Section A-Research paper

Effective Removal and Recovery of Hazardous Dye, Fast Green FCF from Wastewater using Waste Green Adsorbent: Powdered Silk

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Abstract-

The toxic cationic dye Fast Green FCF was studied using powdered silk. Silk is naturally obtained adsorbent and has been used in the powdered form to adsorb Fast Green FCF fast dye from wastewater. Studies have been carried out by observing the effects of pH, temperature, contact time, a concentration of dye, an amount of adsorbent, a particle size of

adsorbent etc. Graphical correlation of various adsorption isotherm models like, Langmuir and Freundlich has been carried out for the adsorbent. The adsorption has been found endothermic and feasible in nature. The different thermodynamic parameters, like, Gibb's free energy, enthalpy and entropy of the adsorption process have been evaluated. The kinetic studies proved that the adsorption process follow pseudo first order kinetics. Results of adsorption experiments showed that powdered silk exhibited high sorption capacities towards dye. The bulk removal of the dye has been carried out by treatment with adsorbent followed by filtration through the syringe filter. Desorption studies have also been put in effect to recover dye by using dilute NaOH.

Keywords: Powdered silk, Fast Green FCF, Adsorption, Desorption, Kinetics, Equilibrium isotherm.

I. **Introduction**:

Freshwater resources are found to be immensely in trouble due to the fast increasing population with their daily living standards. Therefore, the fresh water crisis is the most important problem, which is faced by the living world because of industrial growth. Many countries are already experiencing water scarcity conditions. Many more countries will face a reduced availability of surface water resources by 2050 [1]. Many industries like textile, paper, rubber, plastic, leather, cosmetics, pharmaceutical and foodstuff, use different types of dyes [2]. These dye mingled with water sources, causing increase in chemical oxygen demand (COD), decrease in light penetration and visibility. Such parameters pose adverse effects on aquatic life [3]. The large amount of industrial effluent which is disposed of into water resources without proper treatment and causes a serious threat to the whole human being. Due to the highly toxic nature of dyestuff, this water is unfit for drinking [4]. Considering all this, scientists are trying to develop the suitable adsorbent for removal of dye from wastewater. Various physical, chemical, and biological methods like, coagulation and flocculation, oxidation or ozonation, membrane separation, ultrafiltration, chemical treatments, activated carbon adsorption, photocatalytic degradation, bacterial degradation etc. have been used for the dye removal and degradation [5]. But they are either quite expensive or cannot be applied to large volumes of water. Thus in recent times, alternative methods for the removal of dyes from wastewaters with the use of various low-cost adsorbents is in high demand. Some low-

cost adsorbents such as bagasse fly ash [6], wool [7], fertilizer waste [8], shale oil ash [9], rice husk [10], solid residue of olive mill products [11], red mud [12], etc. have been used by various workers. The benefit of the use of physically modified wool as adsorbents is their low cost, versatility, and easy operations [13]. In recent years many research groups [14–19] have contributed some important and useful research publications on the removal of dye by various materials in search of sustainable processes.

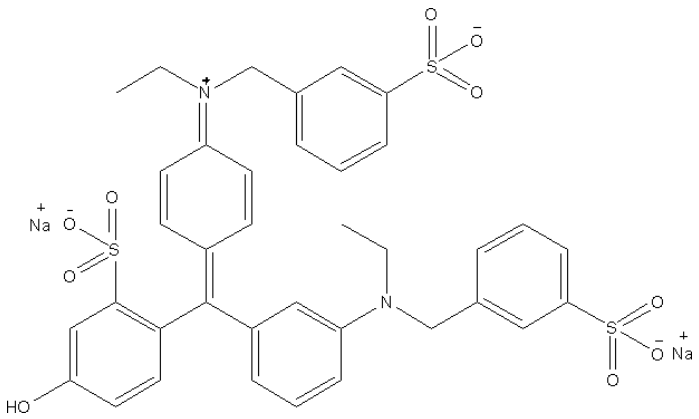


Fig. 1. Chemical structure of Fast Green FCF.

The sea green triaryl methane food dye Fast Green FCF (Fig. 1) (C.I.No. 42053) is also known as Food Green 3, FD and C Green No. 3, Green 1724 and Solid Green FCF with absorption maximum ranging from 622 to 626 nm, Fast Green FCF has a brilliant blue-green color, which is tough to wipe away [20]. After acid extraction of DNA, Fast Green FCF is used as staining agent for histones at alkaline pH. Additionally, it is used in electrophoresis as a protein stain [21]. It is advised in place of numerous other stains, including Light Green SF Yellowish in Masson's trichrome[22]. According to toxicological research, the Fast Green FCF is quite hazardous [23]. It is irritating to people and may irritate their upper respiratory tract, skin, and eye. It also composes as a presynaptic locus by hindering the release of neurotransmitters in the nervous system [24]. It is a known carcinogen and able to induce sarcomas at the site of frequent hypodermic injection [25, 26].

Due to its toxicity, the European Union and many other nations have prohibited its edible use of Fast Green FCF [27].

In this study, we focused on a novel green adsorbent for wastewater treatment. For the purpose of removing Fast Green FCF from wastewater, natural powdered silk was chosen. The silk was characterized using FTIR spectroscopy, SEM, EDX and BET The obtained silk-Fast Green FCF composite was characterized using FTIR spectroscopy, SEM, EDS and TGA. The detailed adsorption study of powdered silk and Fast Green FCF was performed and experimental, influencing various parameters such as pH, contact time, concentration, kinetics, isotherms and dye recovery as measured symmetrically. At the end a possible mechanism was presented. Present work is revealing a sustainable sorbent material as powdered silk for the removal of Fast Green FCF from effluent.

II. Materials and methods:

Fast Green FCF dye, 2-[[4-[ethyl-[(3-sulfonatophenyl)methyl]amino]phenyl]-[4-[ethyl-[(3-sulfonatophenyl)methyl]-azaniumylidene]cyclohexa-2,5-dien-1-ylidene]methyl]-5-hydroxybenzenesulfonate disodium salt, molecular formula C37H34N2O10S3Na2 and molecular weight 808.85 was obtained from M/s HEMIDIA. The silk was purchased from the local market.

Distilled water was used to prepare the stock solution.

A. Material development:

The silk was purchased from the local market. The silk was waste silk left after use as we required in powdered form. In the first stage, silk was washed with distilled water and dried by means of an electrical oven. Manually, silk is cut into very tiny pieces and powdered which is used as adsorbent in further studies. Finally, the adsorbent was sieved to various mesh sizes viz. 90, 150 and 180 BSS mesh and stored separately in desiccators. The distilled water was used to prepare simulated industrial wastewater.

B. Instrumentation:

The FESEM of silk and silk-Fast Green FCF composite analysis was carried out on FEI Nova NanoSEM 450. The EDS of silk and silk-Fast Green FCF composite analysis was performed on Bruker XFlash 6I30. The functional group of silk, Fast Green FCF and silk-Fast Green FCF composite were measured by FTIR spectra (JASCO FTIR-4600) using KBr pellet

technique. The TGA of silk-Fast Green FCF composite analysis was evaluated using TA Instruments Trios V4.4.0.41128. The BET analysis of powdered silk was executed using Quntachrome ASiQwin Quantachrome Instruments Autosorb iQ Station 2 version 3.01. The absorption spectrum was measured using a UV-visible spectrophotometer.

C. Adsorption studies:

Batch studies were performed by taking 10 mL of the dye solution of 100 mg/l in 100 mL volumetric flask at 25 ◦C and definite pH. Desired particle sizes for the adsorbent materials were selected and experiments were performed by changing the adsorbent dosage, concentration of adsorbate, pH of solution, contact time, temperature, particle size etc. After a certain time these solutions were filtered with porafil syringe filter (0.22 μ) and the amount of the dye uptake was analyzed spectrophotometrically at λmax 624 nm.

D. Dye Recovery studies

Dye solution of 100 mg/lit concentration of Fast Green FCF was then shaken with appropriate adsorbent dose till a colorless solution was obtained. The dye adsorbed on the adsorbent was treated with NaOH (pH 8) for desorption and filtered. The amount of dye recovered in solution was analyzed spectrophotometrically at λ max 624 nm.

III. RESULTS AND DISCUSSION:

A. Characterization of adsorbents

Conventional spectroscopic techniques and currently available analytical techniques were used to analyze the powdered silk before and after adsorption.

1) FT-IR data powdered silk, Fast Green FCF and silk- Fast Green FCF:

The functional group of the powdered silk, Fast Green FCF and silk- Fast Green FCF were evaluated by FT-IR. The FT-IR data of the powdered silk was shown in figure 2.

