Experimental Study on Removal of Dye from Aqueous Solution by Adsorption Process Using Low-cost Material

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Abstract: Dyes are the most common types of pollutants which can be even distinguished by the human eye. Dyes shouldn't be disposed in water resources. Usage of many types of treatment technologies are done to avoid that. There are many methods to treat this, but amongst them, adsorption holds a prominent place when it comes to dye removal. The growing need to find efficient and economical treatment method, and importance of adsorption has led to rise of low-cost alternative adsorbents. This thesis work focusses on liquid phase adsorptive removal of organic dyes viz. Crystal violet which represents a class of a basic dye. The adsorbents used was: Sodium carbonate-treated Bamboo (NCB). The characterization and the surface morphology of all the adsorbents were carried out using conventional techniques like Fourier Transform Infrared Spectroscopy (FTIR) and scanning electron microscopy (SEM).

***Index Terms* - Dye removal, Fourier transform infrared spectroscopy, Scanning electron microscope, Sodium carbonate**

I. INTRODUCTION

To keep future of mankind safe, we have to save and protect water which is our top priority right now. With all the advancements in science and technology our world is reaching to new highs. But the cost which we may have to pay in near future is surely going to be too high. Among the consequences of rapid growth is environmental disorder leading to a big pollution problem. Anthropogenic activities have caused much damage to quality of our lifeline. There is condition of crisis of freshwater resources because of faster depletion of the same. It is high time we realize the gravity of the situation as water pollution is now a global concern. Removing pollutants from water has become a top priority right now and to develop an economical and environmentally safe method to achieve this is a challenging task for engineers. After all, it is the future of humans at stake. A dye is usually a substance that bears an affinity to the substrate to which it is being applied to. It is often applied in aqueous solution. It requires a mordant to improve its binding to fabrics. It appears to be colored because it absorbs some of the light waves more than others. Various industries like chemical, refineries, textile, plastic and food processing plants discharge wastewaters. These wastewaters have dyes in them as residues which cause many hazards. Such residual dyes are non-biodegradable as they have a complex molecular structure which makes them more stable and harder to biodegrade. They cause water pollution and pose a grave threat to environment. These residual dyes along with being aesthetically displeasing also stop sunlight from penetration into water thus affecting aquatic ecosystem. Many of them are also toxic in nature which can cause direct destruction or can affect catalytic capabilities of various microorganisms.

II. HARMFUL EFFECTS OF DYES

There are in many harmful effects of dyes on environmental ecosystem such as:

- They can create acute as well as chronic effects on exposed organisms. These effects are different for different exposure time and the dye concentration.
- They can absorb or reflect sunlight which enters the water bodies and thus inhibit the growth of bacteria which disturb the balance in their biological activities.
- They are distinctly visible and so even a small amount may result in abnormal color of water. This appears unpleasant to eyes.
- Because of their complex molecular structures, it is difficult to treat with common municipal treatment process.
- Consume dissolved oxygen and thus affect aquatic ecosystem.
- Sequester metal ions which produce micro toxicity to aquatic lives.

There are many ways to remove dyes from wastewater discharges like membrane separation process, coagulation, chemical oxidation, electrochemical process, reverse osmosis and aerobic and anaerobic microbial degradation. Because of their economic disadvantages and inefficiency many of these processes are not so popular. Coagulations and chemical and electrochemical oxidations are not feasible on large scale plants. Adsorption with its low cost and high performance, is preferred over these processes. Some most commonly used adsorbents are activated carbon, alumina silica and metal hydroxides. Selecting an adsorbent depends on their economic advantages, performance efficiencies and environment, so researchers generally use low-cost adsorbents like char from agricultural wastes and others.

III. ADSORPTION

Adsorption is a process that happens when a gas or liquid solute accumulates on the top of the surface of a solid or a liquid, which in turn forms a molecular or atomic film. In alternate words, adsorption is the adhesion of ions, atoms, molecules or biomolecules of liquid, gas, or dissolved solids on to a surface and this process generates a film of the adsorbate (the atoms being accumulated) on the surface of adsorbent. It is a surface phenomenon which happens due to surface energy. The atoms on the

surface of the adsorbent can attract adsorbates as they are not completely surrounded by other atoms. The exact nature of the bonding depends on the details of the species involved.

