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Removal of Acid Violet 19 Dye from Aqueous Solution by Adsorption onto Activated Charcoal and Polyaniline Coated Charcoal

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Abstarct: In this study, activated charcoal and polyaniline coated charcoal were used as adsorbents for the investigation of the adsorption isotherms of the Acid Violet 19 dye in aqueous solutions at various dye concentrations, contact time, pH and adsorbent dose. The results showed that the percentage removal of dye by Charcoal and Polyaniline coated charcoal increases with increase in agitation time and adsorbent dose. The extent of removal of dyes decreases with increase in initial concentration of dyes and acidic pH was favorable for the adsorption of this dye. The experimental data isotherms were analyzed using the Langmuir, Freundlich equations.

Keywords: Charcoal, Polyaniline coated charcoal, adsorption, dye concentration, pH, Langmuir and Freundlich isotherms.

I. INTRODUCTION

The pollution caused by industrial wastewater has become a common problem for most of the countries. Dyes are synthetic aromatic compounds which are embodied with various functional groups. They are widely used in textile, leather, paper, plastic, and other industries. Some of these dyes may degrade to produce carcinogens and toxic products [1]. Dyes can cause allergic dermatitis, skin irritation, cancer and mutation [2]. Textile industries consume the large volumes of water and chemicals for wet processing of textiles. The chemical reagents used are very diverse in chemical composition, ranging from inorganic compounds to polymers and organic products [3]. The presence of very low concentrations of dyes in effluent is highly visible and undesirable [4]. Commercially available activated carbons (AC) are usually derived from natural materials such as wood, coconut shell, lignite or coal, but almost any carbonaceous material may be used as precursor for the preparation of carbon adsorbents [5,6,7]. Because of its availability and cheapness, coal is the most commonly used precursor for activated charcoal production and can be used as adsorbents for dye removal [8, 9].

In the present work, adsorption of Acid Violet 19 dye onto charcoal and Polyaniline coated charcoal has been investigated and the obtained experimental data were analyzed using adsoption isotherms namely, Langmuir and Freundlich. The effect of initial dye concentration, adsorbent dose and effect of pH has been studied.

II. EXPERIMENTAL METHODS

A. Materials

i. Aniline (Merck) was doubly distilled 182-185 ºC (boiling point 184 ºC)
ii. Ammonium per di sulpate (sd fine chemicals) AR grade was used as received.
iii. Solvents DMSO, NMP, DMF, Acetone (Merck, AR grade), Formic acid was used as received.
iv. Activated charcoal and polyaniline coated charcoal
v. Acid violet 19 dye (Merck) was purchased and used as such.

B. Synthesis of Adsorbents

i) Chemical synthesis of Polyaniline (PANI)

Polyaniline powder was synthesized according to a procedure reported in literature after some modifications [10-12]. In a typical procedure, 5.0 g (0.054 moles) freshly distilled aniline dissolved in 250 ml of HCl 1M. The mixture was cooled to below 5oC by using an ice bath. 250 ml of a pre-cooled 0.3 M (NH4) 2S2O8 solution in HCl (1M) was slowly added under vigorous stirring to monomer solution over a period of 30 minutes. Since the reaction is highly exothermic (ΔH = -372 KJ mol-1), the reaction vessel was placed in an ice bath cooling system during the addition of the oxidant. After complete addition of the oxidant, the reaction mixture was left stirring for about two hours at low temperature (0-5o C) and left unstirred overnight at room temperature. The precipitated polymer (dark green powder) was filtered and washed with distilled water and dilute HCl solution until the washing liquid was colorless. In order to remove the oligomers and other non-polymeric impurities the precipitate was washed thoroughly with methanol and finally with distilled water. The polymer was dried at 50-60oC in an oven, powdered in a mortar and stored for processing. Based on the weight of the monomer used and the product polymer obtained, the polymerization yield was found about 80%.

