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Research Article

REMOVAL OF METHYLENE BLUE USING LOW-COST ACTIVATED CARBONS FROM VARIOUS PLANTS BY ADSORPTION TECHNIQUE

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ABSTRACT
The present study deals with the removal of the textile dye, methylene blue (MB), from aqueous solutions by adsorption using low-cost activated carbons prepared from various plants. Batch adsorption studies were conducted by varying the initial concentration of the adsorbate, adsorbent dosage, contact time, and pH. The effect of pH on adsorption of methylene blue on low-cost activated carbons was studied at pH 4. The percentage removal of dye was measured as a function of both the concentration of the dye (10 - 30 ppm) and the temperature (303 – 323 K). The experimental adsorption data obtained in this study were fitted with Freundlich and Langmuir adsorption isotherms. The adsorption technique using low-cost activated carbons from various plants are found to be an efficient method for the removal of the dye MB from aqueous solutions.

Keywords: *Methylene Blue, Adsorption, Low-cost Activated Carbons*

INTRODUCTION
Industrial, agricultural and domestic wastes, due to the rapid development in the technology, are discharged in several receivers. Generally, this discharge is directed to the nearest water bodies such as rivers, lakes, and seas. Textile dyeing process is an important source of contamination responsible for the continuous pollution of the environment. The volume of waste water containing processed textile dyes is on steady increase. Over 735 tonnes and approximately 10,000 different types of dyes and pigments are produced worldwide annually (Pala *et al.*, 2003). It is estimated that 10–15% of the dye is lost in the effluents during the dyeing process. Colour is a characteristic of wastewater, which is easily detected. Control of water pollution has importance for both organisms, which live in water and those who benefit from water. Many dyes reaching the water source are difficult to decompose and cause many problems due to their carcinogenicity (Safarik *et al.*, 2002; Albanis *et al.*, 2000; Moreira *et al.*, 1998).Consequently, it is important to remove these pollutants from wastewater before their final disposal. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, use of operation and insensitivity to toxic substances (Meshko *et al.*, 2001). Adsorption has been used extensively in industrial process for separation and purification. The removal of colored and colorless organic pollutants from industrial wastewater is considered as an important application of adsorption processes (Al-Qodah 2000). At present, there is a growing interest in using low-cost, commercially available materials for the adsorption of dyes. A wide variety of materials such as peat (Mckay *et al.*, 1980), various silicas (Khokhlova *et al.*, 1997), activated clay (Hsu *et al.*, 1997), banana pith (Namasivayam *et al.*, 1998), natural manganese mineral (Liu *et al.*, 2000), shale oil ash (Al-Qodah 2000), goat hair (Kato *et al.*, 2001), alum sludge (Chu 2001), natural zeolite (Meshko *et al.*, 2001), and mixtures of fly ash and soil (Albanis *et al.*, 2000) have been investigated as low-cost alternatives to activated carbon (Walker *et al.*, 1991). This paper reports the results of adsorption of the dye methylene blue (MB) from aqueous solutions on activated carbons prepared from seven commonly available plants. The plants taken to prepare the adsorbent carbons were of medicinally important and are listed as follows:

Sl. No.	Name of the Plant Botanical	Common	In Tamil	Carbon Prepared	Medicnal Uses
1	*Leucas aspera*	Leucas	Thumbai	Leucas carbon (AC1)	i) used as laxative and anthelmintic. ii) used to cure fever, scabies, coughs and cold.
2	*Curculigo orchioides*	Golden eye grass	Nilappanai kilanku	Golden eye grass carbon (AC2)	i) rysomes of the plant is used in the treatment of decline in strength, jaundice and asthma. ii) roots are used in the treatment of piles, blood related disorders, indigestion *etc*.
3	*Sida rhombifolia*	Indian Hemp	Kurunthotti	Indian hemp carbon (AC3)	i) used internally in dermatopathy. ii) good for rheumatism, colic, haemotherma, athritis and diarrhoea.
4	*Cissus quadrangularis*	Bone setter	Pirandai	Bone setter carbon (AC4)	i) used to cure injuries, muscular pain, sprains, stomach ailments ulcer and asthma. ii) the ash of the plant is used as bandage in treating bone fractures.
5	*Tephrosia purpurea*	Wild indigo	Kattu kolinchi	Wild indigo carbon (AC5)	i) the roots are useful in inflammations, skin diseases, elephantiasis, bronchitis anaemia *etc*. ii) the leaves are useful in syphilis, gonorrhoea and bruises.
6	*Hibiscus rosa sinensis*	Hibiscus	Semparuthi	Hibiscus carbon (AC6)	i) soothes internal and external wounds and sores. Also soothes the alimentary tract and relieves inflammation. ii) lowers body heat.
7	*Cyanoden dactylon*	Bermuda grass	Arugampul	Bermuda grass carbon (AC7)	useful in the treatment of bleading piles, breathing problems, eye ailments and heart diseases.

MATERIALS AND METHODS

Reagents

Reagents include methylene blue (MB) (Merck), hydrochloric acid (Merck) and sodium hydroxide (Merck). All chemicals used in the present investigation were of spectroscopic grade.

Preparation of Adsorbent Carbons

The whole plants of *Leucas aspera*, *Curculigo orchioides*, S*ida rhombifolia*, *Cissus quadrangularis*, *Tephrosia purpurea*, *Hibiscus rosasinensis*, and *Cyanoden dactylon* were collected, washed with water, and dried under shadow. The dried materials were powdered and treated with concentrated sulphuric acid. The carbonized materials were washed repeatedly with distilled water to remove free acid and dried at 110^{o} C. The dried carbons [AC1, AC2, AC3, AC4, AC5, AC6, and AC7] were finally crushed and sieved through 75, 150, 300, and 425 µm sieves. The chemical analysis of carbons was done by standard methods (Vogel, 1961; Snell *et al.*, 1994).

Experimental

Batch adsorption experiments were conducted by shaking 0.1g each of carbons derived from the plants with 50 mL aqueous solution of dye (MB) at different concentrations, temperatures, and pH values. The pH values ranged from 2 to 10. 1.0 N HCl and 1.0 N NaOH were used for pH adjustment. The adsorbents were removed by centrifugation and the concentration of dye in the supernatant liquid was determined spectrophotometrically.

RESULTS AND DISCUSSION

Effect of Contact Time

The effect of contact time on the amount of dye adsorbed was observed at the optimum initial concentration of dye. The time dependent behavior of the dye adsorption was examined by varying the contact time between MB and the seven low-cost activated carbons (AC1-AC7) in the range of 10 to 60 min (Tables1a-7a). The concentration of MB was kept at 10 ppm while the amount of adsorbent added was 0.1g of charcoal from the plants. Preliminary experiments indicated that the adsorption of the dye reached equilibrium in approximately 50 minutes (Fig.1). Being very short, the equilibrium time is an economically favorable condition for the prepared carbonaceous adsorbents described here. In the subsequent experiments, the adsorption of the tested dye was performed for one hour.