IV. MATERIALS AND METHODOLOGY

All glass instruments like measuring cylinders, beakers, conical flask etc.) were produced by Borosil. All the instruments/apparatus which are used in this experiment are listed below:

Table 1 List of all instruments used

Instrument	Function
Electronic weight balance	To measure weight
Oven	To dry the samples / to maintain the temperature
Shaker	To shake the samples in dye solutions
Spectrophotometer (UV/ Vis)	Absorbance
Scanning Electron Microscope((SEM)	Morphology
Fourier transform infrared spectroscopy (FTIR)	To identify the presence of the functional group in the samples.

Crystal Violet (CV)

Basic dyes have amino groups, or alkylamino groups having overall positive charge, as their auxochromes. The colored portion of molecule is the cation. Even though the whole molecule that is charged, the molecule charge is generally shown on a specific atom in structural formulae. They are most fluorescent among all other synthetic dyes. They have very poor light and wash fastness.

- IUPAC Name: Tris(4-(dimethylamino)phenyl) methylium chloride
- Molecular formula = C25N3H30Cl
- Molar mass = 407.979 g mol-1
- Appearance = blue-violet colour
- Melting point = 205°C (with decomposition)

Crystal Violet is used as dye, especially for paper and as a component of navy blue and black inks for printing, ball-point pens and ink-jet printers. It is used to colorize different products such as anti-freezes, fertilizers, and detergents. The dye is also used particularly in Gram's method for classifying bacteria as a histological stain. Crystal violet has antibacterial, antifungal, and anthelmintic properties. However, in large quantities, crystal violet may lead to ulceration of a baby's mouth and throat and is linked with mouth cancer. Crystal violet has also been linked to cancer in the digestive tract of animals.

Preparation of bio-adsorbent

Bamboo was taken from the local market and was crushed into small pieces. Once the crushed bamboo was ready, it was then sieved through 425–600 microns. It was washed properly with distilled water so as to remove any kind of impurities and oven-dried at 60 °C for 24h. It was kept in an airtight vessel to avoid getting in contact of moisture. A certain amount of distilled washed Bamboo was then treated with 0.1 M Na_2CO_3 (sodium carbonate) solution separately for 6 h at 200 rpm (rotation per minute) in a rotary shaker and kept overnight. Then the excess of Na_2CO_3 was washed of with distilled water so as to maintain the pH between 7 and 7.5. It was then oven-dried at 60 °C for 24 hours and kept in an airtight vessel. SEM was carried on NCB to understand the surface characteristics. FTIR analysis was done in order to elaborate the role of the functional group present in adsorption mechanism.

Fig. 1 Preparation of bio-adsorbent

Batch Isotherm Experiments

Investigation of adsorption on CV on NCB was done in batch adsorption experiment. Batch adsorption study was done in 250 ml glass flask containing known amount of adsorbent and known concentration.

Fig. 2 Batch Isotherm Experiments

Effect of Contact Time

150 ml of the working solution was put in each different conical flask. All the flasks were put on the shaker at 150 rpm for a predetermined time period ranging from 5 minutes to 150 minutes. Then, flasks were withdrawn from the shaker, solution was separated from adsorbents and then % absorbances were estimated by using spectrophotometer (JASCO UV/Vis- 550, RPM=101, temp=26oC) at the wavelength corresponding to maximum absorbance, (λ_{max}=618).

Effect of pH

150 ml of the working solution was put in each different conical flask. The pH of the dye solutions was adjusted with dilute HCl (0.1N) or KOH (0.1N) solution by using a pH meter (EUTECH Instrument, pH 510) with pH of solutions being 4,6,8,10. All the flasks were kept on the shaker at 150 rpm for 180 minutes, the flasks were withdrawn from the shaker and the dye solutions were separated from adsorbents and the final % absorbances of dye solutions were measured using UV spectrophotometer (λ_{max}=618).

Effect of Initial Concentration on Crystal Violet

Three solutions of dye were prepared in distilled water in conical flasks with different concentrations of dye-5mg/1L, 10mg/1L and 15mg/1L. NCB was put into the solutions (with concentration 1mg/ml) and were put into the shaker (RPM=101, temp=26oC) for 2 hours. Their % absorbances were determined using Spectrophotometer.