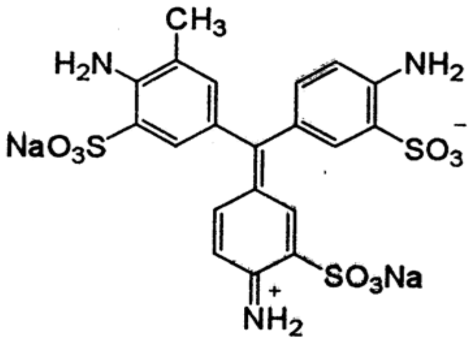
ii) Synthesis of charcoal

Raw sawdust was completely immersed in 2N NaOH aqueous solution for a period of 8 h. Thereafter, it was washed with several times with distilled water to remove the lignine content and excess of NaOH and then dried. It was observed that a dark red solution was generated during this treatment , which indicate the removal of lignine from the adsorbent material. Sawdust was repeatedly washed with double distilled water till no red colouration was observed. It was then immersed in 0.2N sulphuric acid for a period of 8 h to remove traces of alkalinity and other impurities. The acid treated saw dust material was thoroughly washed with double distilled water to remove excess of sulphuric acid and other colouring materials till the wash water was colourless. After this, the treated sawdust adsorbent material was dried in the sunlight and stored for use as an adsorbent [13].

iii) Synthesis of Polyaniline coated charcoal

In order to make Polyaniline soluble in formic acid for coating and composite formation, the polymer was treated with 0.5M NaOH solution for 2 hours. Then it was washed with distilled water and dried in an oven at 60 C.0.50g of base treated Polyaniline, emeraldine base (EB) was dissolved in 50 ml of formic acid. The polymer solution was filtered in order to remove any non-dissolvable solids. For preparation of Polyaniline coated charcoal, 5 g charcoal were mixed with 50 ml of EB in formic acid in a beaker and stirred for two hours at room temperature and left for another 2 hours without stirring. The excess of the solvent was evaporated by heating the product at 60 C in an oven.

iii) Structure of Acid Violet 19 dye



III. RESULTS AND DISCUSSION

A. Results

i) Characterization of Polyaniline

Polyaniline was synthesized by chemical oxidation method and coated with activated charcoal is used as adsorbent for the removal of Acid violet 19 dye.

ii) Solubility

Solubility of Polyaniline was investigated in various solvents. Polyaniline is partially soluble in polar solvents like DMSO, DMF, and NMP but it is insoluble in solvents like acetone, methanol, ethanol and water.

iii) UV-Visible Spectral Analysis

UV-Visible spectrum of Polyaniline was recorded in SYSTRONICS Double Beam UV-Visible spectrophotometer. DMSO was used as a solvent. The spectrum show two absorption band, one in UV-region and other one in visible region. The UV region absorption 312 nm is due to excitation of π-electrons present in the aromatic ring system of the polymer and the peak at (618 nm) visible region is due to the excitation of unpaired present in N-atom of polymer matrix.

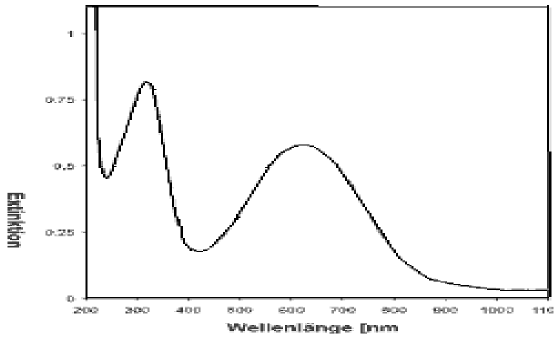


Figure 1: UV-Visible Spectrum of Polyaniline

iv) FT-IR Spectral Analysis

FT-IR spectroscopy is a vast tool to analysis the structure and end groups of the polymer with great accuracy. The adsorption band of polymer is tabulated in the table and the FT-IR Spectrum is shown in the figure 2.

