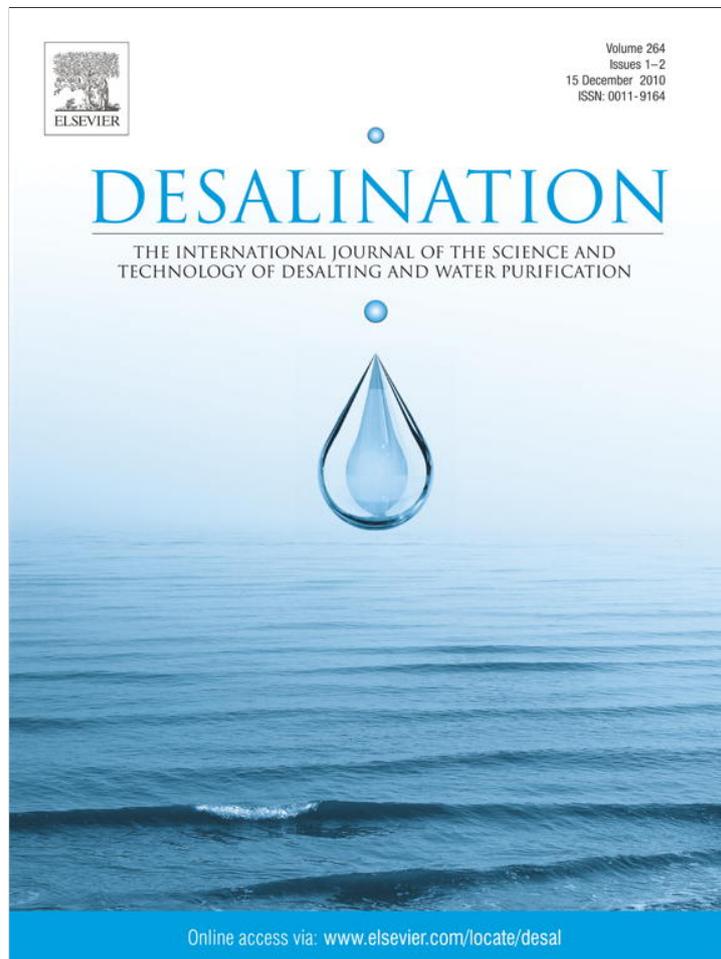


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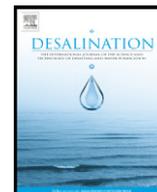
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The influence of pH and the structure of the dye molecules on adsorption isotherm modeling using activated carbon

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ABSTRACT

The main aim of the study was to find out the influence of pH and the molecular weight of the dye molecules on adsorption isotherm models using activated carbon in a single solid–liquid system. In this study we derived activated carbon from the waste biomass of wood apple rind. Batch mode experiments were carried out in order to assess the influence of the initial pH and molecular weight of the dye on adsorption capacity of the carbon. Two basic dyes namely Methylene blue and Crystal violet having different molecular structures have been chosen. To find out the pH effect on the adsorption capacity of the activated carbon, the equilibrium isotherm experiments were carried out by varying the pH of the dye solutions by fixing the carbon dose as constant. A separate study was carried out to note down the change in pH of the dye solution during the adsorption of cationic dye molecules on the activated carbon surface. The adsorption capacity of the activated carbon increased while increasing the pH of the dye solution. The structure of the dye molecules and the nature of pores present on the surface of the activated carbon also decide the adsorption capacity of the carbon.

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1. Introduction

The release of huge amount of dyes into water bodies by textile industries creates serious health problems due its persistent nature. The degradation products of textile dyes are often carcinogenic. [1,2]. Presence of this dye in water leads to various health effects like eye burns, and irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. It may lead to methamoglobinemia, cyanosis and dyspnea, if inhaled directly. It also may cause irritations to the skin [3,4]. Various conventional methods have been tried for several years for textile dye effluent treatment. Among the various techniques, adsorption method is the most effective and economic one to remove the dyes from waste water. In order to design a treatment plant for textile industries' effluent, it is a must to know the adsorption isotherm models and the important factors which affect the isotherm models to a great extent. Compared to other factors like initial concentration of the dye, carbon dose, temperature etc., the pH of

