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EFFECTIVE REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTION BY SULPHONATED *SOLANUM VIRGINIANUM* CARBON

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ABSTRACT

This study reported the accumulation of Methylene Blue (MB) by sulphonated *Solanum virginianum* carbon (SSVC) using batch technique. Adsorption studies are conducted in altered initial dye concentrations, adsorbent doses, pH, contact time and temperature. The removal of MB increases with decrease in concentration of dye. The experimental data was analysed by Langmuir, Freundlich and Temkin models. The adsorption capacity (Q_o) of SSVC was found to be 24.12 mg/g. The process of dye accumulation follows second order kinetics. From the effect of temperature, thermodynamic parameters such as the free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were determined.

Keywords: Adsorption isotherm, Batch process, Exothermic, Pseudo second order, Thermodynamic parameters.

1. INTRODUCTION

Agricultural, industrial and household wastes are discharged into several receivers. Generally, this release is channelled to the adjacent water resources. Dyeing process is a major source of pollution responsible for the environmental pollution. Many dyes have deadly as well as carcinogenic, mutagenic and teratogenic effects [1] on aquatic life and to human [2]. Therefore, removal of dyes is an important aspect of wastewater before discharge. There are several physical and chemical methods such as coagulation, floatation, chemical oxidation, solvent extraction, precipitation, flocculation etc., have been employed in the removal of dyes from wastewater. But they are unsuccessful because dyes are stable to light and oxidizing agents and they involve high equipped cost and aerobic absorption [3,4]. Adsorption has been introduced and found a better technique [5] compared to other methods of wastewater treatment in terms of expenditure, ease of design & function, availability, effectiveness and their insensitivity to toxic substances. Adsorption of dyes against granulated activated carbon (GAC) or powdered activated carbon is a common practice [6-8]. Though, the technology for manufacturing good quality of activated carbon is still extremely cost prohibitive and the regeneration or disposal of the carbon is often problematic. Numerous novel materials have been developed as adsorbents in recent years particularly from various plant materials with the objective of replacing activated carbon with cheaper, more effective and recyclable alternatives. Such low cost adsorbents have been used for treatment of various pollutants in wastewater [9]. Biosorbents collected from biological sources such as pineapple stem [10], banana peel [11], coir pith [12], Orange peel [13], guava leaf powder [14] etc., have been shown to give satisfactory results in removal of commercial dyes from aqueous solution.

The present work is a non-conventional; adsorbent developed from a well-known bio resource, the leaves of *Solanum virginianum*, to remove Methylene Blue from aqueous medium. Actually, it is an easily available plant species. *Solanum virginianum* (Family solanaceae) is a vital ingredient in various ayurvedic preparations [15]. Methylene Blue is a cationic dye and its structure is quite familiar. The dye is not regarded as severely toxic, but it can have a negative effect. On inhalation, it can lead to short periods of rapid or difficult breathing. A large amount of dye creates abdominal, chest pain and severe headache. Workers handling MB are for injuring of photoirradiant contact dermatitis (PICD). Methylene blue [16] may also allow in hemolytic anemic, hyperbilirubinemia and acute renal failure.

2. EXPERIMENTAL

The adsorbent employed in the present work was *Solanum virginianum* leaves powder. *Solanum virginianum* leaves were collected from a number of Solanum virginianum Plant in Sivaganga district. They were washed repeatedly with water to remove dust and solute impurities and were allowed to dry first at room temperature in a shade and then in air oven at 343-353 K for a long time till the leaves became crisp that could be fine powdered in a mechanical grinder. The dried Solanum virginianum was carbonized and sulphonated with Conc. Sulphuric acid kept at ambient temperature for overnight and heated to 90°C in a hot air oven for 6 h. It was then cooled, washed with distilled water for many times and finally washed with double distilled (DD) water in order to remove excess free acid (tested with $BaCl_2$ to give clear solution) and dried at 70°C for 12 h. Finally the powder was preserved in glass bottle and labelled as sulphonated *Solanum virginianum* carbon (SSVC) for the use. As an adsorbent, Methylene blue (Merck) was used without further purification. All the solutions were made in double distilled water. The acidic and basic buffer solutions were prepared from Sodium Acetate, Acetic acid, aqueous Ammonia and Ammonium Chloride. The buffer solutions were used to maintain pH of the solutions in the range from 3.6 to 10. The batch adsorption was carried out in 250 ml narrow mouth bottle by mixing a pre-weighed amount of the SSAC with 100 ml of the aqueous dye solution of particular concentration. The NM bottles were kept in shaker, at constant temperature and were shaken for a pre-determined time interval at a fixed speed (1420 rpm). The adsorbent dose, contact time and temperature of adsorption were carefully controlled. After adsorption was over, the mixture was rapidly centrifuged in a laboratory centrifuge (REMI centrifuge). The adsorbent settled quickly and the remaining unadsorbed content was determined spectrophotometrically and the percentage of dye removal was calculated using the following formula:

$$\% R = C_i\text{-}C_e/C_i \times 100 \quad \text{---------- (1)}$$

The amount of MB adsorbed (mg/g) mass calculated based on a mass balance equation as given $q = (C_i\text{-}C_e)$ V/m, Where, q is adsorption capacity in mg/g, C_i is initial dye concentration in mg/l, C_e is final dye concentration in mg/l, V is volume of final solution in ml and m is quantity of adsorbent in gram. The parameters such as pH, time of contact, adsorbent dose, dye concentration and temperature were varied during different sets of batch experiments.

3. RESULTS AND DISCUSSION

3.1. Kinetic study

The kinetics of adsorption was studied by determining the amount adsorbed at different agitation times for various amount of adsorbents at constant MB concentration. The Kinetics were tested with respect to pseudo-first order model of Lagergren is given by

$$\log (q_e - q_t) = \log q_e - k_1 t/2.303 \quad \text{---------- (2)}$$

The second order kinetics model is given by

$$t/q_t = 1/h + t/q_e \quad \text{---------- (3)}$$

Where q_t and q_e are the amount adsorbed at time t and at equilibrium, k_1 is the pseudo first order rate constant, $h = k_2 q_e^2$, k_2 is the second order rate constant. The intra particle diffusion model, when adsorption takes place inside the pores by diffusion mechanism, is also tested with the help of the following equation.

$$q_t = K_i\, t^{0.5} \quad \text{---------- (4)}$$

Where, K_i is the intra-particle diffusion rate constant.

3.2. Adsorption isotherm studies

Freundlich isotherm (equation 5) is widely used to explain adsorption on a surface having heterogeneous energy distribution. The Langmuir adsorption isotherm (equation 6) is strictly applicable to mono layer chemisorptions. The Temkin isotherm (equation 7) can be expressed in its linear form.

$$q_e = K_F C_e^{1/n} \quad \text{---------- (5)}$$

K_F and n are indicators of adsorption capacity and adsorption intensity respectively.

$$\frac{1}{qe} = \frac{1}{q_m K_l C_e} + \frac{1}{q_m} \quad \text{---------- (6)}$$

By plotting $1/q_e$ versus $1/C_e$ the Langmuir constant can be obtained.

$$q_e = B_T \ln A_T + B_T \ln C_e \quad \text{---------- (7)}$$

Where $B_T = RT/ b_T$, T is the absolute temperature in Kelvin and R is universal gas constant, 8.314 J/mol/K. The constant b_T is related to the heat of adsorption [17].

3.3. Characterization of SSAC - FTIR Spectra

FTIR spectra of SSAC were recorded before and after dye adsorption (Fig. 1a and I b). The FTIR spectra obtained revealed that there were various functional groups detected on the surface of the SSAC sample before and after adsorption. The following functional groups are likely to be present in the adsorbent, -OH (3421 cm^{-1}), >C=O (1707cm^{-1}) and >C=C< (1625cm^{-1}). The polar groups on the surface of the SSAP are such as to determine the adsorption characteristics of SSAC as these groups give rise to considerable cation exchange capacity [18]. There are

some peaks which were shifted, disappeared after dye adsorption and also new peaks were detected.

