ACID VIOLET 43 REMOVALS FROM AQUEOUS SOLUTION USING POLYPYRROLE AS ADSORBENT

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ABSTRACT: *In situ chemical oxidation method was followed to synthesize the polypyrrole, and was used to remove the acid violet 43 from aqueous solution. The prepared Polypyrrole and dye loaded polypyrrole was characterized by Infrared Spectrophotometery. The IR spectra of polypyrrole were taken before and after adsorption. MAC (Maximum adsorption capacity) of the polypyrrole was determined up to 21.276 mg g^{-1} for acid violet. Results revealed that the adsorption of acid violet 43 on polypyrrole was pH temperature dependent. The kinetic data was well fitted with pseudo-second-order showing chemisorption nature of adsorption process. Both the Langmuir and Freundlich isotherms were followed by the adsorption process. It was concluded that the adsorption process involves complex formation between the adsorbent and adsorbate as the process strongly followed Pseudo-second order kinetics.*

Key Words: Acid Violet 43, Polypyrrole, Langmuir adsorption isotherm, Pseudo-second order.

INTRODUCTION

Dye and pigments are extensively used in different industries like paper, textiles, plastics, food and dye industries. These industries discharge huge amount of colored wastewater which are harmful [1]. It is very important to treat such wastewater as the wastewater causes skin allergy, mutation, cancer and skin irritation [2]. Techniques mostly used to treat dye containing wastewater are coagulation/flocculation, biodegradation, membrane separation, oxidation, selective bioadsorbent, using biological mass, photochemically, electrochemically, ion exchange and adsorption method [3-5]. Acid Violet 43 a synthetic dye, commercially known as Jarocol 43, mostly referred to as anthraquinone generally. It exists in the form of dark violet crystalline powder with a bluish touch in daylight and become slightly red in artificial light. It is specifically used in cosmetic formulations such as hair dyes, colors and coloring rinses. It is allowed in cosmetic products except but can be harmful when comes in contact with mucous membrane. Toxicological study of Acid Violet 43 illustrates that it is a dermal toxicant and imparts corrosion and irritation to skin and eyes if its concentration in cosmetics exceeds from recommended standards. In terms of nomenclature Acid Violet 43 is known as benzene-sulfonic acid, 2-[(9, 10-dihydro-4-hydroxy-9, 10-dioxo-1-anthracenyl) amino]- 5-methyl-, monosodium salt. Empirical formula of Acid Violet 43 is $C_{21}H_{14}NO_6SNa$ and its molecular mass 431.4 g mol^{-1}. At 22 ^{0}C its solubility in water is slightly greater than 1g ml^{-1}. Structure of Acid Violet 43 is given below [6].

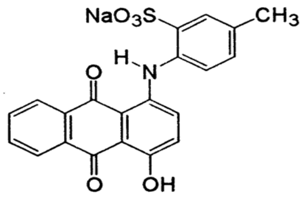

Fig. 1 Molecular Structure of Acid Violet 43 [6]

Adsorption is one of the most efficient methods for the removal of colored pollutant materials from industrial effluents. Among conventional adsorbents, activated carbon is the highly efficient and extensively used adsorbent due to its micro-porous structure and highly active surface area [7]. Others adsorbents are industrial wastes [8], clays [9], kaolinite, talc [10], bentonite [11], chitosan [12], perlite [13], dolomite and calcite [14], zeolites [15] and peat [16].

MATERIALS AND METHOD

Materials

Pyrrole (Unichem Chemicals), Ferric Chloride hexahydrate (Riedel-de-Haen), Acid Violet 43 (Scharlaou Chemicals), Sulfuric acid (Fischer Chemicals), Ammonium hydroxide (Merck) and Distilled water. Analytical grade chemicals were used.

Preparation of Polypyrrole

Polypyrrole was synthesized by following already reported method in which 0.1 moles (16.25g) of $FeCl_3.6H_2O$ was mixed in 50 ml of water in 250 ml flat bottom flask and stirred the solution until whole of the ferric chloride was dissolved in the solution and the solution become uniform. The mixture was stirred for 30 minutes and then, 0.043 mole (2.881 g) of pyrrole was added to stirred aqueous solution. The reaction was carried out for 4 hours on stirring at room temperature [17]. Distilled water used to wash the resultant polymer and dried at room temperature.