Table 1 FT-IR spectral data of Polyaniline

Assignments	Wave numbers (cm^{-1})
N-H Stretching	3391
C-H Stretching (Aromatic)	2920
N-H Deformation	1,54,21,597
C=N Stretching	1636
C-H in plane bending	1,16,01,12,61,018
Aromatic ring Deformation	8,10,880

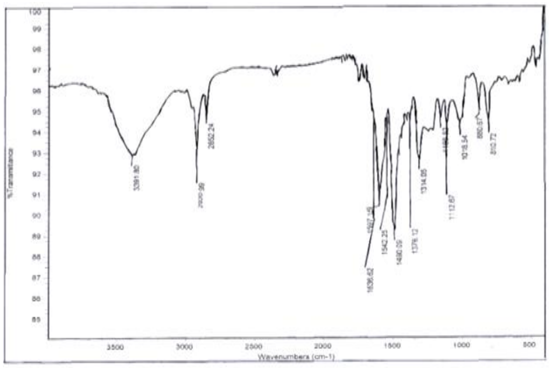


Figure 2: FT-IR spectrum of Polyaniline

v) Thermo gravimetric Analysis

Thermal stability of Polyaniline was determined by Thermo gravimetry. The thermal analysis was carried out between room temperature 27 °C to 800 °C at heating rate of 10°C per min in Nitrogen atmosphere. TGA curve shows the three stage weight loses. First weight is due to the evaporation of absorbed and occluded water form the polymer this weight happened up to 120 °C. The second weight loss is due to the release of dopant ions occurred at 120 – 230 °C. Above 400 °C, the polymer is started to decompose and the residue of 8 % remains at 800 °C.

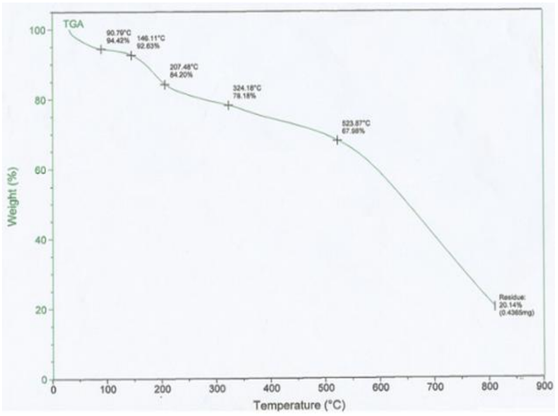


Figure 3 TGA-curve of Polyaniline

B. Batch Mode Adsorption Studies

1. Adsorption studies using charcoal

i) Effect of PH on Adsorption of Acid violet 19 dye

For performing this experiment, Dye solutions of concentration viz.,10, 20, 30, 40 and 50mg/L were prepared from the 1000mg/L stock solution using distilled water. 50ml of the above solution was taken in different 100ml conical flasks. The PH of the sample solutions adjusted from 1 to 10 using dilute HCL and NaOH. 50 mg of the charcoal was treated with the sample solutions and agitated at room temperature (30 ± 1 0C) using mechanical shaker for 120 minutes. The samples were filtered using Whatmann filter paper No. 41 and estimated colorimetrically for the amount of dye adsorbed.

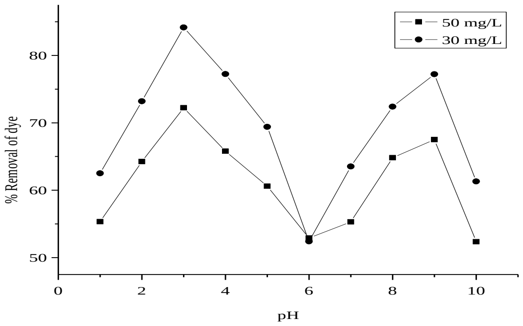


Figure 4: Effect of PH on Adsorption of Acid violet 19 by charcoal

Acid violet 19 is an acidic dye and contains negatively charged sulfonated group (-SO3-Na+). The maximum adsorption of dye was obtained at pH 3. As the pH of the system increases the number of negatively charged adsorbed sites increases and favour the adsorption of the dye by electrostatic attraction. [14]. Consequently the positive charge density would be located more on the dye molecule at pH 3, and this accounts for the higher dye uptake on the negatively charged surface.

ii) Effect of Agitation Time on Adsorption of Acid violet 19 dye

In this experiment different concentration of dye solutions viz.,10, 20, 30, 40 and 50mg/L were prepared and treated with 50mg of adsorbent (charcoal). The samples were agitated at room temperature (30 ± 1 0C) using mechanical shaker. In order to identify the time required to attain the equilibrium adsorption, the investigation was carried out at different time intervals viz.,10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 and 120 minutes. The adsorbate and adsorbent were separated by filtering using Whatmann filter paper No. 41. The filtrates were estimated colorimetrically for the amount of dyes adsorbed.