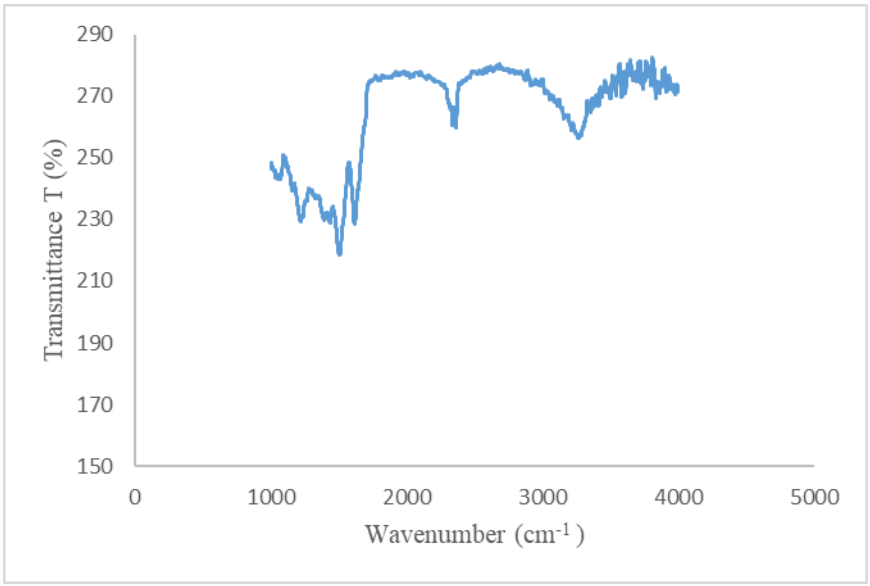


Fig 2: Determination of functional group of the powdered silk by the FT-IR spectra at optimum measurement conditions

The FTIR absorption of silk was recorded. The medium absorption at 1220.71, 1234.21 cm-1 showed C-N of silk. The strong and intense absorption at 1509.98 cm-1 showed β-sheet of silk. The strong and intense absorption at 1617.98 cm-1 showed C=O stretching of amide and β-sheet of silk. The strong and broad band was observed at 3050.83-3502.09 cm-1 indicating O-H, 3417.24-3586.94 cm-1 indicating NH-stretching of silk.

The FT-IR data of the Fast Green FCF was shown in figure 3.

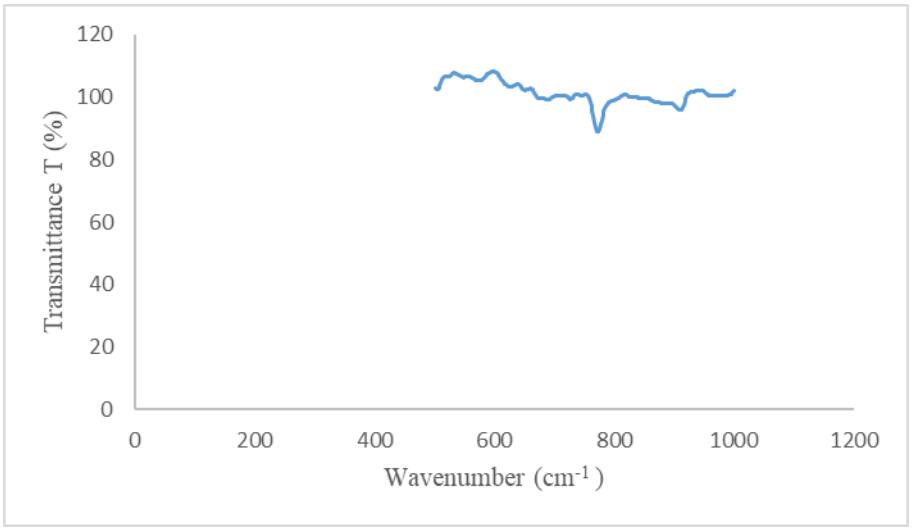


Fig 3: Determination of functional group of the Fast Green FCF by the FT-IR spectra at optimum measurement conditions

The FTIR absorption of Fast Green FCF was recorded. The absorption at 773.31, 910.23 cm-1 shows the ortho, meta and para substituent of Fast Green FCF. The absorption 1025.94-1220.71 cm-1 indicates alkyl amine of Fast Green FCF. The absorption 1388.49 cm-1 indicates symmetric bending vibration –CH3 group of Fast Green FCF. The absorption 1569.77 cm-1 indicates skeletal vibration C=C group of aromatic hydrocarbons of Fast Green FCF. The absorption 3625.51 cm-1 indicates phenolic group of Fast Green FCF. The FT-IR data of the powdered silk-Fast Green FCF was shown in figure 4.

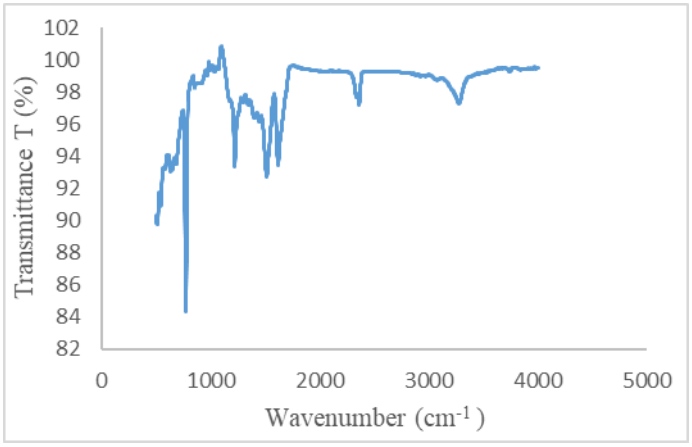


Fig 4: Determination of functional group of the powdered silk-Fast Green FCF by the FT-IR spectra at optimum measurement conditions

The FTIR absorption of silk-Fast Green FCF composite was recorded. The absorption at 684.60, 771.31 and 964.23 cm^{-1} shows the ortho, meta and para substituent of silk-Fast Green FCF composite. The absorption at 1068.37 and 1220.71 cm^{-1} shows the alkyl amine of silk-Fast Green FCF composite. The strong and intense absorption at 1509.98 cm^{-1} was showed β-sheet of silk-Fast Green FCF composite. The strong and intense absorption at 1617.98 cm^{-1} was shown as a C=O stretching of amide and β-sheet of silk-Fast Green FCF composite. The strong, intense and broad absorption at 3073.97, 3272.60 cm^{-1} showed stretching vibrations of intermolecular hydrogen bonding.

2) SEM data silk and silk-Fast Green FCF:

The morphology of all adsorbents on different resolutions was inspected by SEM and presented in Figure 5. The particle size of powdered silk was measured by SEM images as shown in figures 5. The observed particles of powdered silk were less than 200 µm with few particles 50 µm and 5 µm as shown in figure 5. The average particle size is 100 µm. The SEM images of powdered silk exhibited porous network, agglomerated and irregular surface morphology with small fiber like particles judged from figures 5.