the solution is the most important factor that affects the adsorption process [5,6]. Precise monitoring of the initial rapid rate of adsorption is normally not possible because a finite time is required to ensure proper mixing and to separate the solid and solution phases for analysis. The pH of the solution mainly decides the kinetics of the adsorption process and it can be monitored by using the pH meter having ion-selective electrodes [5]. Following the drop in the pH of the dye solution after the addition of activated carbon to the dye solution is a convenient way to studying the rate of adsorption during the first few minutes. The dye removal capacity of the activated carbon generally meant its uptake of dye molecules from solution, which is calculated from fitting the experimental data to the Langmuir isotherm model. This type of approach is feasible only if it exists in the form of plateau. Kurbatov and co-workers [5] were the first people to study about the effect of pH on adsorption studies using activated carbon. The goal of the present work was to study the effect of pH and the molecular structure of the dye on the adsorption isotherm models. The adsorption of Crystal violet and Methylene blue onto a carbon obtained from the wood apple rind was studied at different pH conditions. Two-parameter isotherms, the Freundlich and Langmuir isotherms, as well as one three-parameter isotherm, the Redlich-Peterson isotherm, were examined for their ability to model the equilibrium adsorption data. Non-linear correlation analyses of these three isotherms were applied for the above adsorption of dyes by wood apple rind carbon.

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2. Experimental

The outer rind of wood apple was crushed into smaller pieces and soaked with concentrated H_2SO_4 at 1:1 ratio (wt of raw material/volume of acid) for 48 h and activated at $160\text{ }^\circ\text{C}$ for 6 h. The activated carbon was repeatedly washed with distilled water until the pH of the wash water becomes the pH of the distilled water [7]. The carbon obtained from the wood apple rind (WAC) was dried at $105 \pm 1\text{ }^\circ\text{C}$ for 2 h. All the chemicals used are of analytical grade. The stock solution of 1000 mg/L Crystal violet (CV) and Methylene blue (MB) was prepared and the solutions of the desired concentration were prepared by diluting the stock solution (10 mg/L to 100 mg/L). A calibration graph of absorbance versus concentration was obtained using systronics photometer (model 104) at λ_{max} 595 nm for CV and at λ_{max} 665 nm for MB dye. Batch mode experiments were conducted using screw cap closed containers using ORBITEK shaker at 300 rpm. For isotherm studies 100 mg of WAC and 50 mL of different concentrations of the dye (MB and CV) solution in the range of 20 to 100 mg/L was taken in the closed containers after having adjusted for required initial pH and shaken for 2 h. The required initial pH of the dye solution was obtained by using HCl (0.1 N, 0.01 N, and 0.001 N) and NaOH (0.1 N, 0.01 N, and 0.001 N). A separate study about the change in pH of the solution during adsorption of dye molecules (MB and CV) on WAC was carried out by taking 50 mL of different concentrations of dye solution. The change in pH of the solution was noted after adding the known amount of adsorbent (100 mg) for first 5 to 10 min of time, using digital pH meter having combined glass electrode. After shaking the solution for 2 h, the reaction mixtures were separated and the filtrate was analyzed using spectrophotometer.

The amount of dye adsorbed onto activated carbon was calculated by using the following expression:

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

where q_e was the equilibrium adsorption capacity of dye adsorbed on unit mass of activated carbon (mg/g); C_0 and C_e were the initial dye concentration (mg/L) and dye concentration (mg/L) at equilibrium respectively; V was the volume of the dye solution (L); and m was the weight of activated carbon (g).

3. Results and discussion

3.1. Effect of pH

The effect of pH during the adsorption process and the adsorption performance of WAC were done by taking only a single carbon–dye system. In order to compare the performance of two or more adsorbents, it is a must to carry out the experiments under the same experimental conditions. Particularly it is very important to compare the adsorption performance under the same pH, since isotherm could vary with pH of the solution. For WAC and both the dyes (MB and CV) the pH of the solution decreases suddenly in the initial step of adsorption process. This is mainly due to the ion exchange between the carbon surface and the cationic form of the dye molecule [8]. The changes in pH of the solution were given in Figs. 1a, b, and 2a, and b. The decrease in pH of the dye solution is due to the ion exchange process that released more number of H^+ ions from the surface of the carbon having acidic groups [9]. This type of pH dependence adsorption was presented in an earlier year [5] and in the adsorption of lead onto tree fern [9] and peat [10]. The pH of WAC was found to be 3.91 and after adsorption the pH of the dye loaded carbon was found to be 4.61 for WAC–MB system and 4.41 for WAC–CV system. Initial rate of adsorption is mainly decided by the protons release from the carbon surface [10]. The adsorption capacity of MB is higher than that of CV. This is explained on the basis of the molecular structure and the carbon pore structure. The molecular structure of CV dye is bigger when compared to MB dye (M. wt of MB = 319.85 and