Percentage removal =100(C0 – C) / m

C0 = initial concentration of dye(mg/L)

C = concentration of dye (mg/L)

M = mass of the adsorbent (mg)

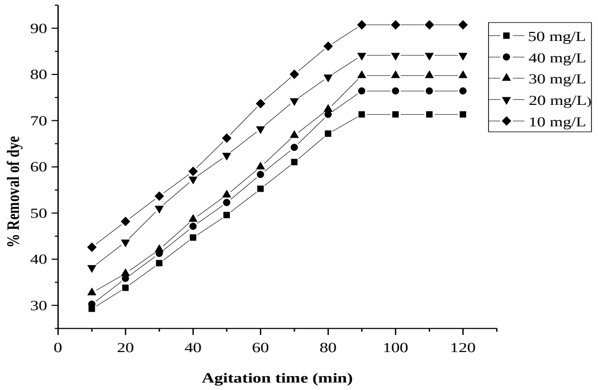


Figure 5: Effect of Agitation Time on Adsorption of Acid violet 19 by charcoal

The time curve shows that the removal of adsorbate is rapid but it gradually slows down until it reaches equilibrium. The equilibrium time was 90 minutes. This is due to the fact that a large number of vacant sites are available for adsorption during the initial stage, and after a lapse of time the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Once equilibrium was attained, the percentage sorption of dyes did not change with further increase of time. So, it was assumed that longer treatment might not have further effect to change the properties of the adsorbent.

iii) Effect of Initial Dye Concentration on Adsorption of Acid violet 19 dye

For this investigation, 50 mg of adsorbent (charcoal) were treated with different concentration of dye solutions viz.,10, 20, 30, 40 and 50mg/L. The samples were agitated at room temperature (30 ± 1 0C) using mechanical shaker for 120 minutes. The samples were filtered using Whatmann filter paper No. 41 and estimated colorimetrically for the amount of dye adsorbed.

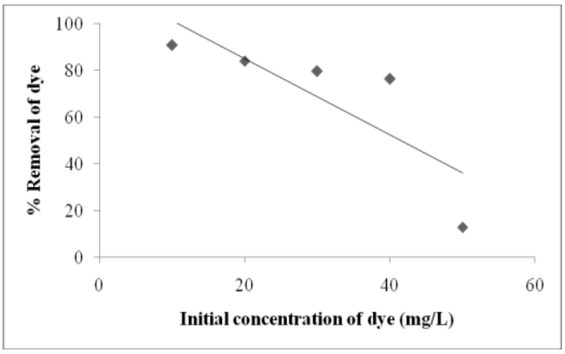


Figure 6 Effect of Agitation Time on Adsorption of Acid violet 19 by charcoal

The equilibrium adsorption capacity of charcoal increase with increase in initial dye concentration, while percent removal of dye showed that the opposite trend [15]. When the initial dye concentration increased from 10 to 50 mg/L the percentage removal decreased from 80 to 30 %

iv) Effect of adsorbent dose on adsorption of Acid violet 19

For performing this research, different amounts of adsorbent (charcoal) viz.,20, 40, 60, 80, and 100 mg were added into the dye solutions of concentration viz.,10, 20, 30, 40 and 50mg/L. The samples were agitated at room temperature (30 ± 1 0C) using mechanical shaker for 120 minutes. The samples were filtered using Whatmann filter paper No. 41 and estimated colorimetrically for the amount of dye adsorbed.