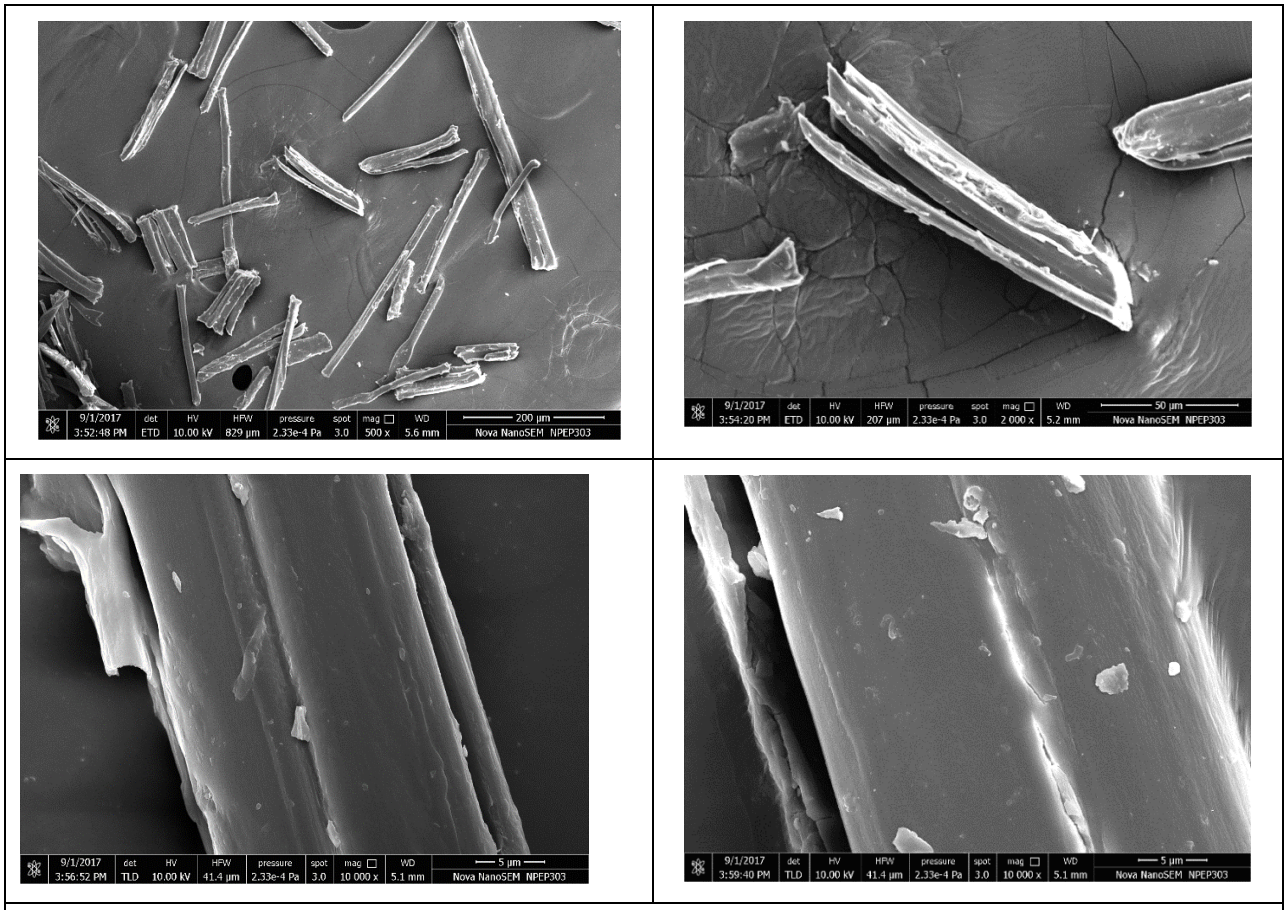


Fig 5: The SEM images of silk particles

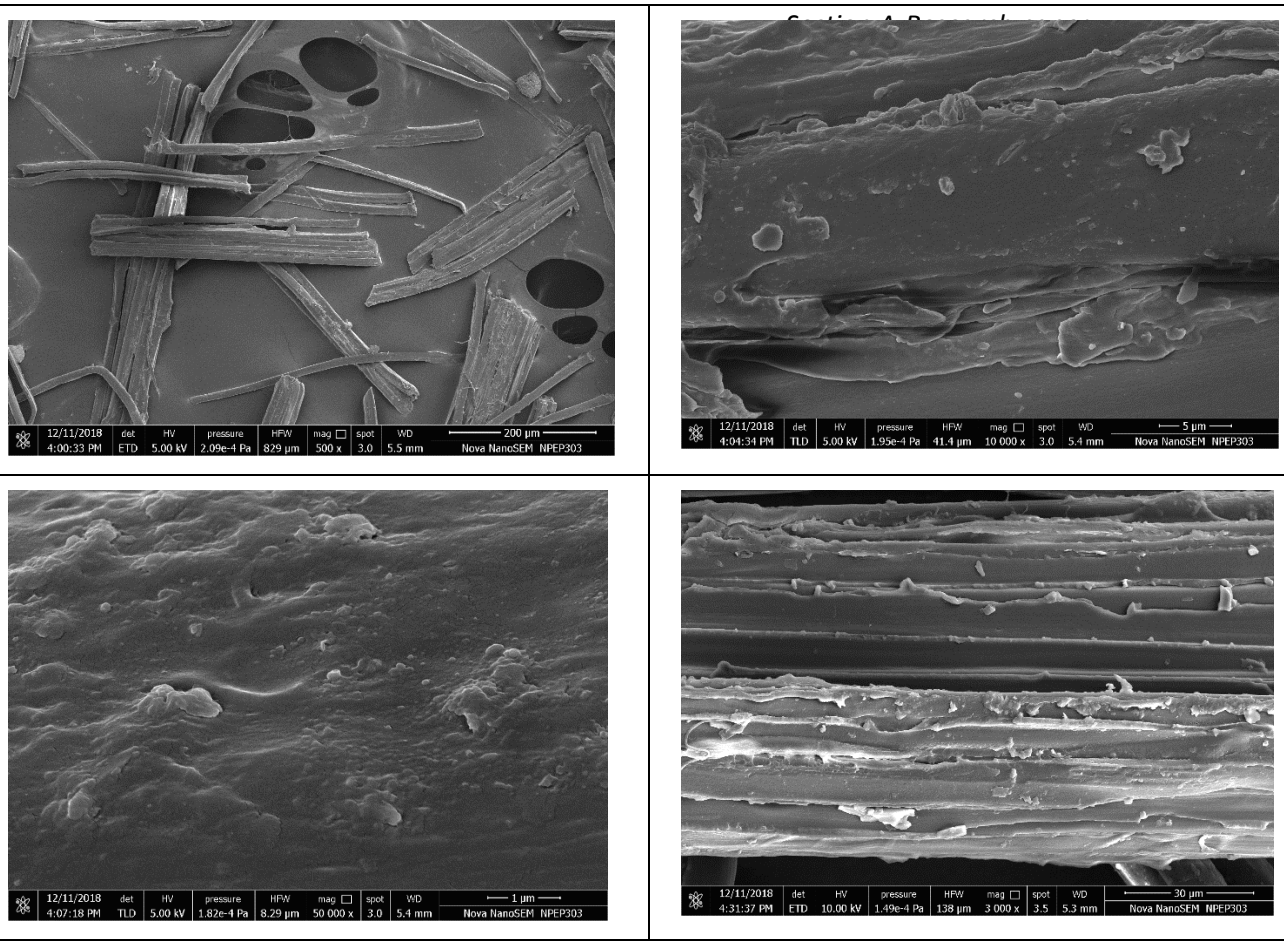


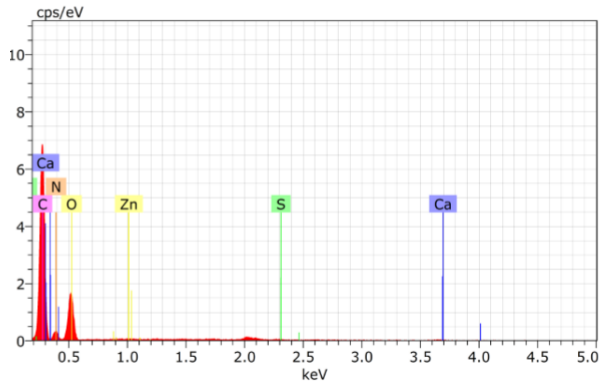
Fig 6: The SEM images of silk- Fast Green FCF composite

The SEM of silk-Fast Green FCF composite is shown in figure 6. The Fast Green adsorption was shown in figure 6. It was apparent that powdered silk has good network structure for the adsorption process. SEM image showed effective adsorption of fast green FCF on powdered silk. It demonstrated that Fast Green FCF is well adsorbed with high homogeneity and agglomeration of many ultrafine particles on powdered silk. SEM image in figure 6, showed the successful deposition of Fast Green FCF on the surface of powdered silk.

3) Energy Dispersive X-ray Spectroscopy (EDS) data:

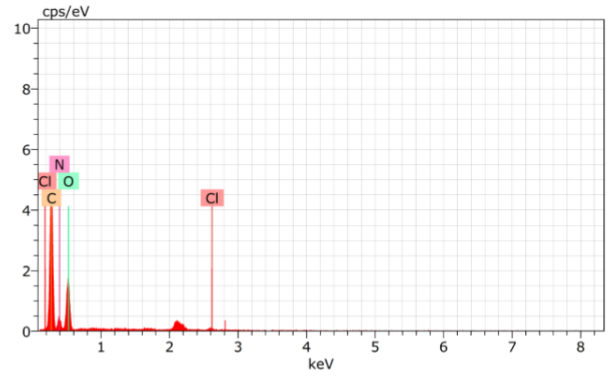
Energy dispersive X-ray spectrum (EDS) of powdered silk before adsorption process, powdered silk adsorbed Fast Green FCF are shown in Fig 8. The result of EDS analysis from an average scanned points showed that the elements of powdered silk are C, N and O Fig 7. After adsorption of Fast Green FCF on powdered silk Fig 8, wt% of N and O increased due to

trapped Fast Green FCF dye molecules which contain sulfonic group and amino group, indicating a chemical interaction of Fast Green FCF-powdered silk. The EDS analysis suggests that the adsorption of Fast Green FCF onto powdered silk processed due the electrostatic interactions between sulfonated amino groups of Fast Green FCF and protonated amino groups of powdered silk.



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	56.87	56.87	62.99	6.73
O	8	K-series	30.48	30.48	25.34	4.11
N	7	K-series	12.10	12.10	11.49	2.21
Ca	20	K-series	0.24	0.24	0.08	0.05
Zn	30	L-series	0.16	0.16	0.03	0.05
S	16	K-series	0.15	0.15	0.06	0.04
Total:			100.00	100.00	100.00	

Fig.7: Energy dispersive X-ray spectrum (EDS):Powdered silk before adsorption process



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	47.92	47.92	54.18	6.52
O	8	K-series	34.68	34.68	29.44	5.42
N	7	K-series	16.57	16.57	16.06	3.55
Cl	17	K-series	0.83	0.83	0.32	0.09
Total:			100.00	100.00	100.00	

Fig.8 : Energy dispersive X-ray spectrum (EDS):Powdered silk adsorbed with Fast Green FCF

4) TGA data of silk-Fast Green FCF composite:

To evaluate the thermostability, thermogravimetric analysis (TGA) was performed. The instrument used was TA Instruments Trios V4.4.0.41128. Figure 9 shows TGA curve of Silk-Fast Green FCF composite. The examination was carried out under nitrogen, heated from 30 oC to 800 ^{o}C with a 10 ^{o}C/min heating rate. The weight of the silk-Fast Green FCF composite remains constant upto 192.70 ^{o}C indicating that silk-Fast Green FCF composite is thermally stable upto a temperature of 192.70 ^{o}C (Fig. 9). At this temperature it starts losing its weight

and this indicates that the decomposition starts at this temperature. Time required for the process is 6.83 min. TGA reveals initial decomposition temperature 192.70 ℃. It exhibits weight loss 0.149 mg and weight percent loss 49.574 %. The result shows high thermal stability of silk Fast Green FCF composite.