Table 1a: Percentage removal of methylene blue (MB) using AC1 at various contact times

Sl No.	Contact time (min)	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	10	10	8.82	1.18	11.8	0.94	1.06	0.02	11.8
2	20	10	7.56	2.44	24.4	0.92	1.22	0.03	24.4
3	30	10	6.13	3.87	38.7	0.80	1.55	0.03	38.7
4	40	10	4.07	5.93	59.3	0.72	1.67	0.05	59.3
5	50	10	2.25	7.75	77.5	0.67	1.72	0.06	77.5
6	60	10	1.57	8.43	84.3	0.61	1.77	0.07	84.3

Table 2a: Percentage removal of methylene blue (MB) using AC2 at various contact times

Sl No.	Contact time (min)	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	10	10	8.87	1.13	11.3	0.94	1.05	0.02	11.3
2	20	10	6.23	3.77	37.7	0.79	1.57	0.05	37.7
3	30	10	5.85	4.15	41.5	0.76	1.61	0.04	41.5
4	40	10	4.49	5.51	55.1	0.65	1.74	0.04	55.1
5	50	10	2.64	7.36	73.6	0.42	1.86	0.06	73.6
6	60	10	0.92	9.08	90.8	-0.03	1.95	0.09	90.8

The removal of MB by adsorption increased with time and attained a maximum value in 50 min and thereafter it remained constant for all the concentrations studied. The percentage removal of MB observed

was 84.3 for AC1, 90.8 for AC2, 92.4 for AC3, 81.4 for AC4, 83.6 for AC5, 84.0 for AC6 and 89.0 for AC7. The percentage removal of MB observed was above 80 in all these plant charcoals. Similar results have been reported in the literature for the removal of the dye MB (Renugadevi *et al.,* 2010).

Table 3a: Percentage removal of methylene blue (MB) using AC3 at various contact times

Sl No.	Contact time (min)	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	10	10	8.53	1.47	14.7	0.93	1.16	0.03	14.7
2	20	10	7.91	2.09	20.9	0.89	1.32	0.02	20.9
3	30	10	6.42	3.58	35.8	0.80	1.55	0.03	35.8
4	40	10	3.56	6.44	64.4	0.55	1.80	0.05	64.4
5	50	10	1.08	8.92	89.2	0.03	1.95	0.10	89.2
6	60	10	0.76	9.24	92.4	-0.11	1.96	0.09	92.4

Table 4a: Percentage removal of methylene blue (MB) using AC4 at various contact times

Sl No.	Contact time (min)	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	10	10	8.04	1.96	19.6	0.90	1.29	0.04	19.6
2	20	10	7.76	2.24	22.4	0.88	1.35	0.02	22.4
3	30	10	6.15	3.85	38.5	0.78	1.58	0.03	38.5
4	40	10	3.16	6.84	68.4	0.49	1.83	0.06	68.4
5	50	10	2.04	7.96	79.6	0.30	1.90	0.07	79.6
6	60	10	1.86	8.14	81.4	0.26	1.91	0.06	81.4

Table 5a: Percentage removal of methylene blue (MB) using AC5 at various contact times

Sl No.	Contact time (min)	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	10	10	9.64	0.36	3.6	0.98	0.55	0.006	3.6
2	20	10	8.71	1.29	12.9	0.94	1.11	0.01	12.9
3	30	10	6.33	3.67	36.7	0.80	1.56	0.03	36.7
4	40	10	3.21	6.79	67.9	0.50	1.83	0.06	67.9
5	50	10	2.52	7.48	74.8	0.40	1.87	0.06	74.8
6	60	10	1.64	8.36	83.6	0.21	1.92	0.06	83.6

Table 6a: Percentage removal of methylene blue (MB) using AC6 at various contact times

Sl No.	Contact time (min)	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	10	10	9.5	0.5	5	0.97	0.69	0.01	5
2	20	10	8.8	1.2	12	0.94	1.07	0.01	12
3	30	10	7.5	2.5	25	0.87	1.39	0.02	25
4	40	10	4.1	5.9	59	0.61	1.77	0.05	59
5	50	10	2.6	7.4	74	0.41	1.86	0.06	74
6	60	10	1.6	8.4	84	0.20	1.92	0.07	84

Table 7a: Percentage removal of methylene blue (MB) using AC7 at various contact times

Sl No.	Contact time (min)	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	10	10	8.5	1.5	15	0.92	1.17	0.03	15
2	20	10	7.4	2.6	26	0.86	1.41	0.03	26
3	30	10	6.2	3.8	38	0.79	1.57	0.03	38
4	40	10	4.2	5.8	58	0.62	1.76	0.04	58
5	50	10	3.2	6.8	68	0.50	1.83	0.05	68
6	60	10	1.1	8.9	89	0.04	1.94	0.08	89

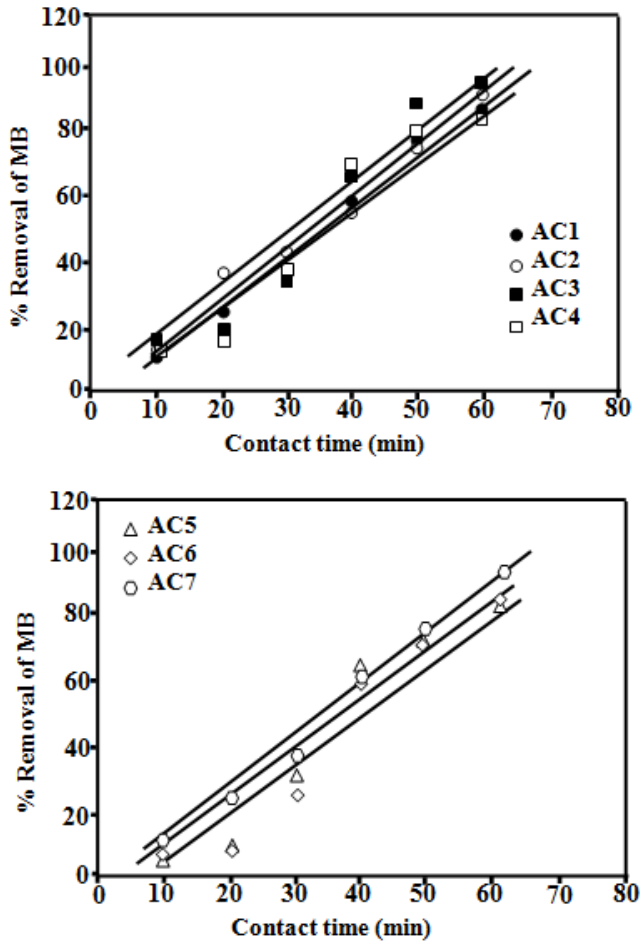

Figure 1: Effect of contact time on the removal of MB

Effect of Adsorbent Dosage

The effect of various adsorbent dosages of AC1-AC7 on MB was studied keeping other parameters, like contact time (50 min), initial dye concentration (10 ppm) and pH 4 as constant at 303 K. The amount of dye adsorbed (in mg/g and percent) is given in Tables 1b-7b. The dye removal capacity plotted as a function of adsorbent dosage is shown in Fig. 2. A significant increase in percentage removal of MB with increase in adsorbent dosage was observed as expected. This has been attributed to the increase in the surface area of carbon that provides more adsorption sites which in turn enhances the percentage of dye removal (Hema *et al.*, 2007). The percentage removal for an initial concentration of 10 ppm of MB for a contact time of 50 min with a dosage of 0.1g of AC1-AC7 was in the range of 89 to 95.