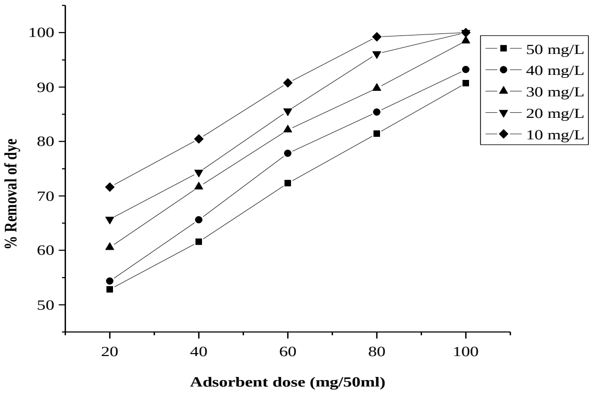


Figure 7 Effect of adsorbent dose on Adsorption of Acid violet 19 by charcoal

From the figure 8, it was observed that, the percentage of dye removal increased from 53 to 99 % .The percentage removal increased with increase the charcoal dosage. The increase in adsorption of dyes with adsorbent dosage can be attributed to increased surface area and the availability of more adsorption sites [16].

2. Adsorbent studies using Polyaniline coated Charcoal

i) Effect of pH on adsorption of Acid violet 19

For performing this experiment, 50 mg of the adsorbent (Polyaniline coated charcoal) l was treated with 10-50 mg/L dye solutions at different pH values (1-10). The PH of the sample solutions adjusted by using dilute HCL and dilute NaOH. The results obtained are shown in figure 9.

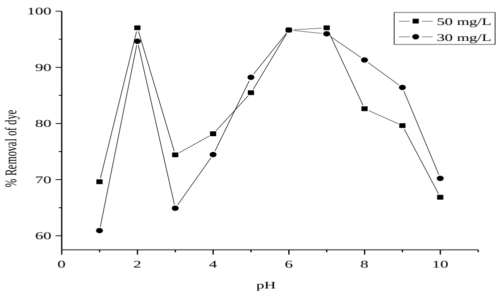


Figure 8: Effect of pH on Adsorption of Acid violet 19 by Polyaniline coated charcoal

ii) Effect of agitation time on adsorption of Acid violet19

For this investigation, 50 mg of adsorbent (Polyaniline coated charcoal) were mixed with 10-50 mg/L dye solutions and agitated at room temperature (30 ± 1 0C) using mechanical shaker. In order to identify the time required to attain the equilibrium adsorption, the investigation was carried out at different time intervals viz.,10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 and 120 minutes. The results are summarized in Figure 10.

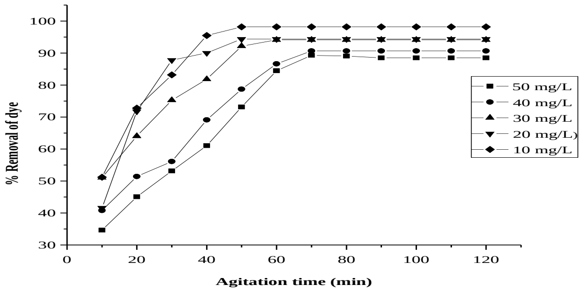


Figure 9 Effect of agitation time on Adsorption of Acid violet 19 by Polyaniline coated charcoal

iii) Effect of initial concentration on adsorption of Acid violet

For performing this experiment, 50 mg adsorbent (Polyaniline coated charcoal) were treated with 10-50 ppm dye solutions and the results are shown in Figure 11.

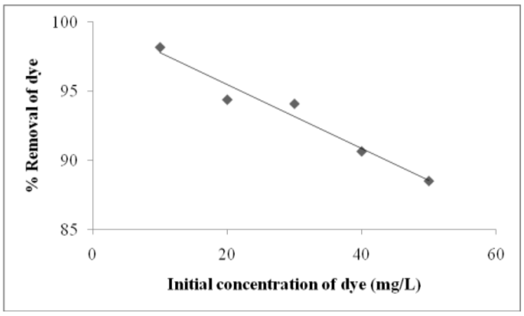


Figure 10 Effect of initial concentration on Adsorption of Acid violet 19 by Polyaniline coated charcoal

iv) Effect of adsorbent dose on adsorption of Acid violet 19

For performing this research, different amounts of adsorbent (Polyaniline coated charcoal) viz.,20, 40, 60, 80, and 100 mg were treated with the dye solutions of concentration viz.,10, 20, 30, 40 and 50mg/L. The results obtained are shown in figure12.