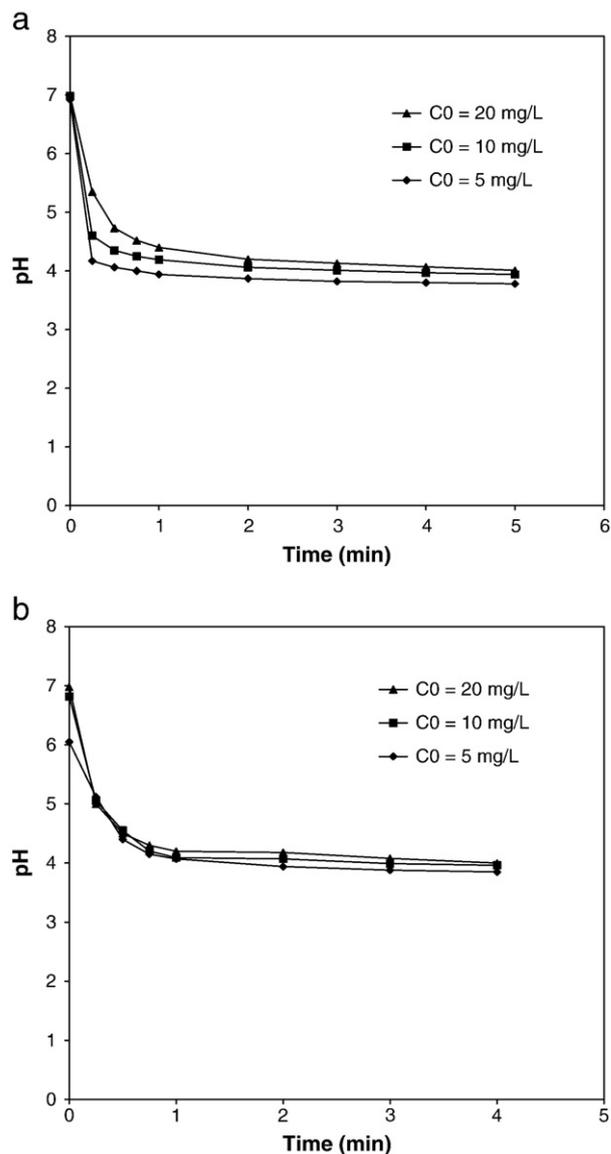


Fig. 1. a. Change in pH during adsorption of MB on WAC for varying MB initial concentrations. b. Change in pH during adsorption of CV on WAC for varying CV initial concentrations.

CV = 408.0). The diffusion of CV molecules finds much difficulty compared to MB molecules on WAC. At room temperature the pore size of WAC is not suitable for the entry of the CV molecules. Increased in the pH of the initial dye concentration increased the uptake of dye molecules from water. The q_m values increased for both the systems. The reason behind this observation is due to the surface modification of carbon takes place if the pH of the dye solution is raised to basic side [11]. Increase of pH which deprotonates the acid groups from the surface of the carbon results more number of negative charge formations on the carbon surface for the attraction of the cationic form of dye molecules from solution [11]. The analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used for designing purposes. The effect of pH on adsorption isotherms has been reported in metal/peat adsorption systems [12,13].

3.2. Isotherm modeling

In order to investigate the effect of pH on adsorption isotherm models, three equilibrium isotherms were analyzed: Langmuir, Freundlich, and Redlich–Peterson. The Langmuir adsorption isotherm