Effect of Adsorbent Dose

Adsorbent dose effect was studied by preparing 5 different solutions of dye and NCB in distilled water in different conical flasks with constant concentration of crystal violet dye and varying dose of NCB 40mgg/150ml, 60mg/150ml, 80mg/150ml, 100mg/150ml, 150mg/150ml. These solutions were prepared in 250 ml conical flasks and put in the shaker (RPM=101, temp=26oC) for 2 hours. Then their % absorbances were calculated by spectrophotometer (λ_{max}=618). And thus, amount adsorbed were calculated.

Fig. 3 Removal of dye observed in different concentrations

V. RESULTS AND ANALYSIS

Plotting calibration curve

Dye solutions in water were prepared with concentrations 4mg/1L, 8mg/1L, 10mg/1L and 12mg/1L and their % absorbances were found out by UV spectrophotometer(λ_{max}=618). The standard calibration curve was plotted with these values. The concentrations for various % absorbance was calculated using the equation of the curve.

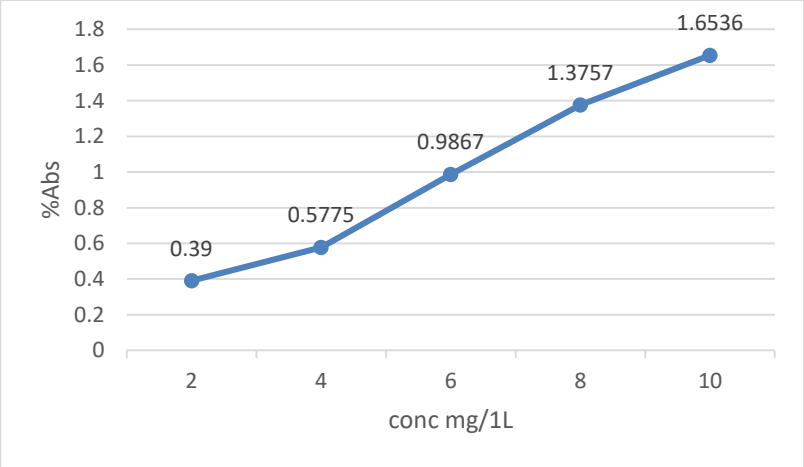

Fig 5. Plotting calibration curve

FTIR Analysis

Infrared spectroscopy is a used to identify the functional groups present and to obtain information on the nature of interactions between adsorbate and adsorbent. FTIR shows the change in properties of the surface on addition of crystal violet dye.

Table 2 FUNCTIONAL GROUPS PRESENT (before)

Alkyl C-H Stretch
Carboxylic Acid O-H Stretch
Ketone C=O Stretch
Aromatic C=C Bending
Aromatic C=C Bending
NO2 (aromatic)
C-O stretch, carboxylic acids
phosphine oxides

Table 3 FUNCTIONAL GROUPS PRESENT (after)

Alkenyl C-H Stretch
Phosphines P-H stretch
Anhydrides C=O stretch
Amides N-H stretch
carboxylic acids O-H stretch
nitro groups NO2 (aliphatic)
phosphine oxides P=O
Aromatics C-H bend (para)