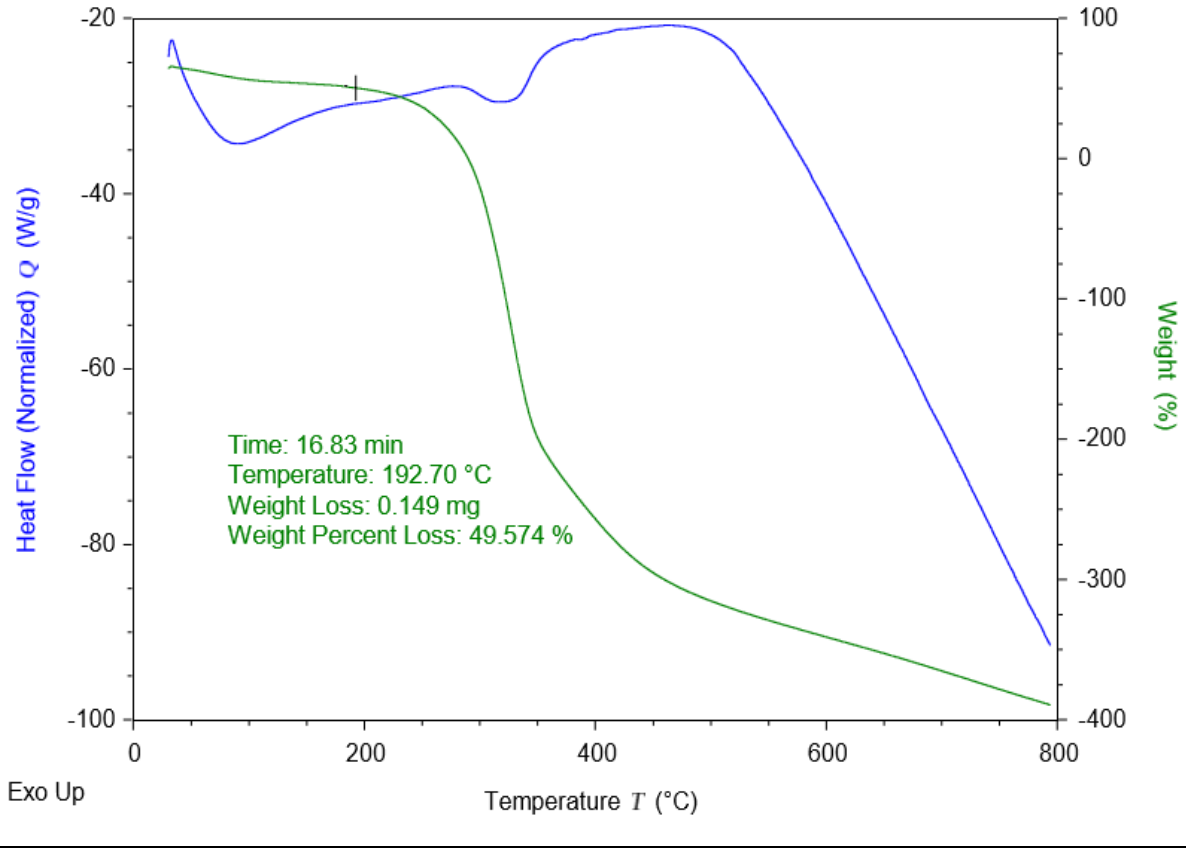


Fig 9: TGA curve of Silk- Fast Green FCF composite

5) BET data of silk:

The property of specific surface area and porosity decide the adsorption capability of conjugated microporous polymers. Brunauer–Emmett–Teller (BET) theory shows average pore radius 8.23112e+01 Å for powdered silk. Barrett-Joyner-Halenda (BJH) adsorption summary shows the surface area 2.629 m^2/g, pore volume 0.014 cc/g, pore radius Dv(r) = 31.148 Å for powdered silk. BJH desorption summary shows surface area 1.211 m^2/g, pore volume 0.012 cc/g, pore radius Dv(r) 22.868 Å. BET summary shows surface area 3.050 m^2/g. Total pore volume is 1.255e-02 cc/g. Pores smaller than 2429.1 Å (Radius) at P/Po is

0.99605. According to the IUPAC classification, the materials give rise to type I nitrogen sorption isotherms which proves the porosity of the material is microporosity (pores<2 nm) and mesoporosity (pores< 11 nm), possessing adsorption capacity.

3.2. Dye Adsorption studies

3.2.1. Effect of pH

In adsorption, pH is a key parameter to control the high uptake to define optimum condition. Therefore, pH has a significant effect on cationic dye of Fast Green FCF adsorption by powdered silk to measure the influence of interaction. In this connection, experiments were carried out to measure the effect of pH on removal of Fast Green FCF by powdered silk absorbent. The solution of Fast Green FCF was 100 mg/l, whereas powdered silk was 100 mg used in each fraction. The dye and powdered silk were taken into a conical flask and stirred for 5 minutes. Then the solution is filtered using a syringe filter where cellulose nitrate porafill paper is used having pore size 0.22 μ. The pH was ranged from 1.0 to 11.0 to define ionization effect in the adsorption operation. The mixed solutions of Fast Green FCF and powdered silk were stirred for 5 minutes. Then solid adsorbent silk-Fast Green FCF were separated and filtrate was analyzed by using UV-Vis spectrophotometry. The results are shown in (Fig 11). The data revealed that dye removal is highly affected by pH of solution. It was cleared that at each pH, the dye solution decolorized effectively. With the increase in pH from 0 to 2.5, adsorption was found to increase after that pH increases, adsorption decreases. (Fig. 10) After pH 4, dye adsorption was decreased on proceeding further till pH 10. Maximum adsorption of dye was found at pH 1.9 after scanning between pH 1.5 to 2.5 (Fig. 11). The decline in adsorption by increasing pH can be elucidated on the basis of protonation and deprotonation of dye molecules as well as sorbent. Protonation of the anionic dye takes place on the addition of acid which allows significant affinity towards the negatively charged adsorbents. On increasing the pH, deprotonation of the dye takes place, which thereby declines the amount of dye adsorbed pH 1.9 has been chosen for the studies on account of the fact that the amount adsorbed in this case is maximum.

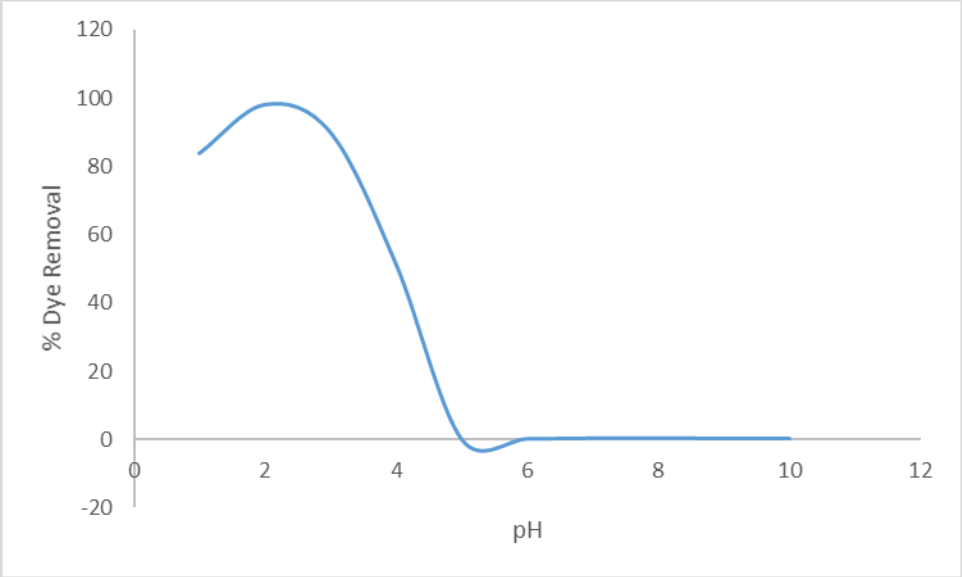


Fig. 10 : Effect of pH on dye adsorption

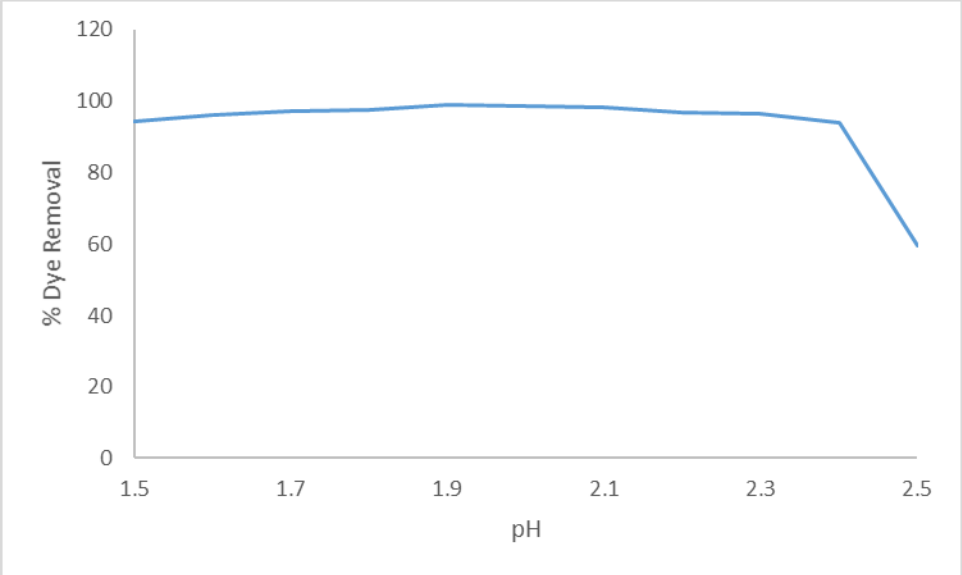


Fig. 11 : Effect of pH on dye adsorption

3.2.2. Effect of contact time

The adsorption kinetics determination by the adsorbent material in waste water treatment is crucial due to major insight into the internal mechanism of reaction kinetics. So sufficient contact time between Fast Green FCF and powdered silk for equilibrium was evaluated. For the evaluation of contact time effect, 100 mg of powdered silk was added with constant initial