Table 1b: Percentage removal of methylene blue (MB) using AC1 at various adsorbent dosages

Sl No.	Adsorbent dosage (g)	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	0.025	10	4.65	5.35	214	0.32	2.49	0.02	53.5
2	0.050	10	3.87	6.13	122	0.26	2.21	0.03	61.3
3	0.075	10	2.71	7.29	97.2	0.09	2.06	0.05	72.9
4	0.1	10	1.62	8.38	83.8	0.03	1.94	0.06	83.8
5	0.125	10	1.23	8.77	70.1	0.02	1.85	0.08	87.7
6	0.150	10	0.86	9.14	60.9	0.01	1.77	0.09	91.4

Table 2b: Percentage removal of methylene blue (MB) using AC2 at various adsorbent dosages

Sl No.	Adsorbent dosage (g)	Initial conc. of MB (ppm)	Final conc.of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	0.025	10	2.41	7.59	303.6	0.38	2.48	0.05	75.9
2	0.050	10	1.84	8.16	163.2	0.26	2.21	0.06	81.6
3	0.075	10	1.43	8.57	114.2	0.15	2.05	0.07	85.7
4	0.1	10	0.94	9.06	90.6	-0.02	1.95	0.09	90.6
5	0.125	10	0.70	9.30	74.4	-0.15	1.87	0.10	93.0
6	0.150	10	0.56	9.44	62.9	-0.25	1.79	0.11	94.4

Table 3b: Percentage removal of methylene blue (MB) using AC3 at various adsorbent dosages

Sl No.	Adsorbent dosage (g)	Initial conc. of MB (ppm)	Final conc. of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	0.025	10	5.79	4.21	168.4	0.76	2.22	0.02	42.1
2	0.050	10	4.82	5.18	103.6	0.68	2.01	0.02	51.8
3	0.075	10	3.47	6.53	87.0	0.54	1.93	0.04	65.3
4	0.1	10	0.79	9.21	92.1	-0.10	1.96	0.09	92.1
5	0.125	10	0.62	9.38	75.0	-0.20	1.87	0.10	93.8
6	0.150	10	0.48	9.52	63.4	-0.31	1.80	0.11	95.2

Table 4b: Percentage removal of methylene blue (MB) using AC4 at various adsorbent dosages

Sl No.	Adsorbent dosage (g)	Initial conc. of MB (ppm)	Final conc. of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	0.025	10	2.11	7.89	315.6	0.32	2.49	0.05	78.9
2	0.050	10	1.82	8.18	163.6	0.26	2.21	0.06	81.8
3	0.075	10	1.25	8.75	116.6	0.09	2.06	0.07	87.5
4	0.1	10	1.09	8.91	89.1	0.03	1.94	0.08	89.1
5	0.125	10	1.06	8.94	71.5	0.02	1.85	0.08	89.4
6	0.150	10	1.03	8.97	59.8	0.01	1.77	0.08	89.7

Table 5b: Percentage removal of methylene blue (MB) using AC5 at various adsorbent dosages

Sl No.	Adsorbent dosage (g)	Initial conc. of MB (ppm)	Final conc.of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	0.025	10	5.42	4.58	45.8	0.73	2.26	0.02	45.8
2	0.050	10	4.53	5.47	54.7	0.65	2.03	0.03	54.7
3	0.075	10	2.87	7.13	71.3	0.45	1.97	0.04	71.3
4	0.1	10	1.68	8.32	83.2	0.22	1.92	0.06	83.2
5	0.125	10	1.39	8.61	86.1	0.14	1.83	0.07	86.1
6	0.150	10	0.98	9.02	90.2	-0.008	1.77	0.08	90.2

Table 6b: Percentage removal of methylene blue (MB) using AC6 at various adsorbent dosages

Sl No.	Adsorbent dosage (g)	Initial conc.of MB (ppm)	Final conc.of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	0.025	10	5.4	4.6	184	0.73	2.26	0.02	46
2	0.050	10	4.9	5.1	102	0.69	2.00	0.02	51
3	0.075	10	4.2	5.8	77	0.62	1.88	0.03	58
4	0.1	10	1.4	8.6	86	0.14	1.93	0.07	86
5	0.125	10	1.3	8.7	69	0.11	1.83	0.07	87
6	0.150	10	0.6	9.4	62	-0.22	1.79	0.10	94

Table 7b: Percentage removal of methylene blue (MB) using AC7 at various adsorbent dosages

Sl No.	Adsorbent dosage (g)	Initial conc.of MB (ppm)	Final conc.of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	0.025	10	5.1	4.9	196	0.69	2.29	0.02	49
2	0.050	10	4.5	5.5	110	0.65	2.04	0.03	55
3	0.075	10	3.9	6.1	81	0.59	1.90	0.03	61
4	0.1	10	2.1	7.9	79	0.32	1.89	0.05	79
5	0.125	10	1.6	8.4	67	0.20	1.82	0.07	84
6	0.150	10	1.1	8.9	59	0.04	1.77	0.08	89