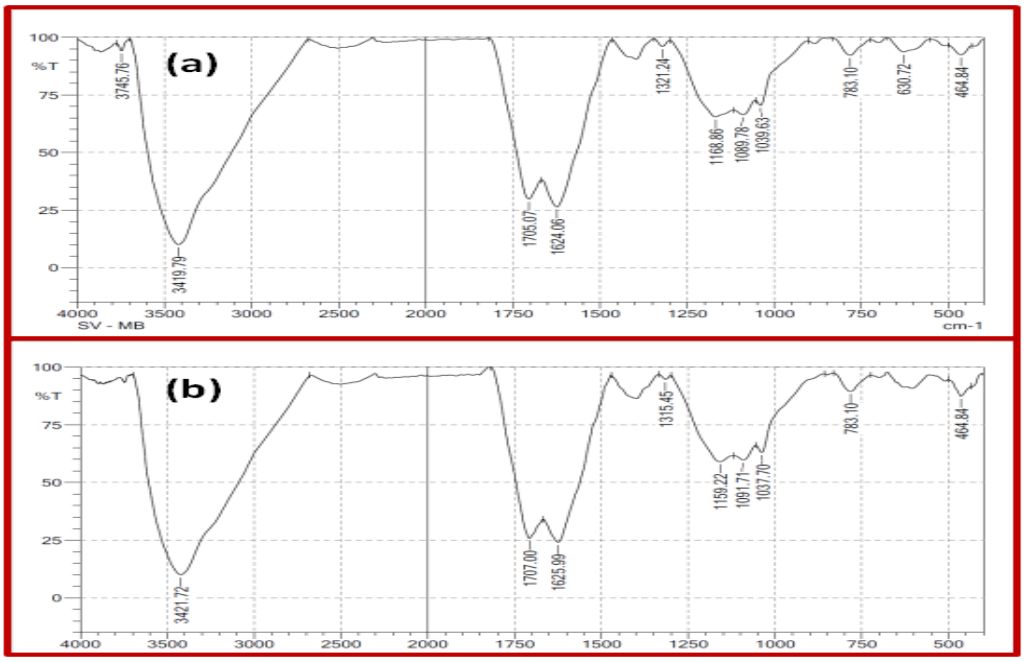


Fig. 1: FTIR spectra of SSAC were recorded (a) before dye adsorption (b) after dye adsorption

3.4. SEM Surface area of SSAC

The SEM micrographs showed that SSAC possesses a rough surface morphology with some pores (Fig. 2a).

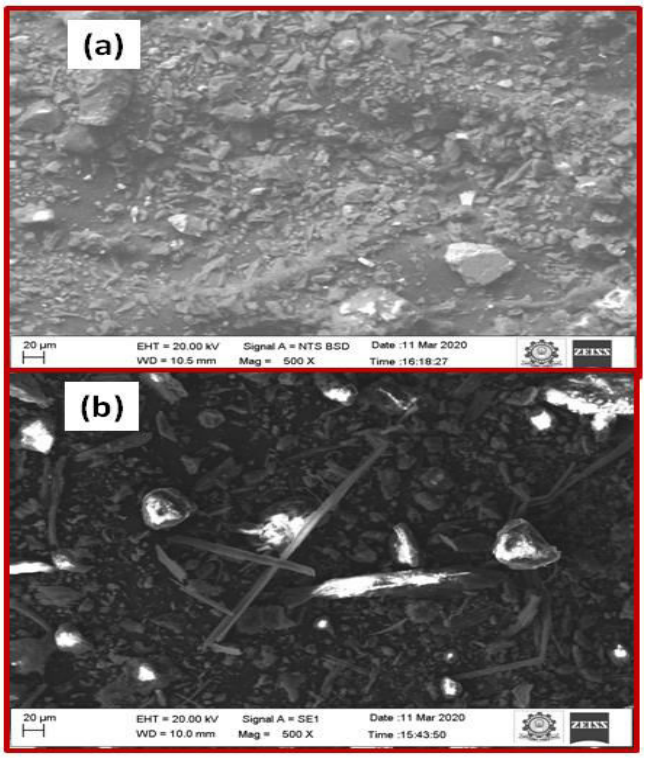


Fig. 2: SEM Morphology of SSAC images (a) before dye adsorption (b) after dye adsorption

The particles have a large number of steps, kinks and broken edges of them these are likely to play an important role as possible active sites for adsorption. Surface morphology of MB loaded adsorbent shows that the surface of SSAC is covered with dye molecules (Fig. 2b).