concentration 100 mg/l of Fast Green FCF at pH 1.9 for different interval time of stirring. The Fast Green FCF adsorption onto the powdered silk with function of time as shown in Fig. 12. The result clarified that adsorption of dye increased with increasing contact time by the adsorbent Fig.12. The Fast Green FCF adsorption efficiency was low at initial and then increases gradually to reach the plateau by the powdered silk adsorbent. With the increase in time the adsorption increases for powdered silk. The percentage adsorption of the dye during the first 3 minutes of contact was almost 98 – 100 %. From experimental data, it is found that this adsorption follows pseudo first-order kinetics (Fig. 13, 14). These results also confirm the endothermic nature of the adsorption. In general, the adsorption process is an exothermic reaction. However, most dye adsorption on powdered absorbent was found to be an endothermic process. Since, adsorption takes place in aqueous media containing both dye and water molecules. For dye to adsorb, water molecules must be desorbed. Since, the molar volume of water is much smaller than dye molecules, a greater number of water molecules are desorbed from the adsorbent surface which results in releasing of greater amount of heat. Hence, the overall process becomes endothermic.

The UV–Vis spectroscopic measurements were carried out to estimate the adsorption of each pollutant by powered silk adsorbent as a function of time from the simulated wastewater having concentrations (100 $mg.L^{-1}$). The adsorption quantity of each pollutant by powdered silk adsorbent increased with time and their initial concentration (Fig.12).The cationic dyes showed higher and faster adsorption than anionic dye. The time required for maximum adsorption (equilibrium time) of Fast Green FCF dye by powdered silk adsorbent increased from 15 sec to 3 min (Fig. 12) for concentration from 100 mg L^{-1}. The adsorption equilibrium time varied for organic dyes and is believed to be governed by their size and charge.

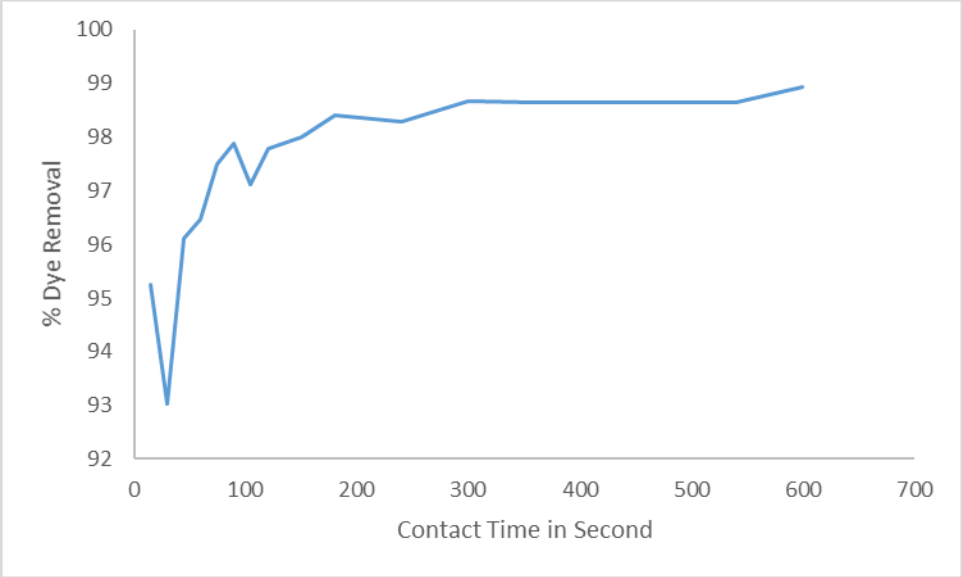


Fig. 12 : Effect of Contact Time on dye adsorption

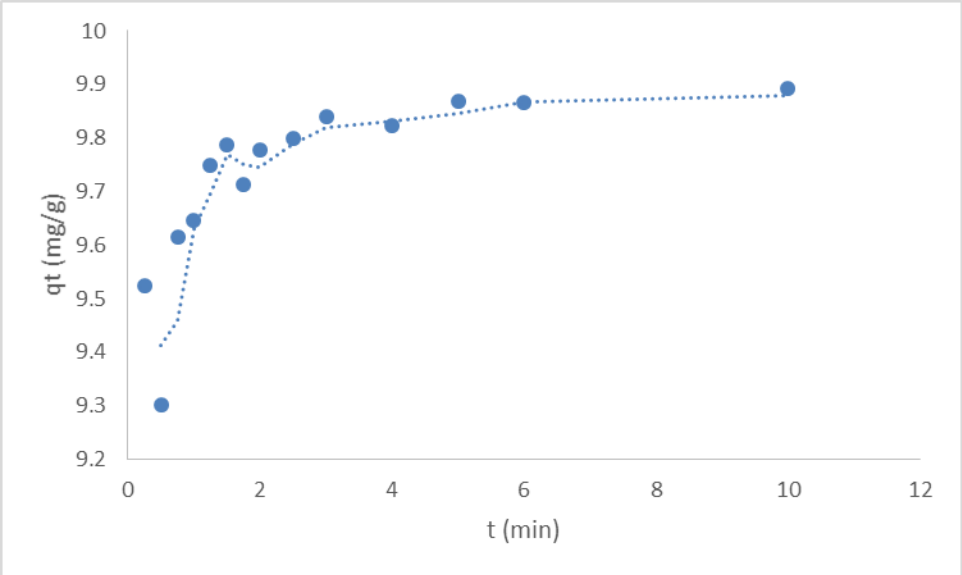


Fig. 13: Nonlinear pseudo first order model for the adsorption kinetics of Fast Green FCF on Powdered silk

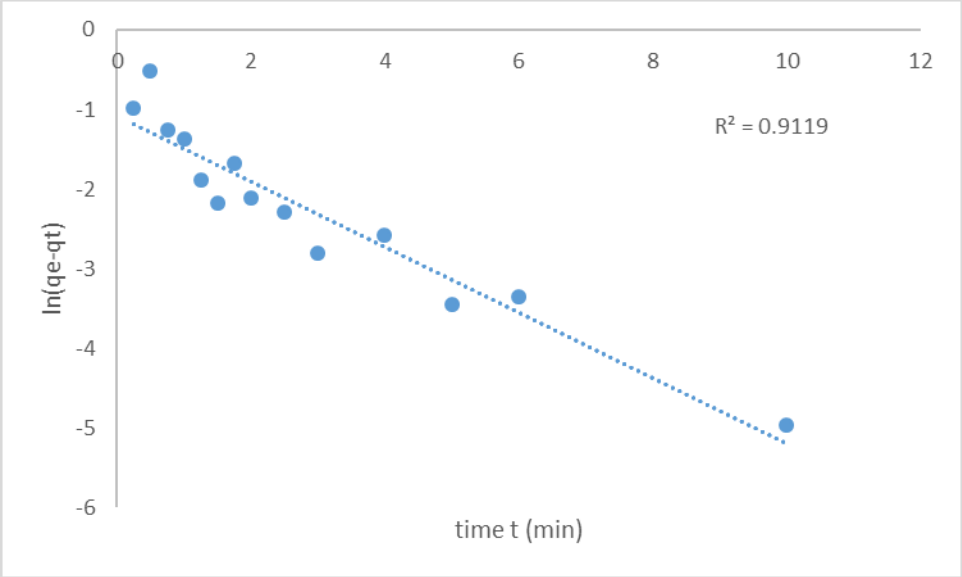


Fig.14 Linear pseudo first order model for the adsorption kinetics of Fast Green FCF on Powdered silk

3.2.3. Effect of temperature

The adsorption of Fast green FCF on powdered silk has been studied from 20^0C to 60^0C (Fig 15).

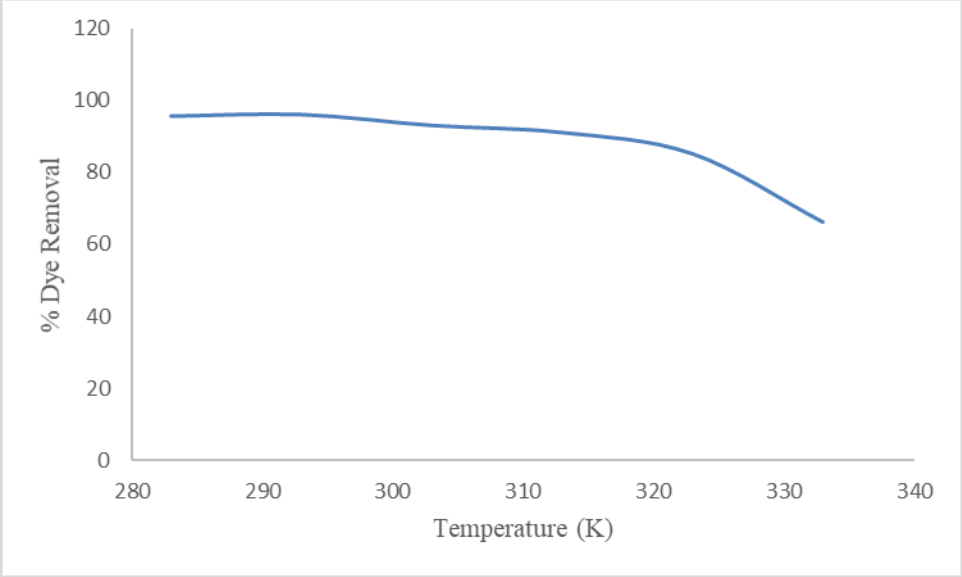


Fig. 15: Effect of Temperature on dye adsorption

At 20^0C, adsorption is observed as maximum. It is also found that for a given mass of powdered silk adsorbent and fixed concentration of Fast Green FCF adsorbate, adsorption decreases with increase in temperature.