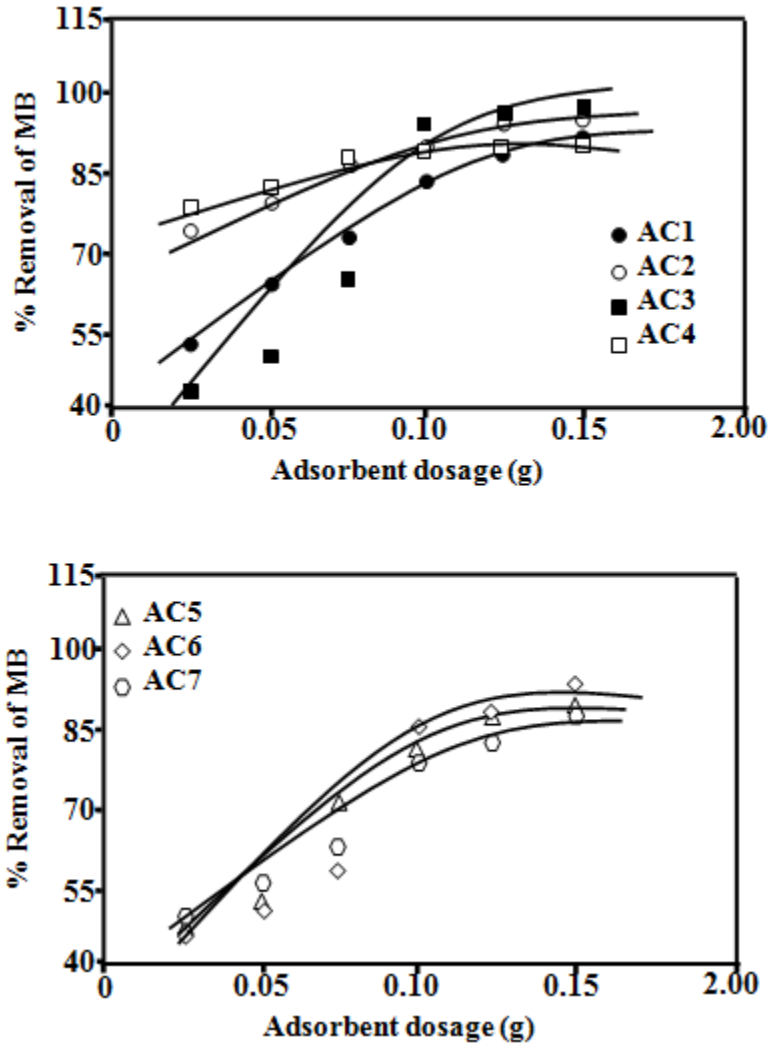

Figure 2: Effect of adsobent dosage on the removal of MB

Effect of pH

Adsorption is also affected by the pH change of the dye solution. The initial pH of dye solution was adjusted to pH 2, 4, 6, 8, and 10. The amount of dye adsorbed (in mg/g and percent) is given in Tables 1c-7c. Dye adsorption was determined by fixing the other parameters as constant and results are given in Fig. 3. The hydrogen ion concentration primarily affects the degree of ionization of the dyes and the surface properties of the adsorbents. Fig. 3 shows that the adsorption of the dye decreased with pH. It is apparent from the figure that the percentage removal of MB was increasing with increase in acidity and no significant increase in the dye removal while increasing the alkalinity (Ravichandran *et al.*, 2010). Hence, throughout the study, the pH of the medium was maintained at 4. The removal of dyes from aqueous solution by adsorption is dependent on pH of the solution, which affects the surface charge of the adsorbent, and degree of ionization, and speciation of the adsorbate (Alkan *et al.*, 2004).

The initial pH of the aqueous solution plays an important role in the whole adsorption process and particularly on the adsorption capacity of adsorbent. The acidity of solution, influencing not only the surface charge of the adsorbent and the degree of ionization of the material present in the solution, but also the solution chemistry of adsorbent (Órfão *et al.*, 2006). Therefore, it is important to indicate the effect of pH on adsorption capacity of prepared carbonaceous adsorbents.

Table 1c: Percentage removal of methylene blue (MB) using AC1 at various pH

Sl No.	pH	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	2	10	1.64	8.36	83.6	0.94	1.94	0.06	83.6
2	4	10	2.03	7.97	79.7	0.91	1.91	0.06	79.7
3	6	10	4.58	5.42	54.2	0.81	1.81	0.02	54.2
4	8	10	4.81	5.19	51.9	0.80	1.80	0.02	51.9
5	10	10	5.13	4.87	48.7	0.79	1.79	0.02	48.7

Table 2c: Percentage removal of methylene blue (MB) using AC2 at various pH

Sl No.	pH	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	2	10	1.24	8.76	87.6	0.09	1.94	0.08	87.6
2	4	10	2.18	7.82	78.2	0.33	1.89	0.05	78.2
3	6	10	3.32	6.68	66.8	0.52	1.82	0.04	66.8
4	8	10	4.39	5.61	56.1	0.64	1.74	0.03	56.1
5	10	10	5.48	4.52	45.2	0.73	1.65	0.02	45.2

Table 3c: Percentage removal of methylene blue (MB) using AC3 at various pH

Sl No.	pH	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	2	10	1.72	8.28	82.8	0.23	1.91	0.06	82.8
2	4	10	1.46	8.54	85.4	0.16	1.93	0.07	85.4
3	6	10	2.81	7.19	71.9	0.44	1.85	0.04	71.9
4	8	10	2.73	7.27	72.7	0.43	1.86	0.04	72.7
5	10	10	3.09	6.91	69.1	0.48	1.83	0.04	69.1

Table 4c: Percentage removal of methylene blue (MB) using AC4 at various pH

Sl No.	pH	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	2	10	1.25	8.75	87.5	0.94	1.94	0.07	87.5
2	4	10	1.83	8.17	81.7	0.91	1.91	0.06	81.7
3	6	10	3.50	6.50	65.0	0.81	1.81	0.04	65.0
4	8	10	3.64	6.36	63.6	0.80	1.80	0.03	63.6
5	10	10	3.73	6.27	62.7	0.79	1.79	0.03	62.7

Table 5c: Percentage removal of methylene blue (MB) using AC5 at various pH

Sl No.	pH	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	2	10	1.84	8.16	81.6	0.26	1.91	0.06	81.6
2	4	10	2.43	7.57	75.7	0.38	1.87	0.05	75.7
3	6	10	3.61	6.39	63.9	0.55	1.80	0.03	63.9
4	8	10	4.23	5.77	57.7	0.62	1.76	0.03	57.7
5	10	10	4.98	5.02	50.2	0.69	1.70	0.02	50.2

Table 6c: Percentage removal of methylene blue (MB) using AC6 at various pH

Sl No.	pH	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	2	10	1.7	8.3	83	0.23	1.91	0.06	83
2	4	10	2.5	7.5	75	0.39	1.87	0.05	75
3	6	10	4.4	5.6	56	0.64	1.74	0.03	56
4	8	10	4.5	5.5	55	0.65	1.74	0.03	55
5	10	10	4.9	5.1	51	0.69	1.70	0.02	51

Table 7c: Percentage removal of methylene blue (MB) using AC7 at various pH

Sl No.	pH	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	2	10	2.1	7.9	79	0.32	1.89	0.05	79
2	4	10	3.2	6.8	68	0.50	1.83	0.04	68
3	6	10	5.2	4.8	48	0.71	1.68	0.02	48
4	8	10	5.4	4.6	46	0.73	1.66	0.02	46
5	10	10	5.5	4.5	45	0.74	1.65	0.02	45