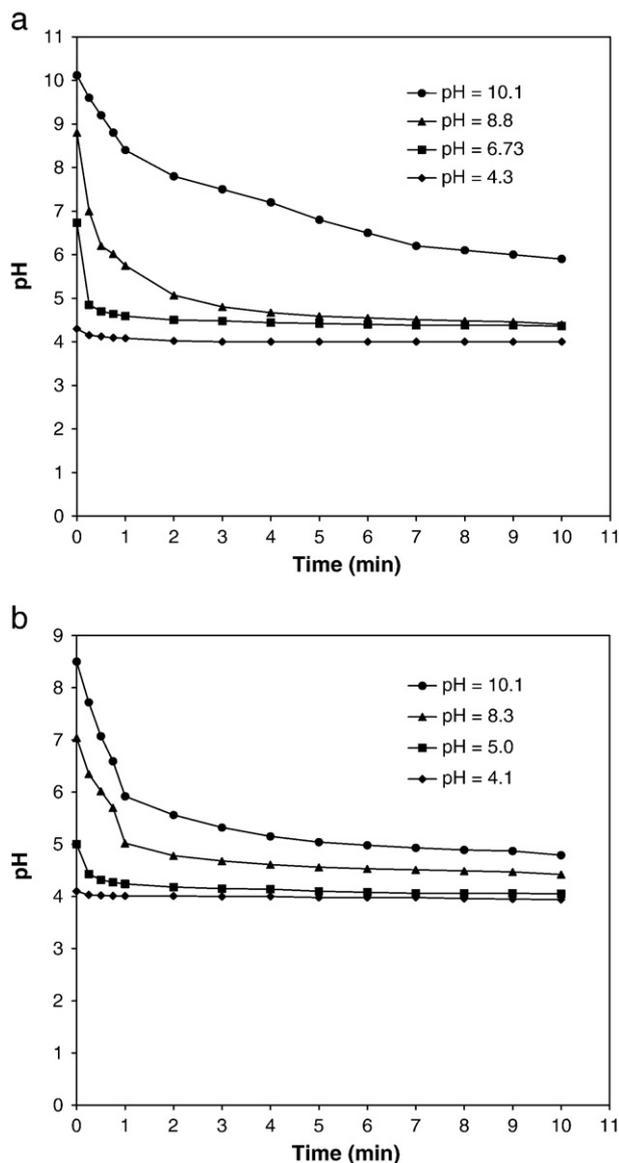


Fig. 2. a. Change in pH during adsorption of MB on WAC for varying initial MB solution pH. b. Change in pH during adsorption of CV on WAC for varying initial CV solution pH.

is perhaps the best known of all isotherms describing adsorption [14]. The theoretical Langmuir isotherm is often used to describe adsorption of a solute from a liquid solution as [14,15]

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (2)$$

where q_e is the equilibrium adsorption capacity, (mg/g), C_e is the equilibrium liquid phase concentration, (mg/L), q_m is the maximum adsorption capacity, (mg/g), and K_a is adsorption equilibrium constant, (L/mg). The Freundlich isotherm is the earliest known relationship describing the adsorption isotherm [16]. This fairly satisfactory empirical isotherm can be used in adsorption from dilute solutions. The ordinary adsorption isotherm is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where C_e is the equilibrium concentration in the solution, (mg/L), q_e is the equilibrium adsorption capacity, (mg/g), K_F and $1/n$ are empirical constants.

The Redlich-Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms [17]. It can be described as follows:

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

It has three isotherm constants, namely, A , B , and g ($0 < g < 1$).

It has been presented that the non-linear method is a better way to obtain the isotherm parameters [18]. A trial-and-error procedure, which is applicable to computer operation, was used to compare the best fit of the three isotherms using an optimization routine to maximize the coefficient of determination r^2 , between the experimental data and isotherms in the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel [19,20]. The coefficient of determination r^2 was

$$r^2 = \frac{\sum (q_m - \bar{q}_e)^2}{\sum (q_m - \bar{q}_e)^2 + \sum (q_m - q_e)^2} \quad (5)$$

where q_m was the equilibrium capacity obtained from the isotherm model, q_e was the equilibrium capacity obtained from experiment, and \bar{q}_e was the average of q_e . In order to assess different isotherms and their ability to correlate with experimental results, the theoretical plots from each isotherm have been shown with the experimental data for adsorption of MB and CV on WAC at the various pH in Fig. 3a and b. The graph is plotted in the form of dyes adsorbed per unit mass of WAC, q_e , against the concentration of dyes remaining in solution, C_e . A comparison of the coefficient of determination for the three isotherms has been made and listed in Table 1. The Redlich-Peterson and Langmuir isotherm models were the most suitable for the data compared to the Freundlich isotherm. The Langmuir and the Redlich-Peterson isotherms had well fitted the adsorption of both MB and CV onto WAC at various pH based on higher r^2 value (Table 1). Fig. 4a and b shows the plots comparing the theoretical Langmuir, empirical Freundlich, and the Redlich-Peterson isotherms with the experimental data for the adsorption of MB and CV onto WAC at a pH of 7. The Redlich-Peterson and Langmuir isotherms overlapped (since the g value in Redlich-Peterson model is one in the case of MB/WAC) and seemed to be the best-fitting isotherms for the experimental results. By using a non-linear method there was no problem with transformation of non-linear isotherm equation to linear forms, and also they had the same error structures [18].