3.2.4 Effect of particle size

For batch adsorption experiments, three different particle sizes viz. 90, 150 and 180 micron mesh were selected. The difference in the amount adsorbed was noticed with the increase in mesh size. (Fig. 16) presents the effect of sieve size of adsorbents on the adsorption at 25°C. Adsorption was found to increase with the decrease in the mesh sizes. This is due to increase in the surface area of the adsorbents and accessibility of the active functional groups towards the dye.

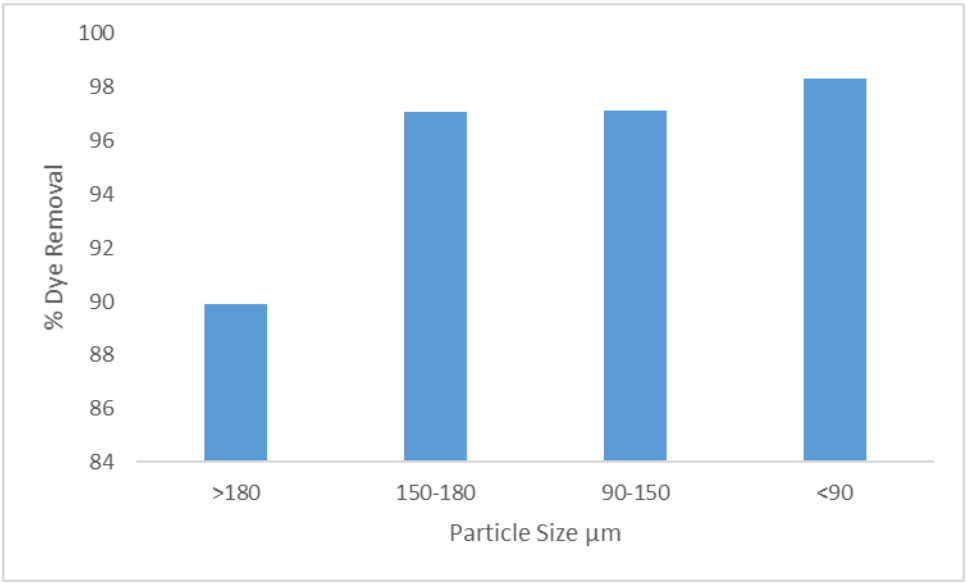


Fig. 16: Effect of particle size on dye adsorption

3.2.5 Effect of adsorbent dose

The effect of adsorbent amount on Fast Green FCF removal efficiency was evaluated by adding various amounts of powdered silk at initial concentration when initial concentration 100mg/l was fixed at optimum pH 1.9. With different adsorbent amounts, Fast Green FCF removal efficiency as shown in Fig 17. The maximum Fast Green FCF removal efficiency

was observed with 100 mg powdered silk when initial concentration was fixed at 100 mg/l. Increasing the adsorbent dose enhances the amount of dye adsorption on adsorbent (Silk) (Fig 17) Increase in adsorbent dose provides more binding sites. It is observed that 80 mg to 140 mg shows maximum adsorption. After 140 mg, adsorption was found to be constant because of adsorption equilibrium between Fast green FCF and silk.

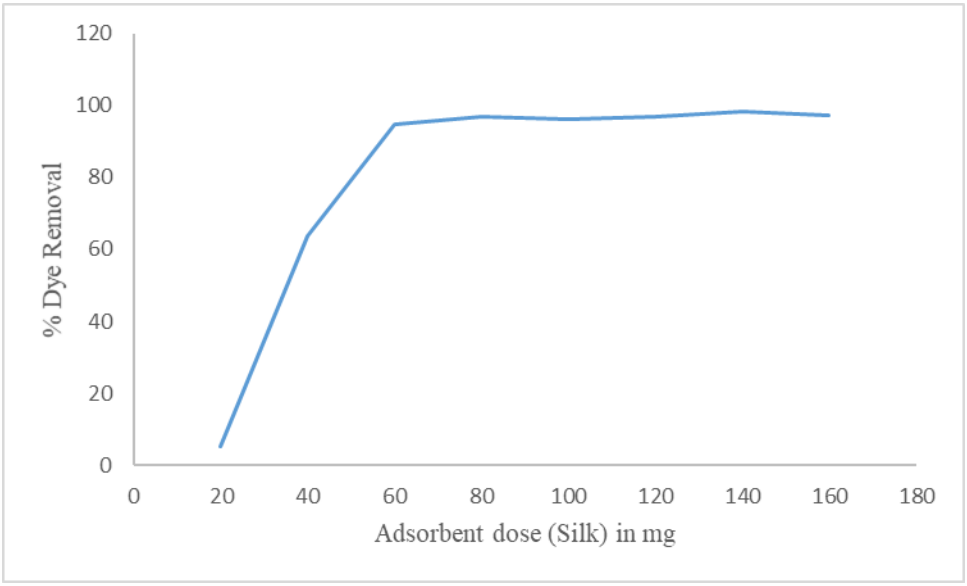


Fig. 17: Effect of adsorbent dose on dye adsorption

3.2.5 Effect of adsorbate dose

If we vary Fast green FCF dose from 50 mg/l to 250 mg/l, it was observed that maximum adsorption of 100 mg/l. 100 mg silk used for the same. See in (Fig 18)

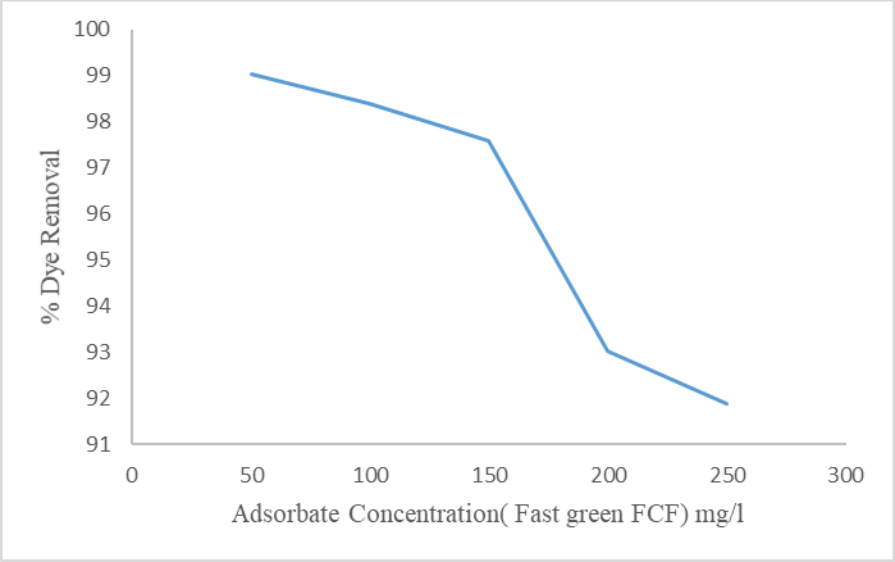


Fig. 18: Effect of adsorbate dose on dye adsorption

3.2.6 Effect of initial concentration and adsorption isotherm

The dye removal performance by the powdered silk adsorbent was assessed as adsorbent amount and removal percentage in the condition of various Fast Green FCF initial concentrations. For the initial concentration, Fast Green FCF removal was enhanced by using powdered silk adsorbent because the driving force to overcome mass transfer resistance between the bulk liquid phase to the solid material phase, and powdered silk adsorbent put up more considerable potential for Fast Green FCF removal quantity. Fig. 10 shows initial dye concentration effect on the adsorption by powdered silk adsorbent and various initial dye concentrations varied from low to high where the other experimental conditions were fixed. It was found that the adsorption of fast Green FCF dye was high in the initial low concentration region then increased gradually to reach an equilibrium state for the determination of maximum adsorption capacity as judged from Fig. 19.

To determine the mechanistic parameters associated with Fast Green FCF dye adsorption by powdered silk adsorbent, this study measured the relationship between adsorbed Fast Green FCF and its residual in aqueous solution at adsorption equilibrium by using Langmuir adsorption model. The Langmuir adsorption isotherm is the best known for all isotherms describing adsorption operations based on material morphology. The linear form of the

Langmuir adsorption isotherm equation is represented by the following equation:

$$\frac{Ce}{qe} = \frac{1}{KL.qm} + \left(\frac{1}{qm}\right)Ce \qquad \text{(linear form)} \qquad \ldots\ldots \qquad (1)$$

Where, Ce is the concentration of Fast Green FCF dye in the solution at equilibrium in mg/l,

qe is the amount of Fast Green FCF dye adsorbed at equilibrium in mg/g,

qm is theoretical maximum adsorption capacity of Fast Green FCF dye in mg/g, and

K_L is Langmuir adsorption constant.