3.5. Effect of dose and the initial concentration of the dye

The adsorption of methylene blue was studied as a function initial dye concentration of in the range of 10-50 ppm (Table 1).

The results obtained were shown in Fig. 3. The percentage adsorption decreases with increase in initial concentration of the dye for sulphonated *solanum virginianum* carbon powder.

Minimum adsorption was 68% for 50 ppm concentration to maximum adsorption value 92% for 10 ppm concentration of dye solution. This is due to decrease in resistance to dye uptake and consequently increase in mass transfer driving force. These results indicated that the profile of dye uptake is a single, smooth and continuous curve leading to saturation due to formation of monolayer coverage on the surface of adsorbent. Initial dye concentration was one of the effective factors on adsorption efficiency. A similar observation was reported for MB adsorption onto tartaric acid modified Swede rape straw [7].

Table 1: Effect of initial dye concentration on the removal of MB by SSAC

Ci	Ce	% Removal	Amount adsorbed
10	0.8000	92.0000	6.13
15	1.4000	90.6667	9.06
20	3.0000	85.0000	11.33
25	7.8000	68.8000	11.46
30	8.2000	72.6667	14.53
50	16.0000	68.0000	22.66

Temp. 303K; Amount of SSAC = 1.5 g/L; pH = 7.0

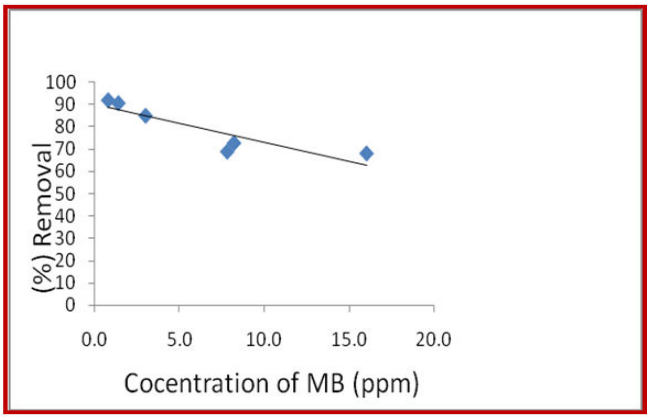


Fig. 3: Effect of initial concentration on percentage removal of methylene blue dye

3.6. Effect of pH

One of the main variables affecting the adsorption process is pH. The effect of initial solution pH was determined by agitating 1.5 g/l of sulphonated Solanum virginianum carbon Powder adsorbent and 100 ml of dye solution of initial basic dye concentration of 25 ppm using water-bath shaker (30°C) at different solution pH ranging from 3.6 to 10 (Table 2). Agitation was provided for 15 min contact time which is sufficient to reach equilibrium with a constant agitation speed of 1420 rpm. The pH was adjusted by adding a few drops of acidic or basic buffer solution. As shown in Fig. 4, the solution pH will have a significant influence on dye adsorption. Adsorption of the dye increases with increasing solution pH.

As the pH is increased, the surface charge density on the sulphonated *Solanum virginianum* carbon powder changes and the adsorbent becomes negatively charged resulting in an enhanced attraction between the positively charged dye molecule and the adsorbent surface [19]. This behaviour is expected for basic dye removal. A similar trend is also observed for the adsorption of MB on coconut coir dust [1], succinylated sugarcane bagasse [5], and activated carbon prepared from Enteromorpha prolifera [6].