RESULTS AND DISCUSSION

FTIR Characterization

Infrared spectra were recorded on Bruker Vector 22 FTIR spectrometer, ranging 4000 cm^{-1} to 400 cm^{-1} wave number. Spectra of pure polypyrrole and dye loaded polypyrrole are shown in following figure 2 and 3.

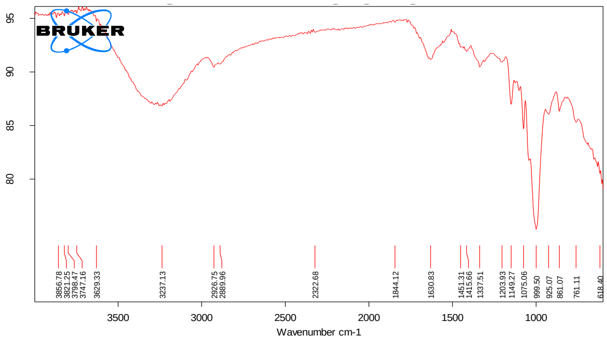

Fig. 2 FTIR Spectrum of Pure Polypyrrole

Absorption band at 1539.08 cm^{-1} was due to characteristics polypyrrole ring stretching mode. -C-C- and -C-H- stretching frequency of polypyrrole ring appeared at 1451.31 cm^{-1} and 925.07 cm^{-1}, respectively. In plane deformation and wagging frequency of carbon hydrogen bond (-C-H-) appeared at 1415.66 cm^{-1} and 761.11 cm^{-1} respectively. Characteristic carbon nitrogen (-C-N-) stretching frequency appeared at 1203.93 cm^{-1}. Absorbance at 3237.13 cm^{-1} attributed to -OH of the water moisture adsorbed on the surface of polypyrrole [18-20].

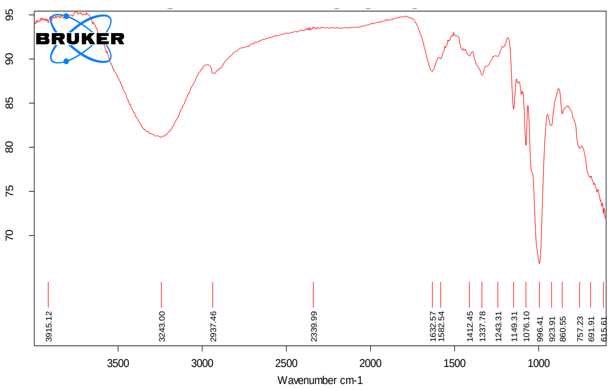

Fig. 3 FTIR Spectrum of Dye Loaded Polypyrrole

Adsorption of acid violet confirmed from change in polypyrrole ring mode frequency. Characteristics polypyrrole ring stretching mode frequency shifted to 1538.39 cm^{-1} from 1539.08 cm^{-1} present in unloaded polypyrrole shows interaction between positively charged dye and lone pair of electron on the nitrogen of the polypyrrole chain. -C-C- and -C-H- stretching frequency of polypyrrole appeared at low values which are 1470.17 cm^{-1} and 930.19 cm^{-1} respectively. In plane deformation and wagging frequency of carbon hydrogen bond (-C-H-) shifted at higher value are 1454.47 cm^{-1} and 752.67 cm^{-1}, respectively.

Adsorption Studies

Different factors affecting the adsorption process were studied by batch experimental technique. Adsorption study was done by shaking of series of 100 ml Erlenmeyer flask. After each batch experiment adsorbed polypyrrole was separated by filtration. The amount of acid violet in the filtrate after adsorption was determined UV-visible spectrophotometrically at its λ_{max} which is 570 nm. The percentage removal of acid violet 43 was calculated as follows:

$$\%\text{age Removal} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

Where C_0 (mg dm^{-3}) and C_e (mg dm^{-3}) are initial concentration and equilibrium concentration of dye in solutions.

Different factors studied were time of agitation, adsorbent dose, adsorbate concentration, pH of the solution and temperature of the medium whose brief descriptions are given here:

Effect of Time of Agitation

Agitation time is very important factors highly affect the adsorption phenomenon. Agitation time factor was studied by varying time from 10 to 100 minutes. 0.1g of adsorbent dose was used against 50 ml of dye solution with concentration of 50 mg dm^{-3}. It was noted that % age dye removal increases with increases in agitation time. Increase in % age removal due to more adsorption of dye molecules on the surface of the polypyrrole surface, as the more time available for adsorption process.