3.3. Adsorption capacity

The adsorption capacity of dyes increased with pH which is typical for the adsorption of most of the dyes from their solution. When the system is in a state of equilibrium, the distribution of dye between the WAC and the dye solution is of fundamental importance in determining the maximum adsorption capacity of WAC for the dyes from the isotherm. The Langmuir, Redlich-Peterson, and Freundlich isotherms constants are shown in Table 1. The maximum adsorption capacity, q_m , and the adsorption constant, K_a , were found to be increased from 36.2 to 40.1 mg/g for MB/WAC and 15.7 to 19.8 mg/g for CV/WAC system. The molecular structure (Geometry) of the CV dye is bigger compared to that of the MB dye (M. wt of MB = 319.85 and CV = 408.0), the diffusion of CV molecules finds much difficulty compared to MB molecules on WAC. So the q_e value for MB/WAC is higher. The K_a value increased from 0.573 to 1.40 L/mg for MB/WAC and 1.37 to 2.34 L/mg for CV/WAC and increased in the solution pH from 5 to 9 respectively. The higher the K_a value, the stronger is the affinity between the carbon surface and the dye molecules. The bond between the WAC and CV is stronger compared to WAC and MB dye molecules based on the K_a values. Similar results were also found in nickel removal from aqueous solution by sphagnum moss peat [13]. The increased in pH of the solution increased the K_a value that shows

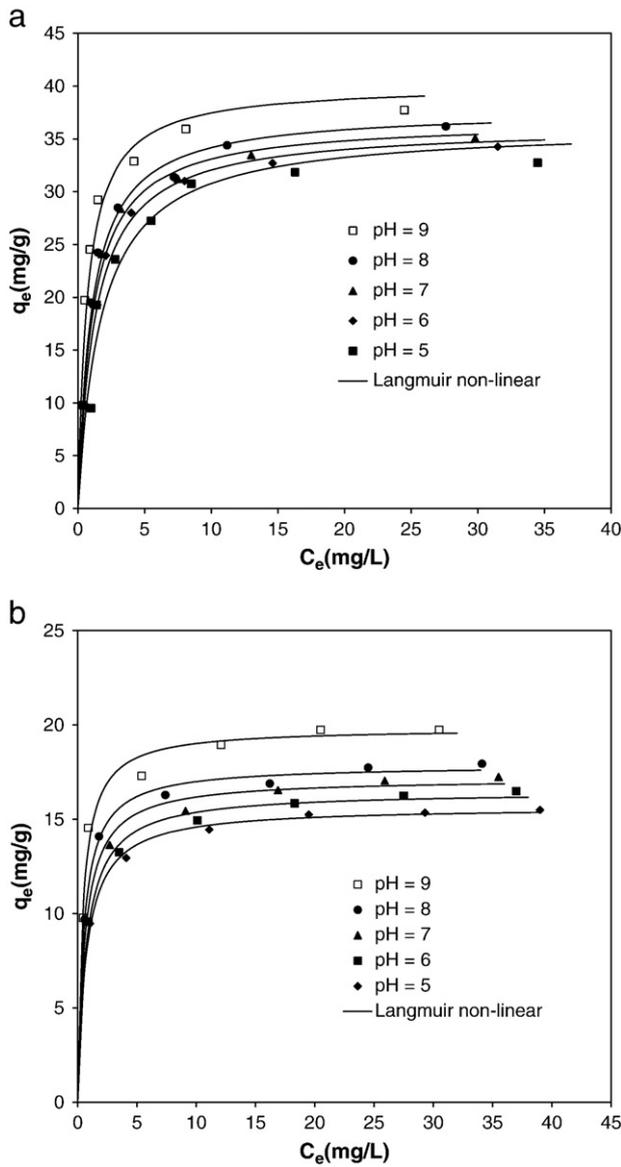


Fig. 3. a. Langmuir isotherms for MB/WAC system at various pH. b. Langmuir isotherms for CV/WAC system at various pH.