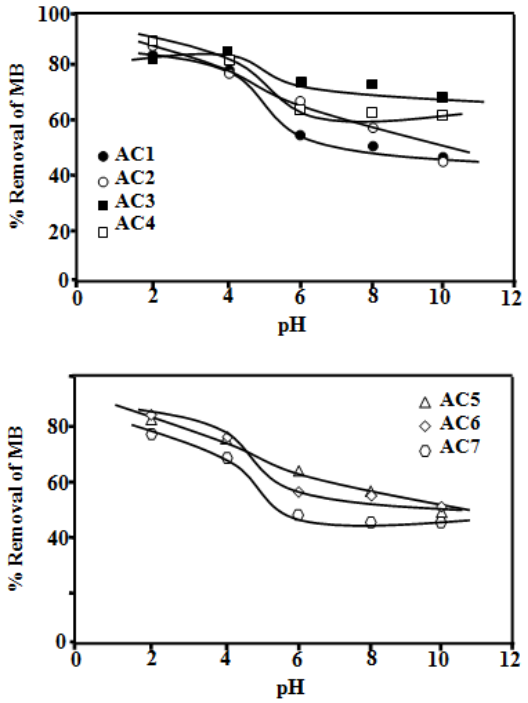

Figure 3: Effect of pH on the removal of MB

Effect of Dye Concentration

The effect of concentration of MB on the adsorbents AC1-AC7 was studied at constant contact time, temperature, and pH. The percentage removal of dye gets increased with increase in concentration of the dye. The initial MB concentrations were taken from 10, 20, 30, 40, and 50 ppm with adsorbent dosage of 0.1g for contact time of one hour. The percentage removal of MB gets increased gradually with the increase in dye concentration. This is due to increase in the driving force of the concentration gradient with an increase in the initial dye concentration. The rate constant for the removal of MB with AC1-AC7 for varying dye concentrations were calculated.

Adsorption Isotherms

The equilibrium adsorption isotherm is one of the most important ways for characterizing carbonaceous adsorbents. In this manner, the Langmuir and Freundlich isotherm equations were used to interpret the mechanism of the adsorption. The Langmuir adsorption, which is the monolayer adsorption, depends on the assumption that the intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation further assumes that adsorption occurs at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Furthermore, the Langmuir equation is based on the assumption of a structurally homogeneous adsorbent, where all sorption sites are identical and energetically equivalent. Theoretically, the sorbent has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further sorption can occur (Ozcan *et al.*, 2004). In this study, two most commonly used isotherms, namely Freundlich and Langmuir, have been adopted. The observed data on the adsorption of the dye at different temperatures have been analyzed on the basis of the Langmuir isotherm model.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_O} \quad (1)$$

where Q_0 = Langmuir constants related to the capacity and b = Langmuir constants related to the energy of adsorption.

The linear form of the Langmuir isotherm equation (Girgis *et al.*, 2007) is presented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (2)$$

Table 8: Langmuir isotherms for the sorption of MB on AC1-AC7

Adsorbent	Temp. K	q_{max}	K_L	r	sd	R_L	X^2
AC1	303	4.197	0.432	0.966	0.010	0.424	0.001
	313	4.432	0.271	0.980	0.014	0.451	0.004
	323	4.561	0.196	0.986	0.027	0.423	0.006
AC2	303	4.054	0.344	0.959	0.015	0.422	0.002
	313	4.111	0.255	0.976	0.017	0.444	0.004
	323	4.343	0.189	0.972	0.030	0.401	0.005
AC3	303	5.023	0.566	0.956	0.013	0.404	0.001
	313	5.112	0.432	0.946	0.019	0.443	0.003
	323	5.246	0.376	0.968	0.025	0.428	0.005
AC4	303	4.132	0.421	0.975	0.016	0.420	0.002
	313	4.354	0.328	0.985	0.018	0.441	0.005
	323	4.430	0.208	0.980	0.028	0.404	0.006
AC5	303	4.789	0.507	0.975	0.013	0.425	0.001
	313	4.876	0.476	0.985	0.015	0.443	0.002
	323	4.908	0.312	0.980	0.025	0.408	0.004
AC6	303	4.655	0.503	0.979	0.014	0.428	0.001
	313	4.788	0.454	0.988	0.015	0.446	0.003
	323	4.876	0.306	0.981	0.024	0.404	0.002
AC7	303	4.987	0.543	0.970	0.019	0.420	0.002
	313	5.045	0.490	0.980	0.022	0.441	0.006
	323	5.132	0.377	0.983	0.031	0.403	0.004

where q_e (mg g^{-1}) is the equilibrium dye concentration on the adsorbent, C_e (mg l^{-1}) the equilibrium dye concentration in the solution, q_{max} the monolayer adsorption capacity of the adsorbent (mg g^{-1}), and K_L is the Langmuir adsorption constant (l mg^{-1}) related to the free energy of adsorption. The plots of Ce/qe versus Ce for the adsorption give a straight line with slope of $1/q_{max}$ and intercept of $1/q_{max}K_L$. The experimental plots of Langmuir adsorption isotherm of MB on carbonaceous adsorbents have been shown in Figs. 4a-10a. Based on the slope and intercepts of these plots, the q_{max} and K_L values for adsorption of MB on prepared carbonaceous adsorbents were calculated and listed in Table 8**.**

Langmuir isotherm (Eq. 2) is found to be obeyed by the dye on all activated charcoals as shown in Figs. 4a-10a. This indicates that the dye is physisorbed on the surface of the activated charcoals. These logarithmic equations for the adsorption studies of dye on activated charcoals gave high linearity with a range of correlation coefficient between 0.966 and 0.988. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites on the activated carbon surface, since the Langmuir equation assumes that the surface is homogeneous.