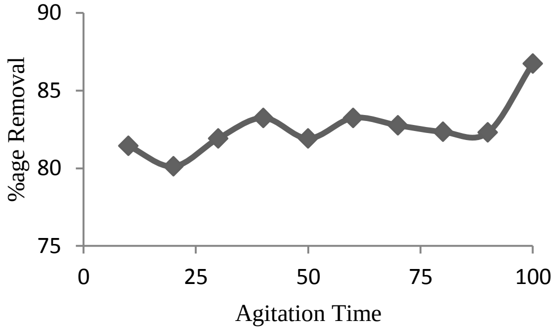

Fig. 4 Effect of Time of Agitation

Maximum percentage removal was achieved after 100 minutes of agitation time which was 86.74. Percentage removal was remained constant after that time.

Effect of Adsorbent Dose

The adsorbent dose effect on % age removal was studied by changing the adsorbent dose from 0.1g to 0.5g. In every batch experiment, 50 ml of 50 mg dm^{-3} dye solution was taken and 5 minutes was given as agitation time. It was observed that removal was increased with increases in adsorbent dose as shown in figure 5. With increase in adsorbent dose, active site available for attachment of adsorbate increases causing increasing %age removal.

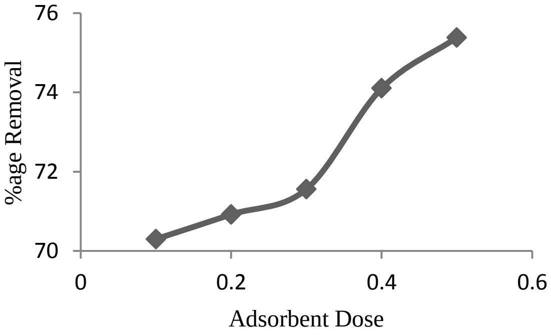

Fig. 5 Effect of Adsorbent Dose

Initial concentration (C_0) taken was 50 mg dm^{-3} during each adsorption experiment. Maximum %age removal achieved was 75.38 against 0.5g of the adsorbent.

Effect of Adsorbate Concentration

Effect of initial adsorbate concentration on the percentage removal was also investigated by varying the concentration from 5 mg dm^{-3} to 30 mg dm^{-3}. Dependency of initial dye concentration on dye removal is depicted in figure 6. Time of agitation given was 10 minute for each batch experiment. Maximum adsorption of dye was observed against 30 mg dm^{-3} which was 95.84. There was no further increase in % age removal with increase in initial adsorbate concentration.

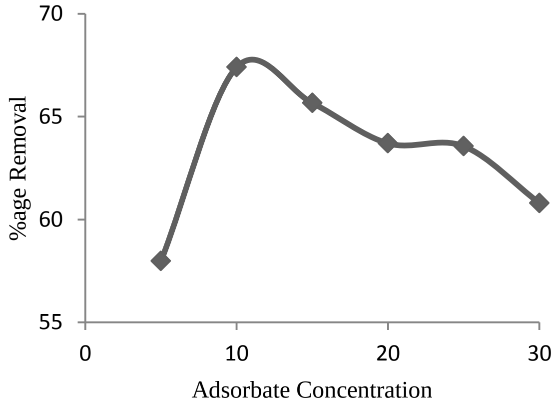

Fig. 6 Effect of Adsorbate Concentration

Effect of pH of Solution

Adsorption characteristics of polypyrrole depend upon the type of charge on the surface of the polypyrrole. Charge on the surface depends upon the concentration of hydrogen ion concentration in the solution. Maximum adsorption was observed at pH 2 and pH 14. At low pH the polypyrrole chain exist as imine form and imine chain doped with negative counter ion of the acid. In this condition ion exchange mechanism was more prominent compared to adsorption. At high pH the, the removal was due the hydrogen bonding in which hydroxyl ion acted as bridge connecting =NH and amino group of the acid violet.