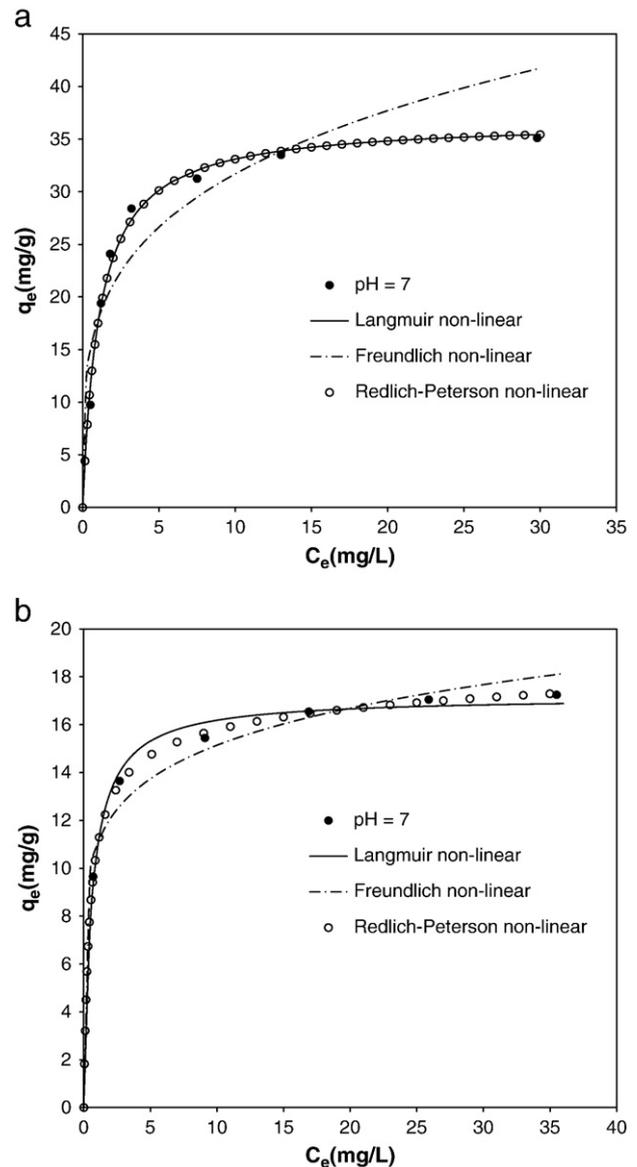


Fig. 4. a. Fitted isotherms for WAC-MB system at pH 7. b. Fitted isotherms for WAC-CV system at pH 7.

there is an increase in the affinity between the carbon surface and the cationic form of dye molecules. In addition, the values of g were also found to be one, which means that the isotherms are approaching the

Langmuir form and not the Freundlich isotherm. The important factor that obtained from Langmuir model is K_R , from this value one can predict whether the adsorption system is favourable [21,22].

Table 1
Isotherm parameters for both the systems at different initial pH of the dye solutions.

pH	Langmuir			Freundlich			Redlich-Peterson				
	q_m mg/g	K_a L/mg	r^2	$1/n$	K_F (mg/g) (L/mg) ^{1/n}	r^2	g	B (L/mg) ^g	A L/g	r^2	
MB/WAC	5 ± 0.1	36.2	0.573	0.935	0.275	15.2	0.794	1.000	0.573	20.7	0.935
	6 ± 0.1	36.2	0.774	0.985	0.257	16.8	0.828	1.000	0.774	28.0	0.985
	7 ± 0.1	36.7	0.912	0.985	0.251	17.8	0.832	1.000	0.912	33.5	0.985
	8 ± 0.1	37.7	0.957	0.973	0.255	18.4	0.837	1.000	0.957	36.1	0.973
	9 ± 0.1	40.1	1.40	0.930	0.246	21.3	0.788	1.000	1.40	56.4	0.930
CV/WAC	5 ± 0.1	15.7	1.37	0.990	0.135	10.0	0.919	0.969	1.91	27.0	0.998
	6 ± 0.1	16.5	1.39	0.982	0.141	10.4	0.941	0.950	2.41	33.7	1.000
	7 ± 0.1	17.2	1.65	0.979	0.141	11.0	0.939	0.948	2.93	42.7	0.998
	8 ± 0.1	17.9	1.96	0.989	0.141	11.6	0.902	0.978	2.43	40.6	0.992
	9 ± 0.1	19.8	2.34	0.966	0.151	12.7	0.894	0.976	2.90	53.6	0.969