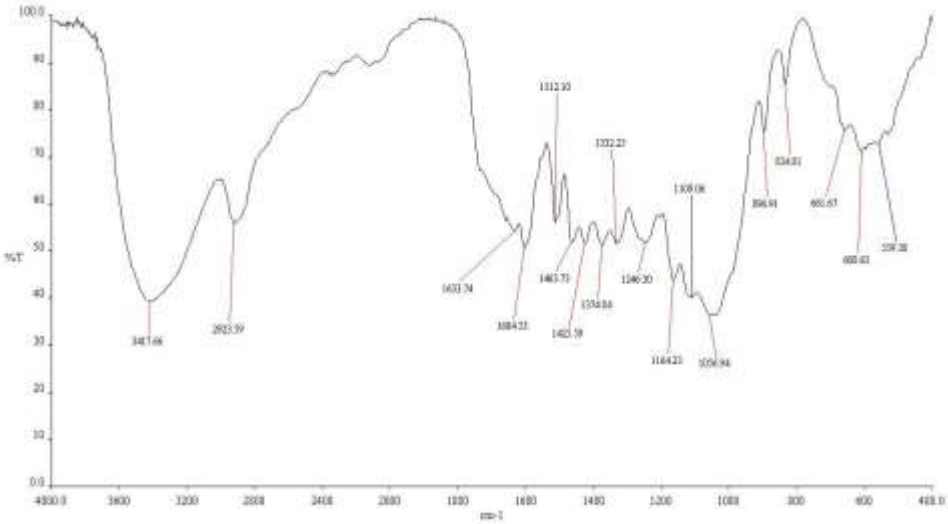

Fig. 6 FTIR Analysis before dye removal

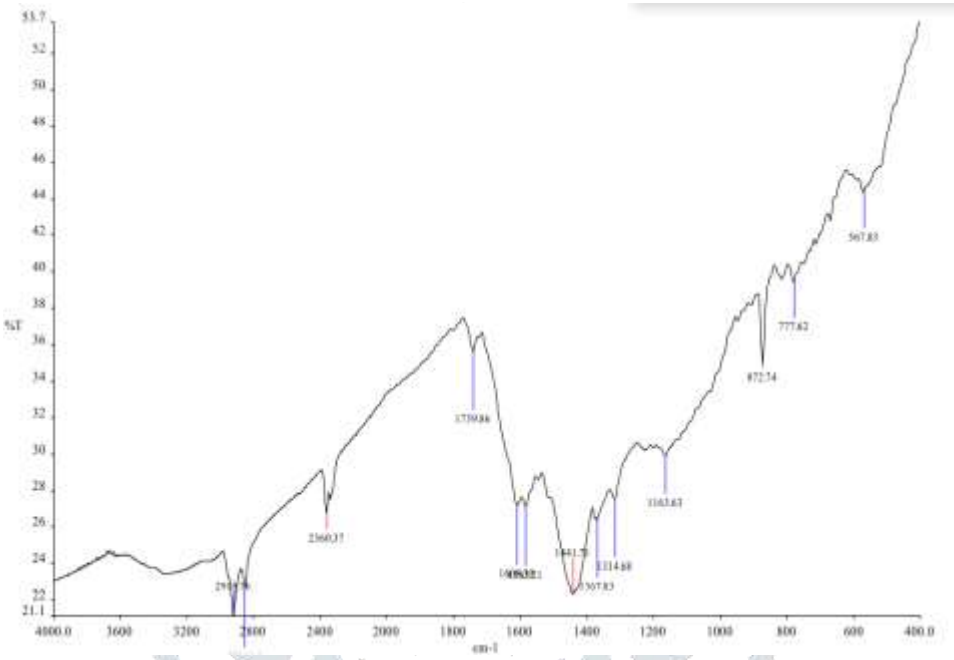

Fig. 7 FTIR Analysis after dye removal

SEM Analysis

Na2CO3 treated bamboo chips are shown in Fig. 8. When we compare the image of raw bamboo pieces and Na_2CO_3 treated bamboo pieces we can clearly see that Na_2CO_3 treated bamboo pieces got more uneven, porous and rough surface. The surface became porous and had cavity-like structure, which is heterogeneous and provides a very large surface area for adsorption. Thus it is confirmed that surface texture of bamboo changed when we treated it with sodium carbonate. The rough surface with ridges like structure shows the presence of macropores which are responsible for the high surface area. After adsorption we can see smooth surface finish. This is because the dye crystal violet molecules were adsorbed and trapped on its surface of it. All porous cavity was filled up by CV during the adsorption.

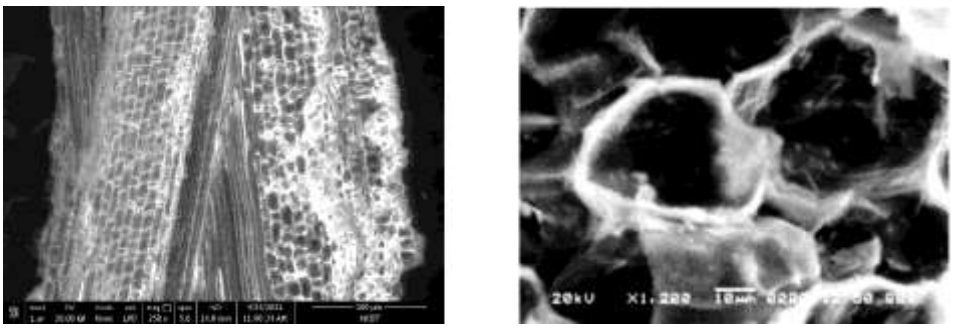

Fig. 8 SEM Analysis

Effect of Contact Time

The effect of contact time can be seen from the figure for the dyes. It is clear that the amount of adsorption is rapid in the early stages and the slows down in later stages till saturation is allowed. The final dye concentration did not vary much after 2 hours from the start of adsorption process which shows that equilibrium was achieved after 2 hours (120 min). Due to saturation of the active site, further adsorption did not take place.