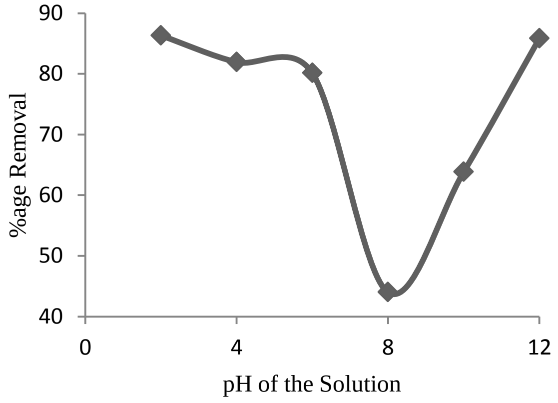

Fig. 7 Effect of pH of Solution

Effect of Temperature

Temperature is one of the major factors affecting the rate of adsorption, as it directly affects the interaction between the adsorbent and the adsorbate. Multiple batch experiments were conducted to study the effect of temperature. Every time 50 ml of dye solution was used against 0.1g of the adsorbent, the temperature was varied from 30 ^{0}C to 70 ^{0}C. Maximum adsorption found was 83.30 which was at 70 ^{0}C. That increase might be due to the increase in mobility of the ions increases the collision rate between the adsorbate and the active surfaces of the adsorbent. After optimum temperature it was found that removal was decrease with further increase in temperature which is actually due to the breakdown of interaction between the adsorbent and the adsorbate.

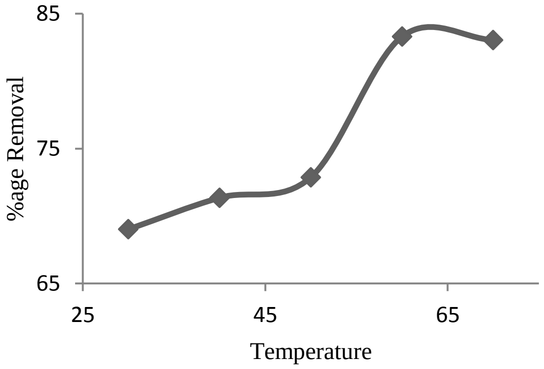

Fig. 8 Effect of Temperature

Adsorption Isotherm

Distribution of adsorbate molecules between liquid phase and solid phase is an equilibrium process. This equilibrium process was studied with the help of two classical adsorption isotherm models, Freundlich and Langmuir. Equilibrium concentration (Q_e) is amount of acid violet in the solution at equilibrium. Equilibrium concentration was calculated by using equation (2):

$$Q_e = \frac{V(C_o - C_e)}{W} \qquad (2)$$

Where "V" (dm^3) is the volume of solution dye containing solution used and "W" (g) is the amount of adsorbent used.

Langmuir Adsorption Isotherm

Langmuir adsorption isotherm is valid for monolayer formation of adsorbate on the surface of adsorbent. The linear expression of Langmuir isotherm is given in equation (3):

$$\frac{1}{Q_e} = \frac{1}{b.Q_{max}\, C_e} + \frac{1}{Q_{max}} \qquad (3)$$

Where Q_e amount of acid is violet in "mg g^{-1}" adsorbed on the adsorbent; C_e is the equilibrium concentration of acid violet in the solution in "mg dm^{-3}" and Q_{max} is maximum possible adsorption capacity of the adsorbent in "mg g^{-1}". Langmuir constant "b" is related to free energy involved during adsorption.

Plot of $\frac{1}{Q_e}$ against $\frac{1}{C_e}$ was plot, which was a straight line. Maximum possible adsorption capacity was determined from the intercept of the graph and Langmuir constant "b" was find out from the slope of the graph. R_L is another very important Langmuir isotherm characteristics known as dimensionless constant separation factor, can be calculated from equation 3.

$$R_L = \frac{1}{1 + (K_L.C_o)} \qquad (4)$$

Different values of R_L shows different characteristics of adsorption isotherm, values of R_L indicate different characteristics isotherm will be linear if $R_L = 1$, favorable if $0 < R_L < 1$, unfavorable if $R_L > 1$ and irreversible if R_L become zero. K_L is Langmuir adsorption coefficient which gives information about binding sites available on the surface of the adsorbent, calculated as:

$$K_L = Q_{max} \times b \qquad (5)$$

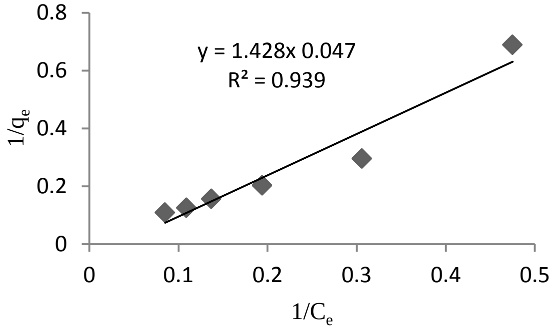

Fig. 9 Langmuir Adsorption Isotherm

Freundlich Adsorption Isotherm

Equilibrium adsorption data was also test by using most simpler and classical adsorption Freundlich adsorption isotherm. Freundlich adsorption isotherm is as below:

$$Q_e = K_f C_e^{1/n} \quad (6)$$

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

Plot of Q_e Vs C_e is linear intercept graph. K_f known as Freundlich constant comes from intercept and “n” adsorption intensity comes from the slope of the linear graph.

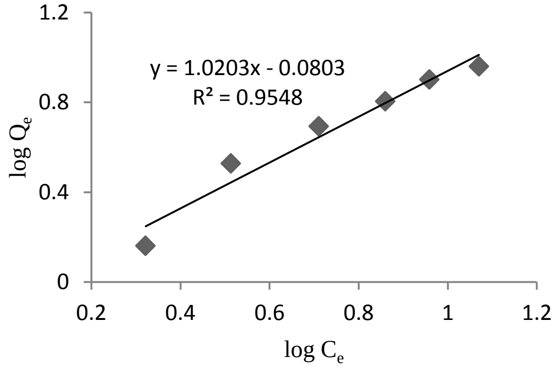

Fig. 10 Freundlich Adsorption Isotherm

Table: 1 Langmuir and Freundlich Constants

Freundlich			Langmuir				
R^2	n	K_f	R^2	Q_{max}	b	K_L	R_L
0.95	0.98	0.83	0.93	21.27	0.05	1.06	0.018

Comparative values of the regression coefficient (R^2) showed the more compatibility of the adsorption data with Freundlich isotherm compared to the Langmuir isotherm. In light of basic assumptions of both the isotherm it can be concluded that the adsorption process occurs both by the heterogeneously and through monolayer formation. The value of “n” is approximate equal to one showing the favorable adsorption process. Langmuir isotherm was also verify by adsorption data as the regression coefficient coming out to be 0.93, which is very greater than the accepted value of regression coefficient i.e. 0.80. So this value also showed the homogeneous surface of the adsorbent and also the adsorption process proceeds without any interaction between the acid violet and polypyrrole. The value of Langmuir characteristic “R_L” coming out from adsorption data was less than one showing the favorable adsorption process.

Table: 2 Adsorption Capacity Comparison of Different Adsorbent for Acid Violet

Type of Adsorbent	Adsorption Capacity
Chitosan/Polyurethane [21]	30
Coir Pith [22]	1.65
Orange Peel [22]	19.88
Coir Pith Carbonized [22]	8.06
Carbon from Cocoa [23]	47.62
Polypyrrole [This Study]	21.276

Other most important parameters used to predict the adsorption capacity derived from Langmuir adsorption isotherm is Q_{max} (mg g^{-1}). Polypyrrole has 21.276 maximum adsorption capacity “Q_{max}” which was much greater than most of the previously used adsorbent as indicated in the table 2.

Adsorption Kinetics

Dynamic adsorption rate were studied by the by using Pseudo first order and Pseudo second order equation in order to find out the nature of adsorption process:

Pseudo-first Order Kinetics

Linear form of Pseudo-order kinetics equation is given in as:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (8)$$

Where "Q_e" is the amount of acid violet in mg g^{-1} adsorbed on the adsorbent. "Q_t" is the amount of acid adsorbed at time t in mg g^{-1}. “t” is time in minutes and k_1 is rate constant for Pseudo-first order model in per minutes.

Pseudo-second Order Kinetics

Pseudo-second order equation is given as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (9)$$

Where "Q_e" is the amount of acid violet in mg g^{-1} adsorbed on the adsorbent. Q_t is the amount of acid adsorbed at time t in mg g^{-1}. “t” is time in minutes and k_2 is rate constant for Pseudo-second order model in g mg^{-1} min^{-1} .