Table 2: Effect of pH on the removal of dye

Initial pH	Ci	Ce	% Removal	Amount adsorbed
3.6	25	12.6000	49.6000	8.266666667
4.2	25	11.8000	52.8000	8.8
5.4	25	10.0000	60.0000	10
7	25	7.8000	68.8000	11.46666667
8	25	1.2000	95.2000	15.86666667
9.2	25	0.6000	97.6000	16.26666667
10	25	0.2000	99.2000	16.53333333

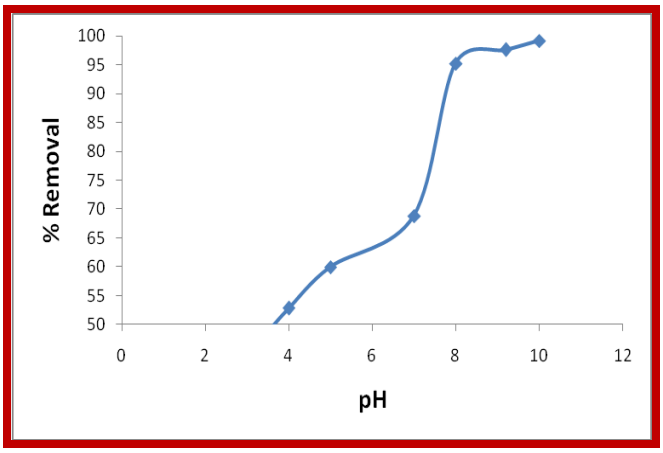
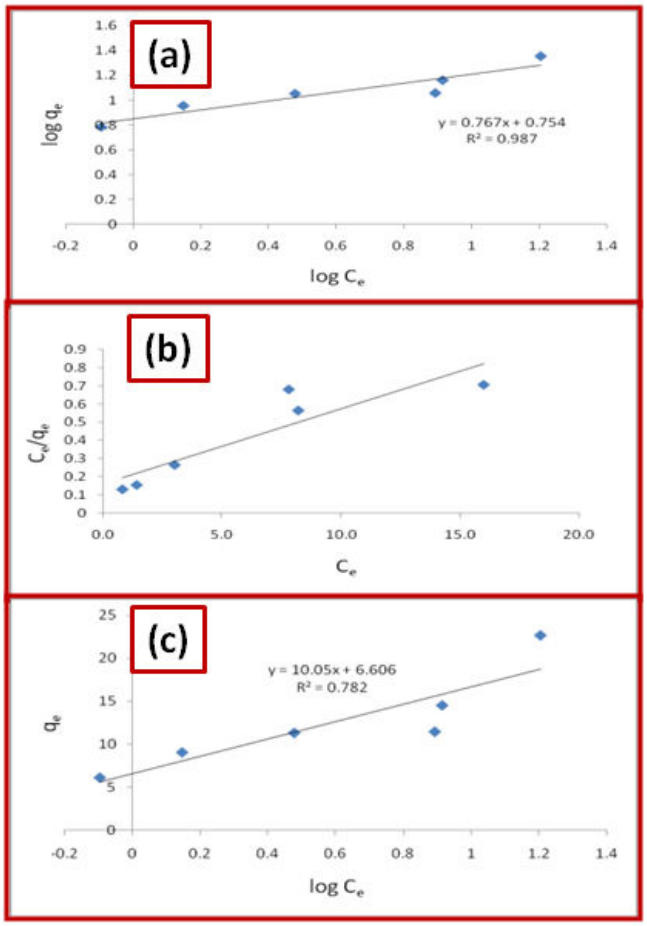


Fig. 4: Effect of pH on the removal of dye

3.7. Adsorption Isotherms

The experimental data yielded good linear plot with Freundlich adsorption isotherm (Fig. 5 (a), r = 0.987), Langmuir adsorption isotherm (Fig. 5 (b), r = 0.902) and Temkin adsorption isotherm (Fig. 5 (c), r = 0.782). The Freundlich coefficient 'n' which should have values in the range of 1<n<10 for favourable adsorption [20] remained in the narrow range of (2.681). The Freundlich adsorption capacity K_f was 7.121 Lg^{-1}. The dimensionless separation factor, R_L has a value of 0.160 in occurrence with the suggested value for favourable adsorption. This isotherm constant indicated that the SSAC had a very good potential as an adsorbent for MB [21-28]. Examination of data shows that Freundlich isotherm shows relatively good correlation (r = 0.987). Langmuir, Freundlich and Temkin isotherm's constants and correlation coefficients for adsorption of MB onto SSAC were presented in Table 3. Table 4 listed a comparison of maximum monolayer adsorption capacity (Q_o) of MB on various adsorbents. SSVC is found to have a relatively large adsorption capacity of 24.12 mg/g and this indicates that it could be considered a promising material for the removal of basic dye from aqueous solution.