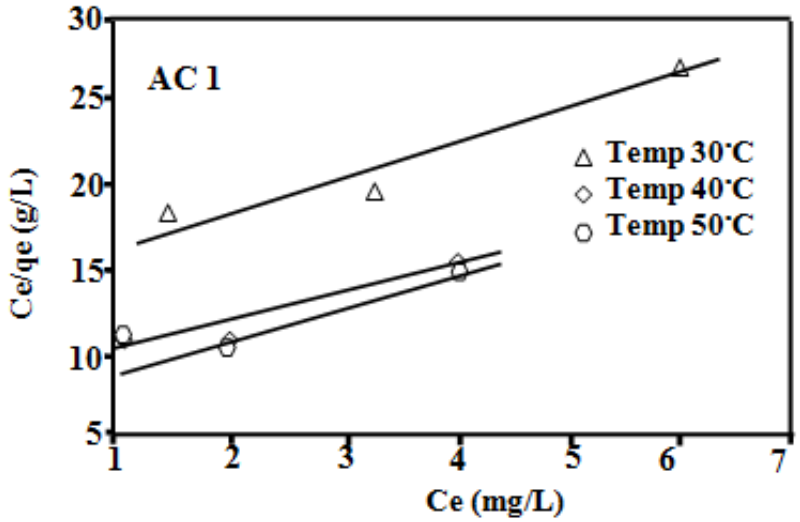

Figure 4a: Langmuir isotherm of sorption of MB on AC1

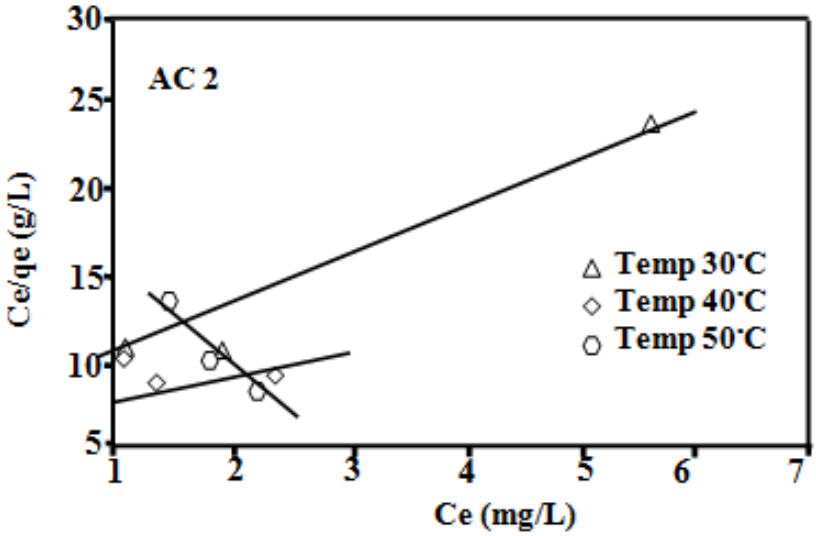

Figure 5a: Langmuir isotherm of sorption of MB on AC2

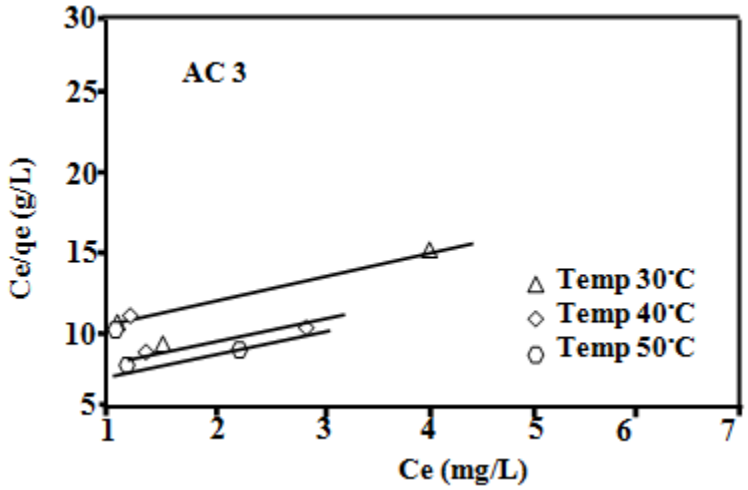

Figure 6a: Langmuir isotherm of sorption of MB on AC3

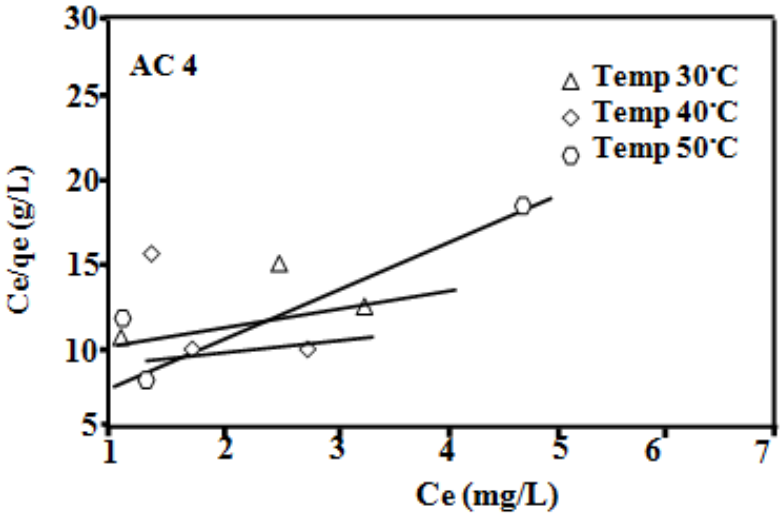

Figure 7a: Langmuir isotherm of sorption of MB on AC4

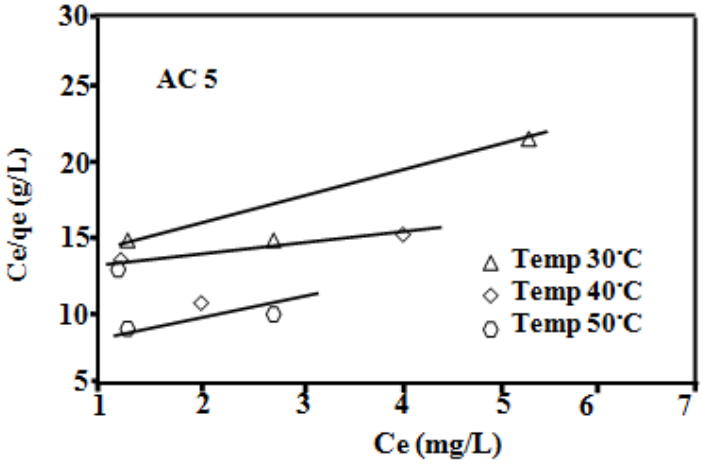

Figure 8a: Langmuir isotherm of sorption of MB on AC5

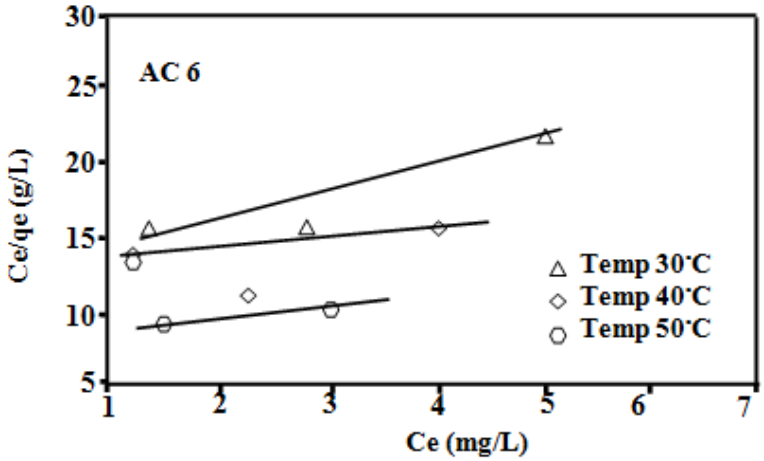

Figure 9a: Langmuir isotherm of sorption of MB on AC6

The equilibrium adsorption data at different dye concentrations are fitted with Freundlich isotherm model (Al-Degs *et al.*, 2007).

$$q_e = K_f C_e^{\,n}$$

$$\log q_e = \log K_f + n \log C_e$$

where *n* and K_f (mg/g) are Freundlich constants related to the intensity of adsorption and adsorption capacity, respectively. The plots of log q_e against log C_e are shown in Figs. 4b-10b. The values of Kf and n are calculated from the intercept and slope of these linearized plots and are listed in Table 9 along with the r values. The r values are very close to unity, which indicate that Freundlich isotherm is applicable.