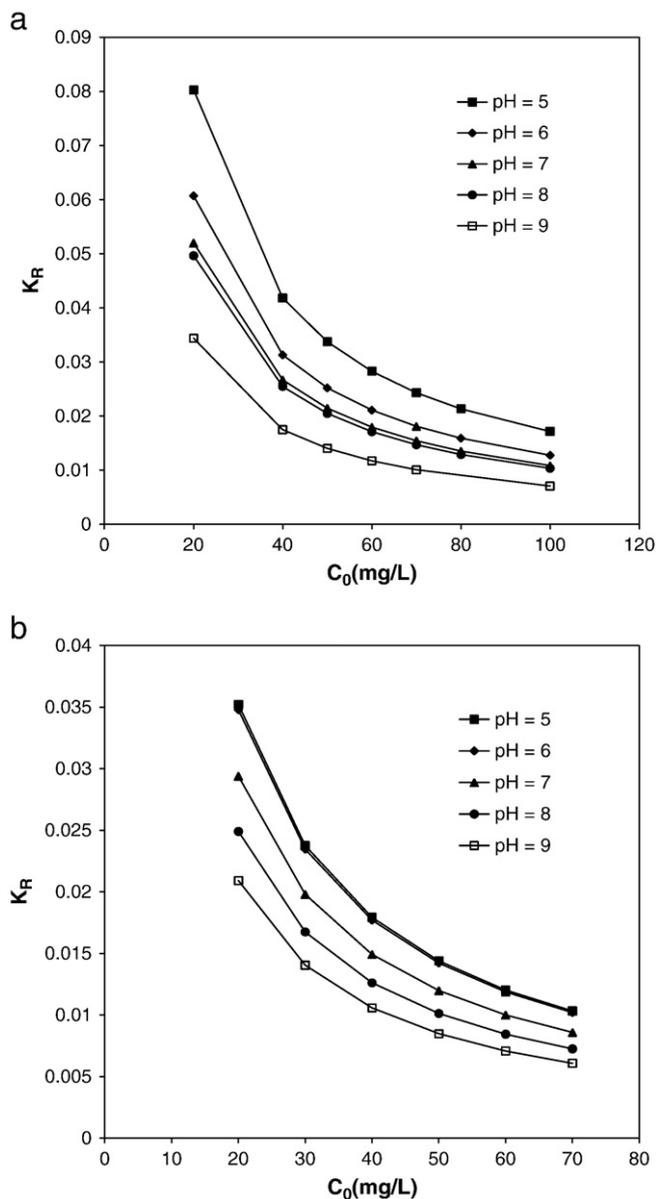


Fig. 5. a. Relation between C_0 and K_R for MB/WAC system at various pH. b. Relation between C_0 and K_R for CV/WAC system at various pH.

According to Hall et al., the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor which is defined by the following relationship.

$$K_R = \frac{1}{(1 + K_a C_0)} \quad (6)$$

where K_R is a dimensionless separation factor, C_0 is the initial dye concentration and K_a is Langmuir constant. The value of K_R , explains the feasibility of the reactions ($K_R > 1$ —unfavourable, $K_R = 1$ —linear, $0 < K_R < 1$ —favourable, $K_R = 0$ —irreversible). The relationship between K_R and C_0 has been presented with Fig. 5a and b for both the systems

[15]. The increased in pH of the dye solution and the initial concentration of the dye solution favours the adsorption process. The values lie between one to zero for both the systems discussed above. The K_a values also increased with increase in pH of the solution.

4. Summary

Effect of the initial pH of the dyes solutions on adsorption of basic dyes onto activated carbons was presented. It is clear that the uptake of basic dyes (MB and CV) from solution using activated carbons (FTPC and WAC) follows Langmuir isotherm model (mono layer coverage), and the pH of initial concentration of the dyes solution played a major role and the reaction is favourable at room temperature. Affinity between the bigger size molecule (CV) and the activated carbon is more compared to the lower size molecule (MB) and the geometry of the molecules also decides the adsorption capacity of the carbon.

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