Here, K_L ($L.mg^{-1}$) denotes Langmuir adsorption constant, q_m denotes optimum adsorption capacity in units of mg g^{-1}. Figure 19 shows the Ce/qe vs Ce plot concerning adsorption of Fast Green FCF dye on powdered silk adsorbent. The estimated values of the above-mentioned quantities are tabulated in Table 1.

Fig. 19 shows the linear adsorption isotherm obtained using the model, and Langmuir isotherm model parameters including the qm value of material. The q_m value of Fast Green FCF adsorption on powdered silk adsorbent indicates better adsorption, which was 24.27mg/g. The adsorbents in this study significantly increased the adsorption capacity due to the surface functional group, interlayer, and porous nature of adsorbent surface. The coefficient (R^2) for Langmuir model was indicated the suitable monolayer coverage by the powdered silk adsorbent.The experimental results shown that the adsorption data are fitted well with Langmuir isotherm, suggesting the monolayer coverage on the adsorbent surface as expected naturally.

It was observed that the value of q_m was evaluated as 24.27 mg g^{-1}. This value of qm indicates the maximum amount of Fast Green FCF that could be removed by one gram of powdered silk adsorbent.

Meanwhile, the Freundlich adsorption isotherm provides information considering multilayer adsorption on a heterogeneous surface in terms of logarithmic dependence of surface energies with surface coverage. This isotherm is often expressed as follows:

$$\ln qe = \ln KF + \frac{1}{n\ lnCe} \qquad \text{(Linear form)} \qquad (2)$$

Here, K_F (L mg^{-1}) and 'n' (mg L^{-1}) designate the capability and intensity of the adsorption,

respectively. The values of $\ln q_e$ are plotted against the values of ln Ce and a linear graph is obtained (Fig. 20). In Table 2, the constants evaluated from the graph are tabulated.

Table 1 : Adsorption isotherms constants for different adsorption models for the adsorption of Fast Green FCF dye on powdered silk:

Isotherm models	Adsorption Isotherm Constants		R^2
Langmuir	K_L =0.4178 L mg^{-1}	q_m = 24.27 mg g^{-1}	0.9828
Freundlich	K_F = 7.484 L mg^{-1}	n = 2.5477 mg L^{-1}	0.9642

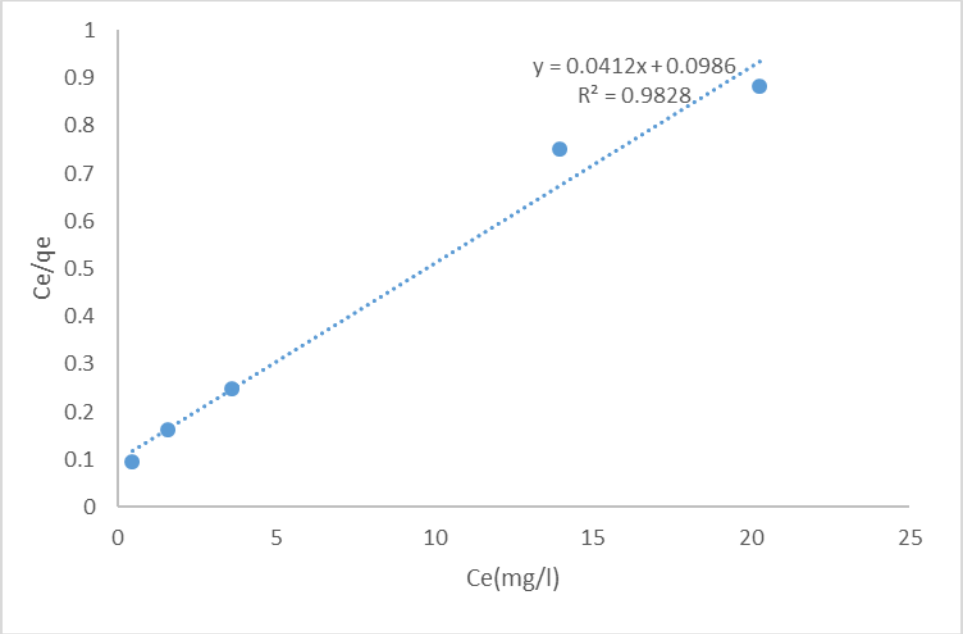


Fig. 19: Linear fitting of Langmuir isotherm models for the silk-Fast Green FCF

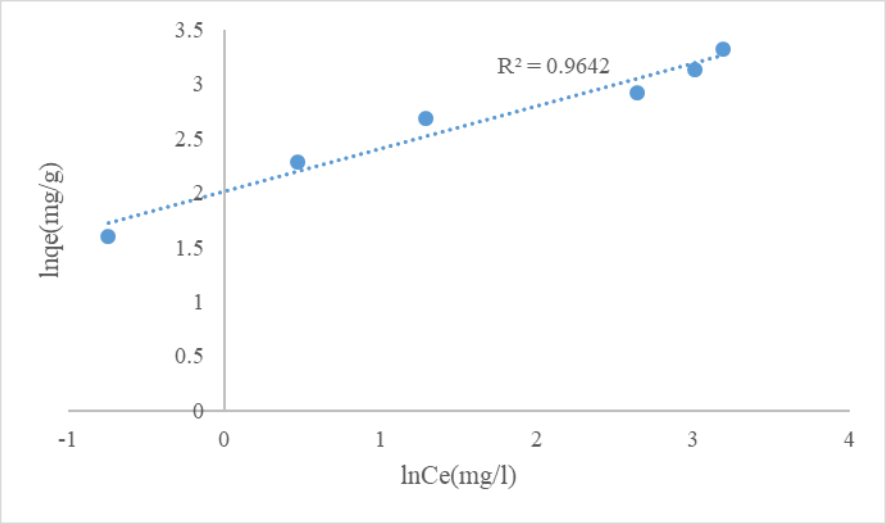


Fig. 20: Linear fitting of Freundlich isotherm models for the silk-Fast Green FCF

Table 2 : Comparison of dye adsorption capacities using different forms of adsorbent materials.

Used adsorbents	Name of dye	Capacity (mg/g)	Ref.
PABA@AC	Malachite green	66.87	28
Fe-BDC MOF	Methylene blue	8.65	29
Pine leaves	Methylene blue	126.58	30
Citric Acid Modified Sawdust	Methylene blue	111.46	31
Cellulose surface	Reactive red dye	78.00	32
Mango seed	Orange 16	52.5	33
Rice flour (RF)	Methyl orange	173.24	34
Graham flour (GF)	Methyl orange	151.27	35
Powdered silk	Fast Green FCF	24.27	This study

Table 3: The dye removal performance comparison between some membranes reported in literatures and this study.

Membrane	Dye	Feed concentration (mgL^{-1})	Dye water flux ($Lm^{-2}h^{-1}$)	Dye removal (%)	Volume (mL)	Ref
Ultrathin graphene	Methylene blue	6.4	21.8	99.2	10/35*	36
Ultrathin GO	Brilliant Blue	20 (methanol)	7.5	100	-	37
MXene/GO	Methylene blue	10	16.69	98.65	~10	38
MXene/GO	Brilliant Blue	10	0.23	100	~5	39
GO/Polyethersulfone	Direct Red 16	30	<13.5	99	~17	40
GO/tannic acid	Methylene blue	100	23.33	97.6	-	41
Graphene/MWCNTs	Direct Yellow/ Methyl Orange	50	4.97-10.11/ 4.61-9.54	99.6-99.9/92.0-98.0	-	42
GO/TiO2	Methyl orange/ Rhodamine B	10	7	≥99	~8	43

Surface modified polysulfone	Cibacron yellow	67	2.5	99.9	~11	44
Surface modified polysulfone	Rhodamine B	50	11.9	98	~37	45
Attapulgite nanorods into GO	Rhodamine B	7.5	16.2	97	-	46
Attapulgite nanorods into GO	Methyl violet B	50	~15	100	-	47
MCM 0.6	Methylene blue	75	44.97 ± 2.19	100 ± 0.1	10**/50	48
MCM 0.6	Methylene blue	15	28.94 ± 0.74	94.63 ± 3.8	-	48
Powdered silk	Fast Green FCF	100	-	98	-	This study

10/35*: The permeation volume was 10mL to the original feeding solution as 35mL after the steady state was reached.

–: There is no specific data shown in the literature.

**: 10mL=0.010L=44.97 ($L \cdot m^{-2} \cdot h^{-1}$) * 10 (min) * 13.84×10^{-4} (m^2).

Adsorption thermodynamics

The Fast Green FCF adsorption on powdered silk has been identified as decreasing with the increase in temperature from 20 to 60 °C at pH 1.9 as shown in Fig. 15. This observation is an indication of an involvement of an exothermic process [49]. At the equilibrium, the Gibbs free energy change was estimated using Eq. (3) by evaluating equilibrium constant (K_L) as is discussed in the previous section for Langmuir isotherm.

$$\Delta G^{\circ} = -RT \ln K_L \quad (3)$$

In thermodynamics, the Gibbs free energy change is often employed to correlate with the enthalpy change (ΔH°) and entropy change (ΔS°) as per the following equation which is known as van't Hoff equation.

$$\ln K_L = \frac{\Delta S0}{R} - \frac{\Delta H0}{RT} \quad (4)$$

Plotting the values of ln K_L with respect to the reciprocal of temperatures, a linear graph is obtained (Fig.22). Then the thermodynamic quantities were evaluated from the slope and intercept and tabulated in Table 3.