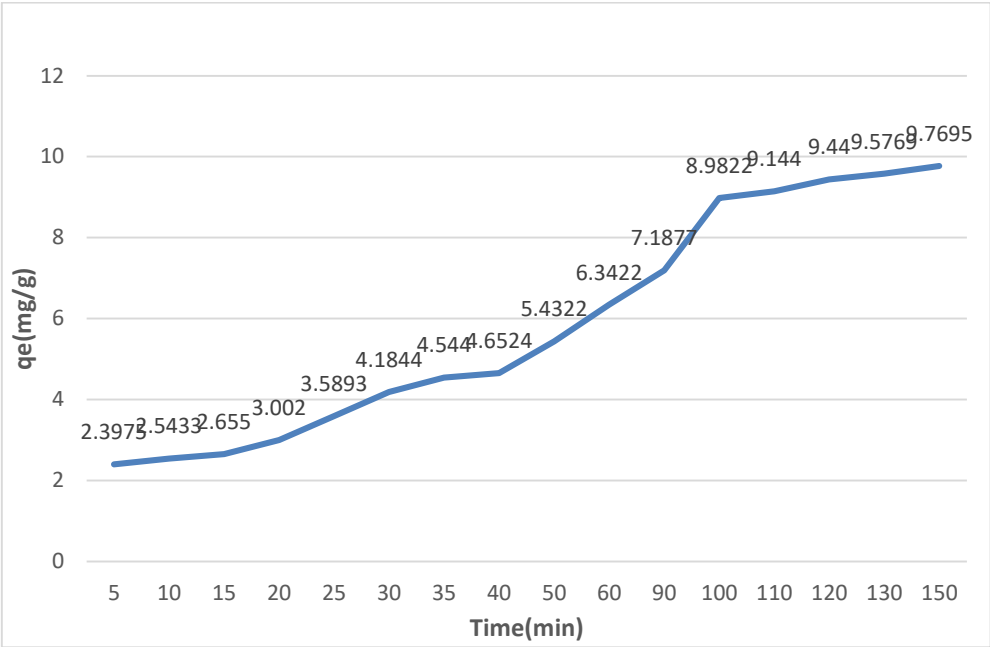

Fig. 9 Effect of Contact Time

Effect of pH

The effects of initial pH on dye solution of three dyes removal were observed by varying the pHs 4, 6,8,10. At pH - 4 the dye removal was found to be minimum and it increased as initial pH of dye solutions were increased. It was maximum at pH = 10 as seen in the graph of qe Vs time. With increase in negative charges on the surface, adsorption of CV dye which is a cationic dye would obviously increase. So as the pH increases, more negatively charged surface was available thus increasing the dye removal.