(a) Freundlich adsorption isotherm for the removal of MB, (b) Langmuir adsorption isotherm for the removal of MB and (c) Temkin adsorption isotherm for the removal of MB dye

Fig. 5: Results of Adsorption Isotherms

Table 3: Langmuir, Freundlich and Temkin isotherm constants and correlation coefficients for adsorption of MB onto SSVC

Correlation Analysis	Methylene Blue
Langmuir isotherm	
Correlation coefficient	0.902
Slope	0.041
Intercept	0.160
Q_o	24.12
B	0.260
R_L	0.160
Freundlich isotherm	
Correlation coefficient	0.987
Slope	0.767
Intercept	0.754
K	7.121
Temkin isotherm	
Correlation coefficient	0.782
Slope	10.05
Intercept	6.606

3.8. Kinetics of adsorption

The study of adsorption kinetics is important because it provides valuable insight into the reaction pathways and into the mechanisms of the reactions. Experiments with different interaction times were carried out with a constant amount of adsorbent dose and initial concentration of dye as 25 ppm at 303 K. Fig. 6 (a) showed that the time necessary for MB to reach saturation on the SSVC surface was just over 30 min. An approximately 80 % of the dye was removed at the equilibrium time. The circulation of the dye in the liquid - solid interface at equilibrium is important in order to establish the adsorption capacity of SSVC for the dyestuff [29]. The relatively short equilibrium time of 20 min and a high percentage removal indicates that SSVC possessed a high degree of affinity for the dye MB. The plot of q_t *versus* $t^{1/2}$ and Fig. 6 (b) gives more than one slope. The initial sharp portion is likely to symbolize fast adsorption on the external surface, and the second nearly flat portion a slow diffusion into the interior surfaces of the particles [30]. The second portion of the plot might also be due to adsorption on the steps and crevices of the surface as saw from the SEM measurement. The kinetics of MB adsorption on SSVC is verified with respect to Natarajan and Kalf in Fig. 6 (c), pseudo first order rate equation of Lagergren in Fig. 6 (d), Bhatacharrya & Venko in Fig. 6 (e) and second order kinetics in Fig. 6 (f).

$$\log (q_e - q_t) = - (k_1/2.303)t + \log q_e \quad \text{-------- (8)}$$

Where q_t and q_e are the amounts adsorbed per unit mass at time t and equilibrium time, and k_1 is the first-order rate constant. Plot of $\log (q_e - q_t)$ *versus* t, which provides a straight line, is utilized to obtain obtain k_1. The pseudo-first order Lagergren plot (Fig. 6d) yield first order rate constant of 4.41 x 10^{-2} min^{-1} indicating a significantly fast reaction. It was seen that the experimentally found q_e values matched those determined from pseudo-second order plot. Therefore, the adsorption of MB on SSVC might take place through a pseudo second-order mechanism. Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particulates followed by dispersion of the solute molecules into the interior of the pores, which may be the slowest and rate-determined step. Application of the liquid film diffusion model involving diffusion from the bulk liquid phase to the surface of the adsorbent provides similar conclusions. The liquid film diffusion model could be applied with advantage,