Note that, irrespective of the temperature, ΔG° values were found to be negative indicating that the Fast Green FCF dye adsorption onto powdered silk is a spontaneous process. Additionally, the negative sign of ΔH° that was estimated as 29.449 KJ mol^{-1} which implied the endothermic nature of Fast Green FCF dye adsorption onto powdered silk. At the same time, the obtained value of 0.1086 J mol^{-1} K^{-1} for entropy change shows that the adsorption caused the increasing disorder. Similar phenomenon was reported by other researchers [50] (Figs. 21, 22).

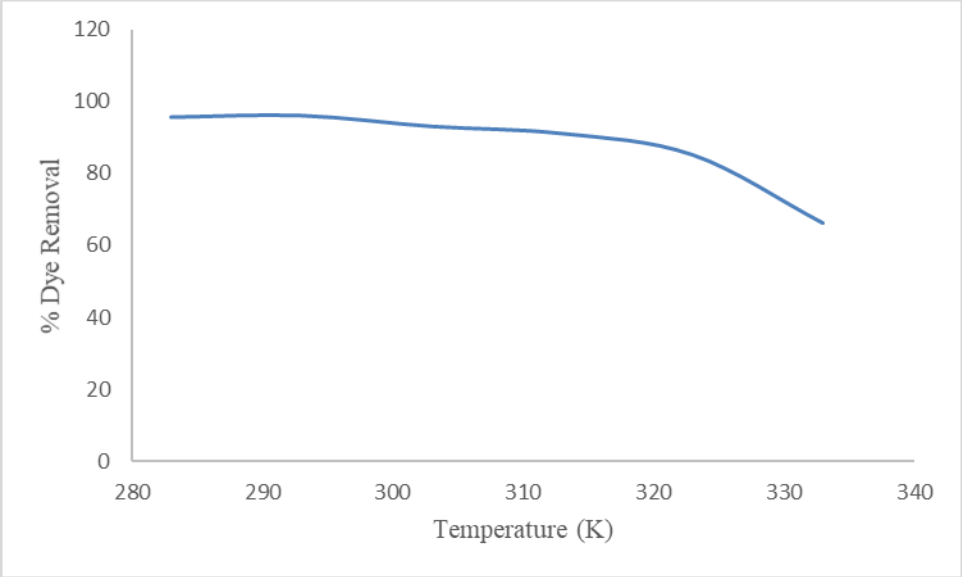


Fig. 21: Plot of %Dye Removal at different temperatures

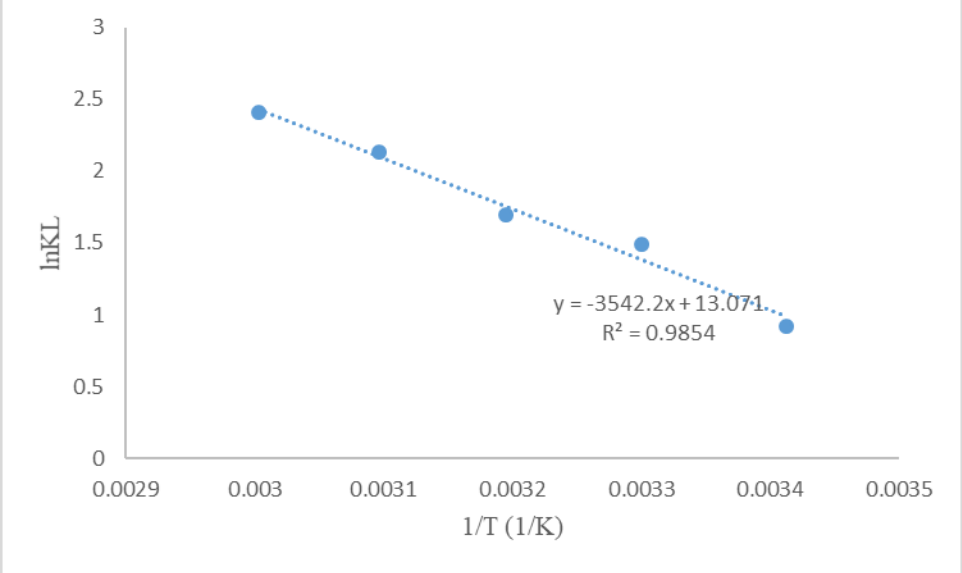


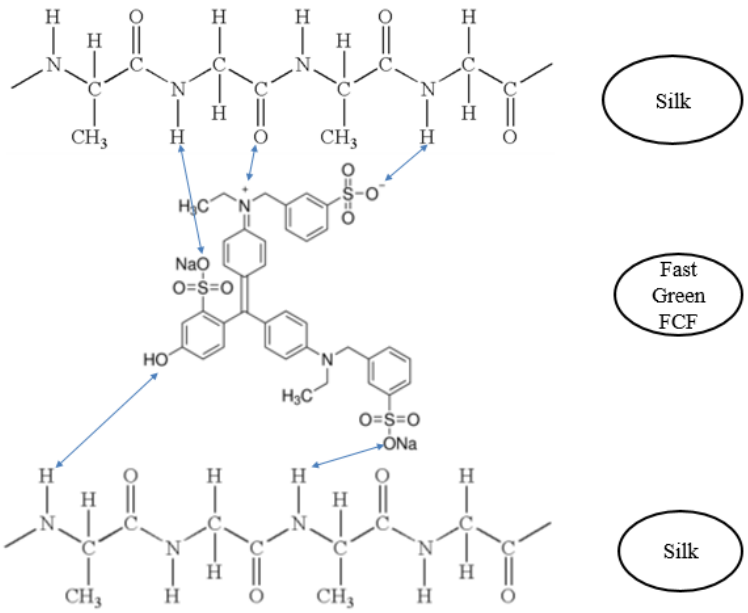
Fig. 22: Van't Hoff's plot of lnK vs 1/T

Table 4: Thermodynamic parameters for the adsorption of Fast Green FCF dye onto powdered silk

T(K)	ΔG°(KJ mol^{-1})	ΔH°(KJ mol^{-1})	ΔS°(KJ $mol^{-1}K^{-1}$)
293	-2.248385476	29.449	0.1086
303	-3.754032877		
313	-4.418945117		
323	-5.718840242		

Possible mechanism for dye adsorption

In the understanding of the bonding mechanism, the adsorption process clearly presents the nature of selectivity and sensitivity. The functional group associated in powdered silk was measured based on FTIR measurement. In addition, the mechanism of toxic dye adsorption and organic compound anchoring by the functional group adsorbent material may be clarified by considering the solution acidity, degree of dissociation of dye species and surface functionality presenting the charges of the functional adsorbent materials. From the hydroxyl availability in powdered silk adsorbent, the anionic Fast Green FCF dye might be associated as hydrogen bonding and covalent bonding as shown in scheme 1. Based on bonding ability, powdered silk adsorbent was able to adsorbed the anionic Fast Green FCF with high efficiency.



Scheme 1: Possible bonding mechanism between powdered silk and Fast Green FCF

3.3. Dye recovery

Desorption is an important criterion in adsorption process to make the adsorbent cost effective and promising. Therefore, desorption of Fast Green FCF dye from the powdered silk was evaluated. The recovery of dye from silk-Fast Green FCF composite was examined using pH parameter and contact time. Silk-Fast Green FCF composite was taken into the conical flask and solution of pH 7 to 11 was added to it. Keeping contact time of 5 minutes, the solution was stirred and filtered by using a syringe filter. Filtrate was evaluated by using UV-visible spectrophotometry. It was found that at pH 8 the NaOH solution gave complete desorption of dye from silk. To study the contact time, silk-Fast Green FCF composite was taken into the conical flask at pH 8 and contact time was varied from 1 to 6 minutes. It was found that desorption of dye was effective at 4 minutes. Therefore for complete desorption of Fast Green FCF from powdered silk, NaOH of pH 8 and contact time of 4 minutes was required. The percentage recovery of the dye 99-100%.

IV. CONCLUSION

Thus it can be revealed powdered silk used as low cost adsorbent for removal of Fast Green FCF from wastewater. It can be concluded that adsorption process depend on the effects of

pH, concentration of dye, particle sizes of powdered silk, amount of adsorbents, temperature and contact time. The optimum process conditions for the Fast Green FCF adsorption on powdered silk were pH 1.9, contact time 3 minutes, adsorbate concentration 100mg/l, adsorbate 100 mg and temperature 20^0C. Fast Green FCF was found to adhere endothermically, spontaneously, and practically to the powdered silk. According to the adsorption isotherms, the adsorption of Fast Green FCF over the powdered silk fit the Langmuir model. The monolayer adsorption capacity 24.27 mg/g. There is evidence that chemisorption is effective. The dye adheres to material according to pseudo first order kinetics. On the basis of mass transfer studies, it is also concluded that transportation of the dye towards adsorbent materials rapidly exhibits good affinity towards the dye. Bulk removal of the dye has been carried out and percentage 98 – 100 %, respectively. The dye recovery is made by NaOH of pH 8 and as per spectrophotometric estimation, about 99-100% of the dye is recovered from powdered silk.

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