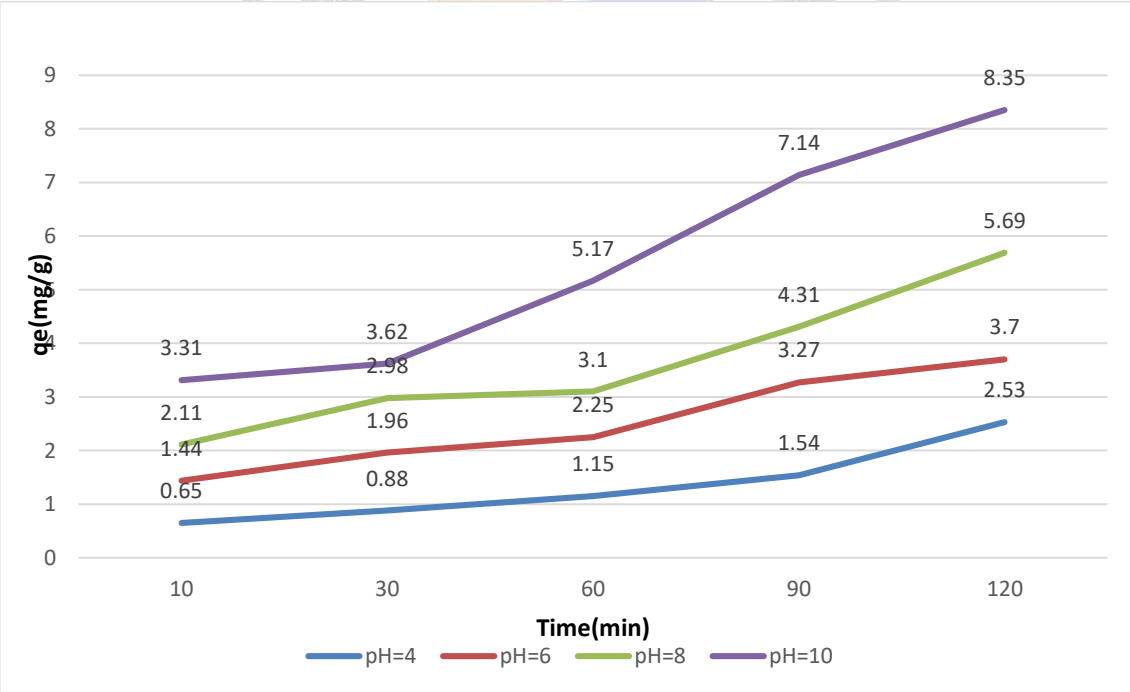

Fig. 10 Effect of pH

Effect of Initial CV Concentration

Results show that when we increase the adsorbate dose, the adsorption increases, optimum dose for the dye being 10g/1L. Though we find that at 15mg/1L, there is a a little increase in qe value but this is almost same as we get in 10 mg/1L adsorbent dosage so opting for 15mg/1L will be expensive and create much loss of adsorbent. So initial concentration of 10mg/L is optimum and cost effective.

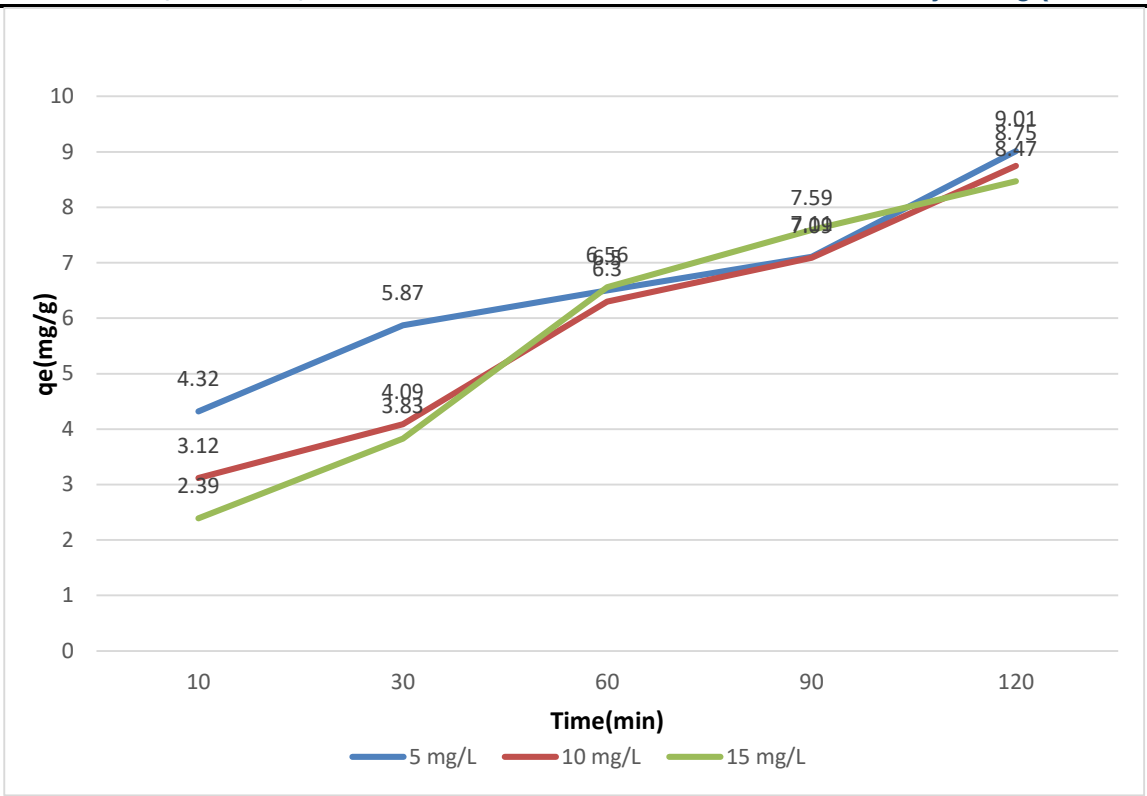

Fig. 11 Effect of Initial CV Concentration

Effect of Adsorbent Dose

Effect of adsorbent dose was studied with adsorbent dose varying in the range of 40 mg/150ml, 60mg/150ml, 80mg/150ml, 100mg/150ml and 150 mg/150ml. We take 100mg/150ml as the optimum dose of adsorbent as with concentration 150mg/150ml we find nearly same adsorption so using this dose will only be cost inefficient and loss of NCB.