$$\ln(1-F) = - k_{fd}t \quad \text{---------- (9)}$$

Where F is the fractional attainment of equilibrium (= q_t/q_e) and K_{fd} is the film diffusion rate coefficient. A linear plot of log (1-F) *versus* t with zero intercept shows that the adsorption process is monitored by bulk mass transfer processes. In the present study, the plot log (1-F) *versus* time was linear (r = 0.956) with intercept -0.349 (Fig. 6e). The line did not pass through the origin as required by the model, but very small intercept indicates that diffusion of the MB molecules from the liquid phase to the adsorbent surface might have some significant role in deciding the rate processes. The film diffusion rate coefficient is 1.9×10^{-2} min^{-1}. From the above result, it appears that the kinetics of adsorption of MB on SSVC has been mostly controlled by mass transfer from solid - liquid interface to the surface of the SSVC particles although some roles for transfer from bulk liquid phase to the solid-liquid interface. The plot does not pass through the origin. Thus the liquid film diffusion is not the predominant mechanism for MB adsorption on SSVC.

The plot of t/q_t *versus* t gives a straight line for the initial concentration of 25 ppm (Fig. 6f) confirming the applicability of the pseudo second order equation. The values of k_2 and equilibrium adsorption capacity q_e were calculated from the intercept and slope which presented in the Table 4.

Table 4: Comparison of adsorption capacity of various adsorbents for Methylene Blue

Adsorbent	Q_o (mg g^{-1})	Temperature (K)	Reference
Wheat shell	16.56	303	20
Activated carbon from Coconut coir	15.59	303	21
Tartaric acid modified wheat Bran	25.18	303	22
Banana peel	20.80	303	23
Neem leaf powder	8.76-19.6	303	9
Beer brewery Waste	4.92	303	24
Sugarcane dust	3.75	303	25
Date stones	12.8	303	26
Fly ash	13.4	303	27
Orange peel	18.6	303	23
Clay	6.30	303	28
SSVC	24.12	303	This study