Table 9: Freundlich isotherms for the sorption of MB on AC1-AC7

Adsorbent	Temp. K	1/n	n	K_f,mg/g 1/n(L/mg)	r	sd	X^2
AC1	303	0.265	0.921	0.345	0.985	0.018	0.006
	313	0.293	0.868	0.258	0.978	0.046	0.006
	323	0.324	0.849	0.243	0.983	0.035	0.008
AC2	303	0.242	0.911	0.332	0.985	0.019	0.006
	313	0.276	0.857	0.276	0.979	0.045	0.007
	323	0.297	0.834	0.240	0.984	0.036	0.008
AC3	303	0.236	0.926	0.333	0.986	0.017	0.007
	313	0.285	0.867	0.250	0.978	0.045	0.007
	323	0.291	0.821	0.243	0.983	0.033	0.008
AC4	303	0.240	0.896	0.322	0.983	0.019	0.006
	313	0.263	0.842	0.244	0.975	0.047	0.006
	323	0.289	0.784	0.201	0.980	0.038	0.009
AC5	303	0.297	0.894	0.320	0.982	0.020	0.005
	313	0.256	0.854	0.241	0.979	0.049	0.006
	323	0.212	0.843	0.225	0.981	0.038	0.007
AC6	303	0.253	0.896	0.324	0.987	0.021	0.006
	313	0.277	0.842	0.246	0.970	0.049	0.008
	323	0.290	0.784	0.205	0.986	0.039	0.009
AC7	303	0.244	0.899	0.328	0.983	0.019	0.007
	313	0.261	0.847	0.247	0.972	0.047	0.007
	323	0.285	0.789	0.205	0.980	0.036	0.007