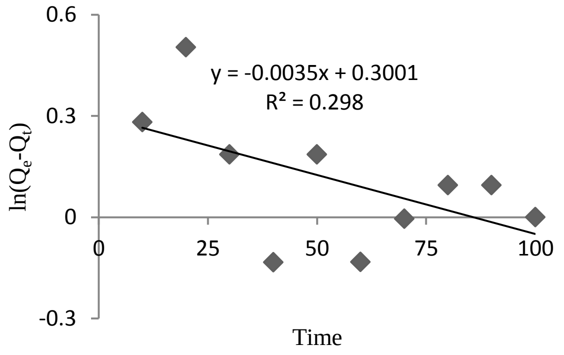

Fig. 11 Pseudo-first order kinetics

Figure 11 showed that the adsorption kinetics did not followed the Pseudo-first order kinetics as the regression coefficient comes out 0.298. Rate constant comes out was 3.0 $\times 10^{-3}$ min^{-1}

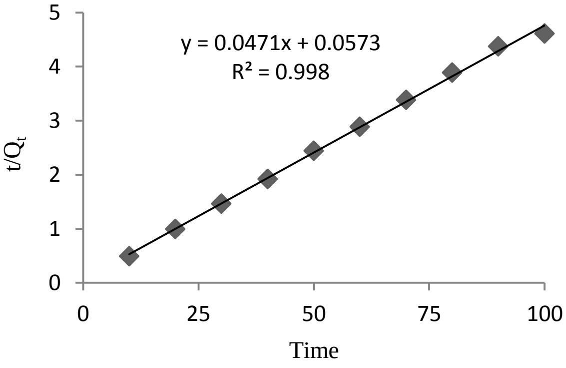

Fig. 12 Pseudo-second order Model

Regression coefficient (R^2) coming from pseudo-second order plot was 0.998, which showed that the adsorption rate strongly followed by the pseudo-second order kinetics. Rate constant for second order kinetics was found to 3.4 $\times 10^{-3}$ g mg^{-1} min^{-1}. Relative values of regression coefficient indicated that the adsorption process was strongly chemisorption process, might be due to the strong attraction between the adsorbent and the adsorbate. Relative values of different kinetics parameters are given in table below:

Table: 3 Kinetics Parameters

Pseudo-first order model		**Pseudo-second order model**	
R^2	0.298	R^2	0.998
K_1	3.0×10^{-3} min^{-1}	K_2	3.4×10^{-3} g mg^{-1} min^{-1}
Q_e	1.35 mg g^{-1}	Q_e	21.27 mg g^{-1}

Thermodynamics Study

As the adsorption process is an equilibrium process, was used to study the thermodynamics of the adsorption process. Equilibrium constant (K_d) a dimensionless parameter was calculated from the initial concentration (C_0) and equilibrium concentration (C_e) by using equation 10. Change in standard Gibbs free energy was calculated by using equation "11" with the help of equilibrium constant value. There is linear relation between ΔG^0 and temperature can be used to find out the standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) of adsorption process.

$$K_d = \frac{C_e}{C_o} \qquad (10)$$

$$\Delta G^0 = -RT\ln K_d \qquad (11)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (12)$$

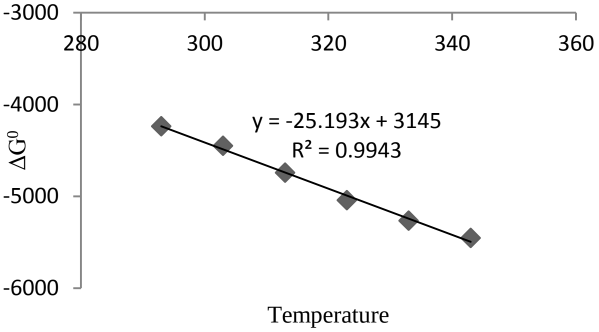

Fig. 13 Thermodynamic study

Entropy of the adsorption process calculated from the slope of the graph was 25.19 $Jk^{-1}mol^{-1}$, was indication of favorable spontaneous adsorption process. Enthalpy of the process calculated from the intercept of the graph was 3145 kJ mol^{-1} indicate the endothermic adsorption process.

CONCLUSION

The removal of Acid Violet 43 using polypyrrole was studied under different physical conditions. Both the Langmuir and Freundlich isotherm model were verified and the adsorption capacity was found to be very high for acid violet 43. Acidic condition was more favorable for dye removal. The high adsorption capacity of prepared showed that this adsorbent could be used as an alternate for acid violet removal.

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