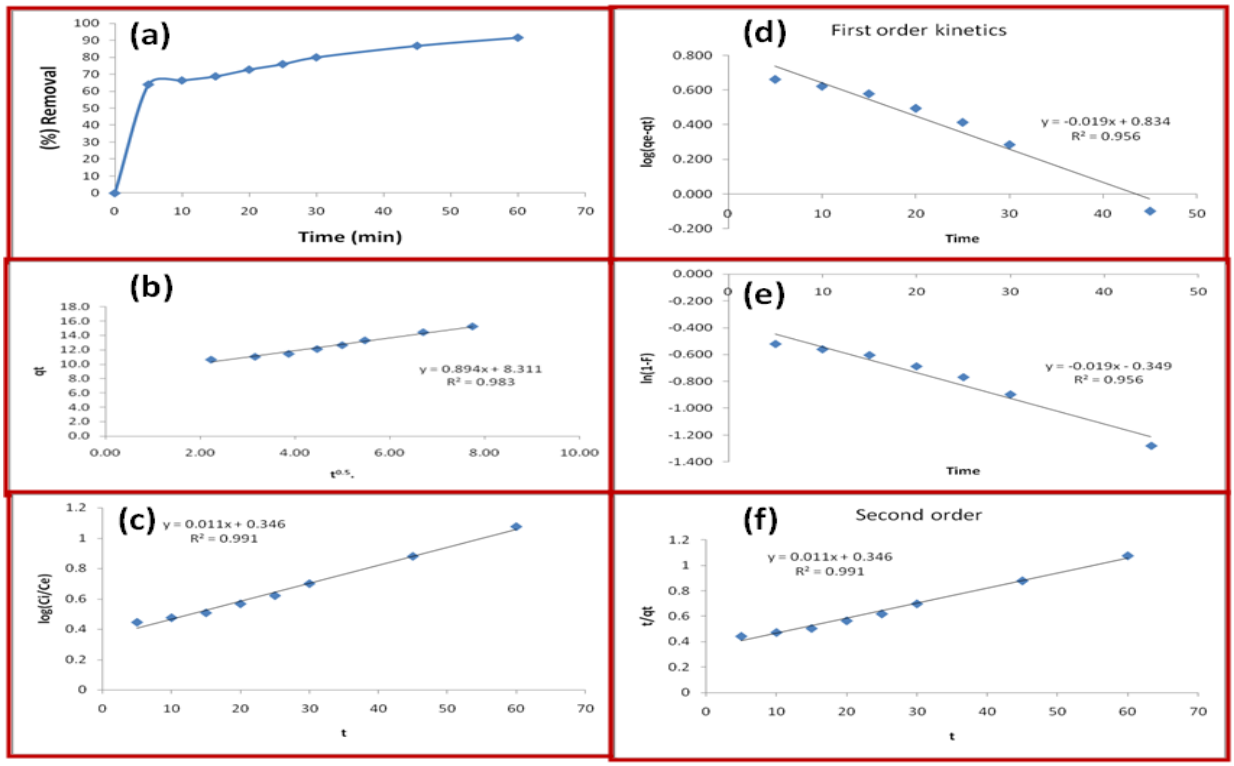


Fig. 6: Effect of contact time on the removal of MB (a), Intra particle diffusion model for the removal of MB (b) by SSVC, Natarajan and Kalf plot (c), Lagergren plot (d), Bhattacharya And Venkobacher plot (e) and Second order kinetics plot (f)

3.9. Effect of temperature and Thermodynamic parameters

The thermodynamic parameters for the adsorption process namely Gibbs free energy change (ΔG°), enthalpy change of adsorption (ΔH°) and entropy change of adsorption (ΔS°) are determined by carrying out the adsorption at six different temperatures and using the following equations,

$\Delta G° = \Delta H° - T\Delta S°$ ---------- (10)

$\text{Log } q_e/C_e = (-\Delta H°/2.303RT) + (\Delta S°/ 2.303R)$ ---------- (11)

Where q_e/C_e is called the adsorption affinity i.e. the ratio of q_e, the amount of adsorbate adsorbed per unit mass (mg/g) to C_e, equilibrium concentration of the adsorbate (mg/L). The values of ΔH° and ΔS° were determined from the slope and intercept of Van't Hoff plot of log q_e/C_e against 1/T respectively (Fig. 7). From ΔH° and ΔS° values we can calculate ΔG°. Table 5 listed the thermodynamic parameters associated with the adsorption of MB onto SSVC powder. The negative values of ΔG° show the feasibility and spontaneity of the adsorption process and the positive value of ΔH° indicated that the endothermic nature of the adsorption process. The positive value of ΔS° shows the increasing randomness of the adsorbate - adsorbent and adsorption medium interface during the adsorption.

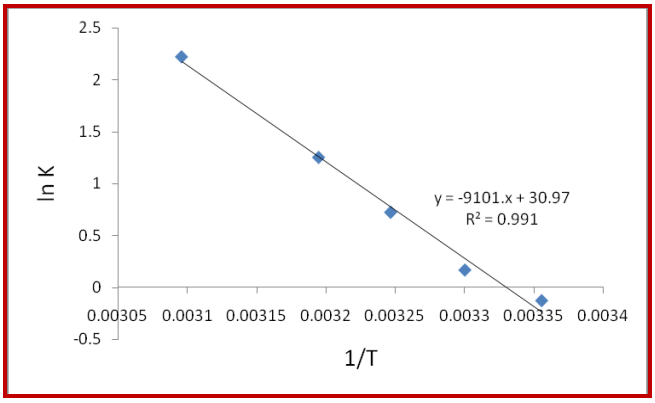


Fig. 7: Van't Hoff plot for the adsorption of Methylene Blue on SSVC powder

Table 5: Values of thermodynamics parameters for MB adsorption on SSVC powder

Temperature (K)	ΔG° (KJ /mol)	ΔH° (KJ /mol)	ΔS° (KJ /mol)	R^2
298	-2.414	174.3	0.593	0.991
303	-5.379	177.2	0.603	1.008
308	-8.314	180.1	0.613	1.024
313	11.309	183.1	0.623	1.041
323	17.239	188.9	0.643	1.074

4. CONCLUSION

The present investigation showed that SSVC is an effective adsorbent for the removal of MB from aqueous solution. The data reported may be very useful for designing an economically cheap treatment process using batch process for the accumulation of MB in aqueous solution.

5. ACKNOWLEDGEMENTS

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