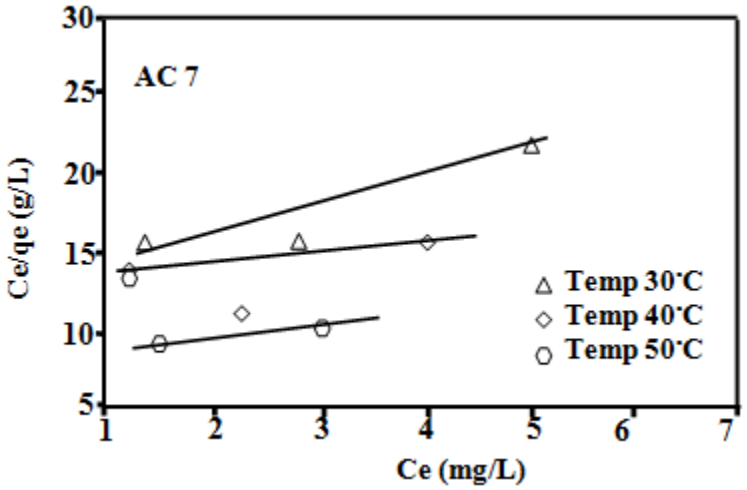

Figure 10a: Langmuir isotherm of sorption of MB on AC7

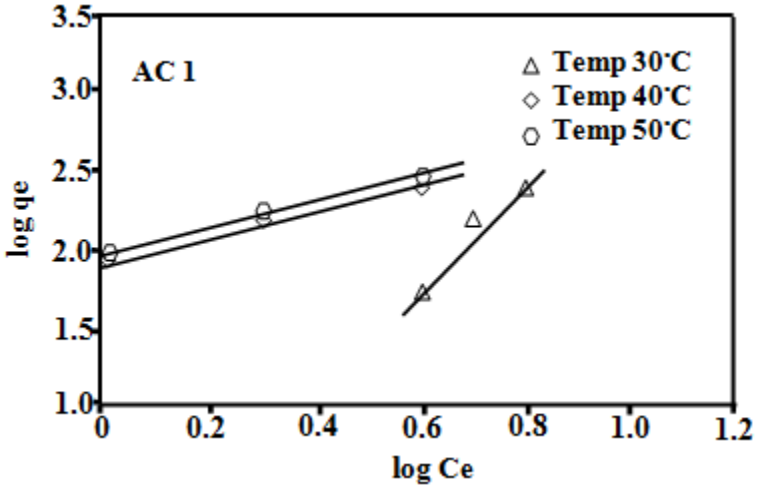

Figure 4b: Freundlich isotherm of sorption of MB on AC1

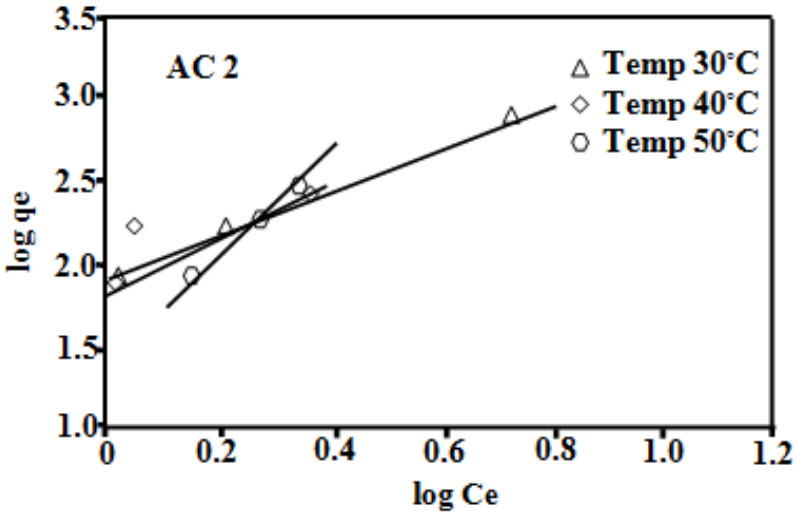

Figure 5b: Freundlich isotherm of sorption of MB on AC2

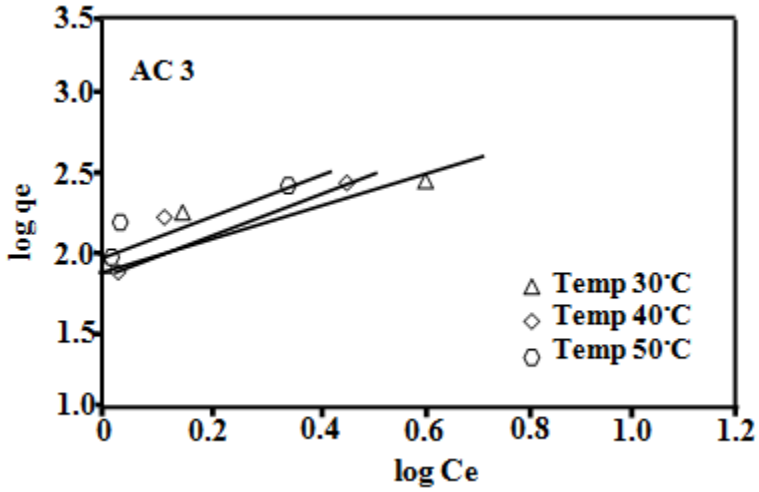

Figure 6b: Freundlich isotherm of sorption of MB on AC3

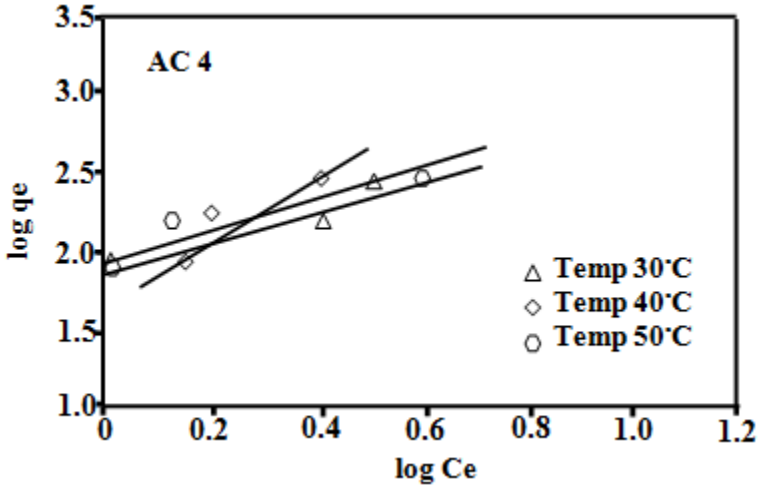

Figure 7b: Freundlich isotherm of sorption of MB on AC4

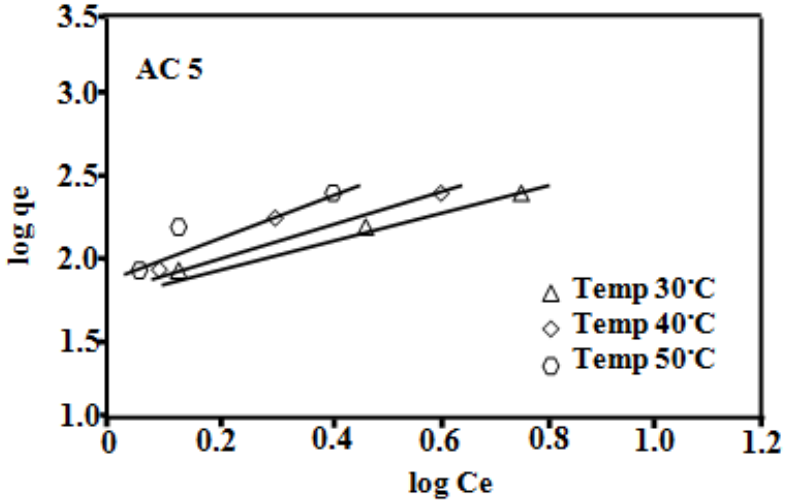

Figure 8b: Freundlich isotherm of sorption of MB on AC5

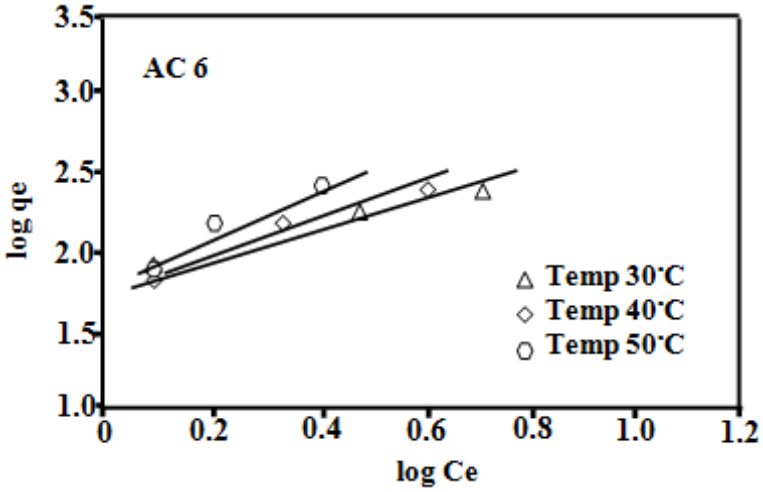

Figure 9b: Freundlich isotherm of sorption of MB on AC6

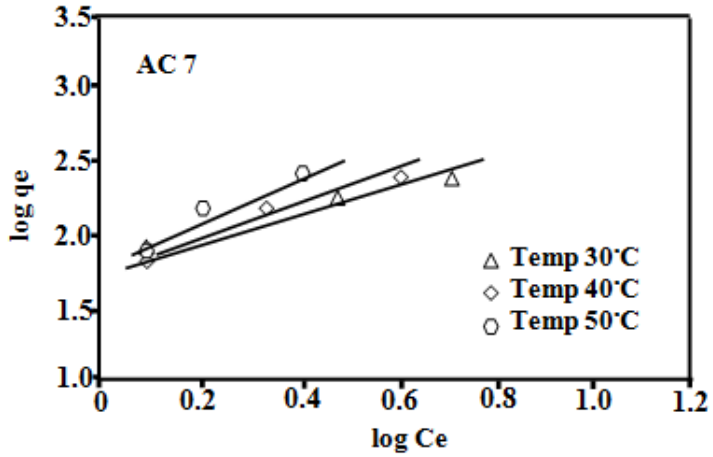

Figure 10b: Freundlich isotherm of sorption of MB on AC7

The values of K_f and q_{max}, the respective Freundlich and Langmuir constants decrease with increase in temperature, showing the temperature dependence of the rate of sorption. The decrease in adsorption with increase in temperature suggests weak adsorption between the surface and sorbents, which supports physisorption. From the r values, it is found that the Langmuir model is the best-fit model for the adsorption of MB onto the adsorbents AC1-AC7 than the Freundlich model.

Adsorption isotherms were obtained at 303, 313, and 323K for MB with the adsorbents AC1-AC7. The isotherms are shown in Figs. 4-10. The isotherms are of L-type, indicating that MB has high affinity for the adsorbents AC1-AC7. The initial sharp rise in the extent of adsorption with increasing dye concentration shows that the bombarding solute molecules find difficulty in accessing vacant sites on the adsorbent as more and more sites are filled up.

It may be noted that the value of K_f and n decrease with an increase in temperature for all the dye on the adsorbents AC1-AC7 indicating that adsorption is favourable at low temperature. The value of K_f is related to the degree of adsorption. The dye having the greater value of K_f has high affinity toward the adsorbent as compared to other having low K_f value. In the present study, it is found that methylene blue has the highest value of K_f indicating its highest affinity towards the adsorbents studied. The value of n in all the cases is slightly less than unity indicating that the adsorption is more significant with all these adsorbents.

Conclusion

Activated charcoal is efficiently utilized as an adsorbent for the removal of hazardous dyes from the aqueous solutions. The adsorption of MB dye was found to decrease with the increase in temperature. The adsorption also decreased with the pH. The adsorption of methylene blue on all adsorbents is explained well by the Langmuir and Freundlich isotherm models. The fitness of Langmuir's model indicates the formation of monolayer coverage of the adsorbate on the outer surface of the adsorbent. The removal of dye between 65 and 96 percent is quite significant in all the adsorbents and it indicates that all adsorbents are moderately good for the removal of color from textile wastewater.

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