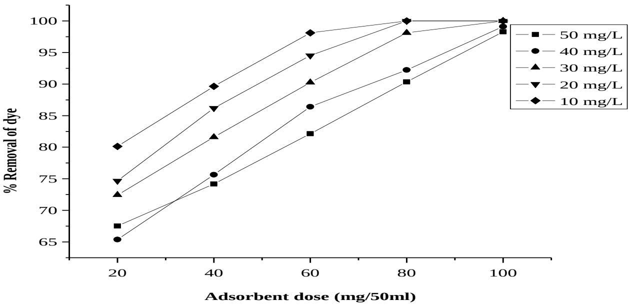


Figure 11 Effect of adsorbent dose on Adsorption of Acid violet 19 by Polyaniline coated charcoal

3. Adsorption isotherms

i) Langmuir isotherm

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The data of the equilibrium studies for adsorption of Acid violet 19 onto charcoal and Polyaniline coated charcoal may follow the following form of Langmuir model,

$$C_e/Q_e = 1/Q_o b + C_e/Q_o$$

Where, C_e is the equilibrium concentration (mg/L) and Q_e is the Langmuir equilibrium constant and b is the amount of adsorbate required to form a monolayer. Hence, a plot of C_e/Q_e vs. C_e should be a straight line with a slope of $(1/Q_o)$ and an intercept as $(1/bQ_0)$.

The values of constants Q_0 and b were calculated and reported in the table 3. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter (R_L), also known as the separation factor, given by

$$R_L = 1/(1+bC_o)$$

The value of $\mathbf{R_L}$ lies between 0 and 1 for favourable adsorption and the high values of correlation coefficient ($\mathbf{R^2}$) indicate a good agreement between the parameters and confirm the monolayer adsorption of Acid violet 19 onto the adsorbents [17].

Table 2 Isotherm parameters for removal of Acid violet 19 by charcoal and polyaniline coated charcoal

S. No	Initial concentration of Acid violet 19 (mg/L) C_0	charcoal		Polyaniline coated charcoal	
		C_e (mg/L)	C_e/Q_e (g/L)	C_e (mg/L)	C_e/Q_e (g/L)
1	10	0.92	0.10	3.89	0.64
2	20	3.17	0.19	13.51	2.08
3	30	6.07	0.25	24.92	4.91
4	40	9.43	0.31	33.80	5.46
5	50	14.33	0.40	43.53	6.73
	Slope	0.021332		0.157303	
	Intercept	0.105282		0.199746	
	R^2	0.987686		0.983759	

Table 3: Langmuir isotherm constants

Dye in solution	Q_o(mg/L)	b(l/mg)	R_L
Acid Violet 19 dye	4.6772	6.4713	0.0061

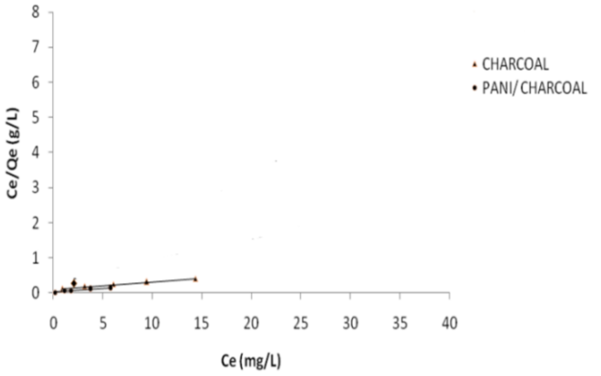


Figure 12 Langmuir plot of adsorption of Acid violet 19

ii) Freundlich isotherm

The Freundlich adsorption isotherm presents the relationship between the amount of dye adsorbed per unit mass of the adsorbent Q_e and the concentration of the dye in solution at equilibrium. The Freundlich adsorption isotherm is

$$Q_e = K_F C_e^{1/n}$$

The equation can be linearized by taking logarithm to find parameters K_F and n.

$$\mathrm{Log}_{10} (x/m) = \log_{10} K_f + (1/n) \log C_e$$

The logarithmic plot of the Freundlich expression for the amount of dye adsorbed per unit mass of the adsorbent (Q_e) and the concentration of the dye at equilibrium (C_e). The values of K_F and n were calculated from the slope and the intercept of the plot. Where x is amount of dye adsorbed (mg), m is the weight of the adsorbent used (g), Ce is the equilibrium concentration of the dye solution (mg/l), K_f and n are constants incorporating all factors affecting the adsorption process (adsorption capacity and intensity) Linear plot of log $_{10}$(x/m) vs. log $_{10}$ Ce shows the adsorption the Freundlich isotherm .

$$Q_e = C_0 - C_{e\,/}\ m$$

Qe = Dye adsorbed per unit mass of the adsorbent

Ce = Equilibrium concentration (mg/L)

Co =initial concentration of the dye solution (mg/L)

m = Amount of adsorbent (mg)

Table 4: Isotherm parameters for removal of Acid violet 19 by charcoal and polyaniline coated charcoal

S. No	Amount of adsorbents (mg/50ml)	Charcoal		Polyaniline coated charcoal	
		log C_e	log Q_e	log C_e	log Q_e
1	20	1.3725	1.4219	1.6556	0.6776
2	40	1.2838	1.4883	1.6472	0.7497
3	60	1.1415	1.5582	1.6248	0.8954
4	80	0.9680	1.6098	1.5783	1.0839
5	100	0.6675	1.6567	1.5126	1.2418
	Slope	0.31955		3.86128	
	Intercept	1.894217		7.121973	
	R^2	0.9536		0.97737	

Table 5: Freundlich isotherm constants

Concentration of dye in solution	K_F	n	R^2
50 mg/L	11.5624	0.5783	0.9912

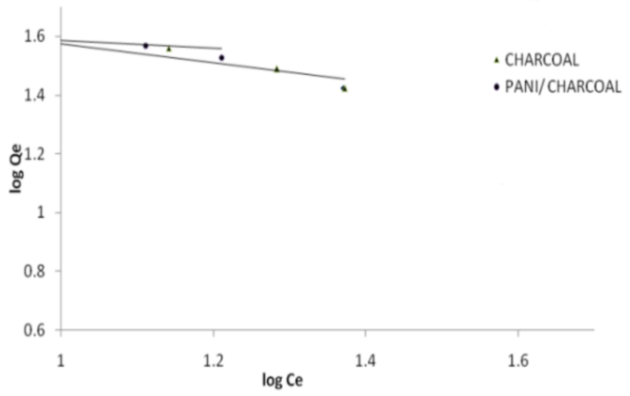


Figure 13: Freundlich plot of adsorption of Acid violet 19

Freundlich adsorption isotherm deals with the multilayer adsorption of the substance on the adsorbent. The related parameters were calculated and reported in the table. The Freundlich adsorption isotherm is an indication of surface heterogeneity of the adsorbent and thus is responsible for multilayer adsorption due to the presence of energetically heterogeneous adsorption sites. In general, higher the values, greater will be the adsorption capacity [18].

CONCLUSIONS

Equilibrium studies were performed for the adsorption of Acid Violet 19 dye, from its aqueous solutions by charcoal and Polyaniline coated charcoal. The results show that charcoal and Polyaniline coated charcoal can be used as an effective adsorbent to remove Acid violet 19 dye from the aqueous solution. The percentage removal of dyes by charcoal and Polyaniline coated charcoal increases with increase in agitation time (contact time between adsorbent and adsorbate) and obtain equilibrium concentration finally. The optimum contact time is found to be 80 – 90 minutes. The extent of removal of dyes decreases with increase in initial concentration of dyes. pH is an important factor that controls the sorption of dyes from aqueous solutions on to solids. The maximum adsorption of dye was obtained at pH 3. The obtained results showed that the adsorption equilibrium data fitted well to the Langmuir and Freundlich isotherms. The correlation coefficient (R2) indicate a good agreement between the parameters and confirm the monolayer adsorption of dyes onto the adsorbents.

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