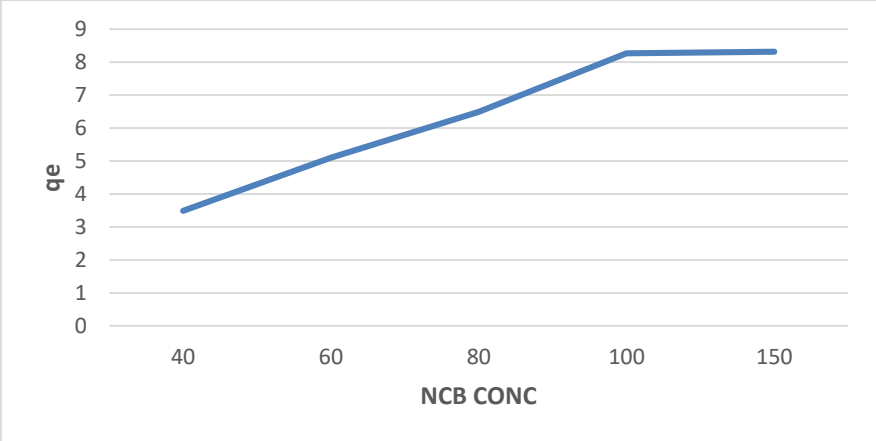

Fig. 12 Effect of Adsorbent Dose

Adsorption Kinetics

We observe that for first order equation qe value calculated corresponds well with the experimental value; also the R2 value is very high. For the second order the calculated qe value differs very much from the experimental value. The R2 value is also very less as compared to the pseudo-first-order model. So we can conclude that pseudo-first-order is the best fitting kinetic model.

Table 4 PSEUDO 1st Order

Co (mg/L)	Qe,exp (mg/g)	Qe,cal(mg/g)	K1(1/min)	R2
10	9.8	13.40	0.029	0.973

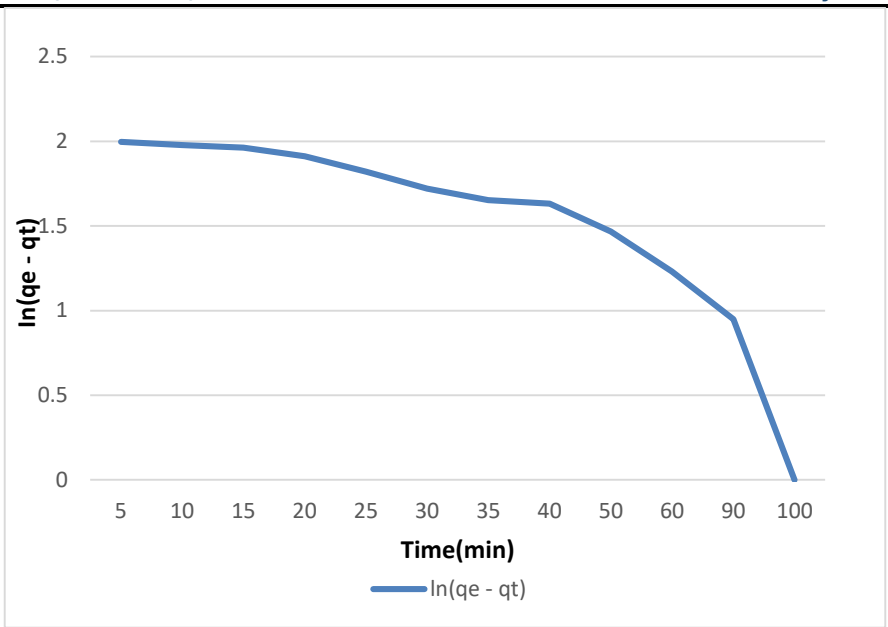

Fig. 13 PSEUDO 1st Order

Table 5 PSEUDO 2nd Order

Co (mg/L)	Qe,exp (mg/g)	Qe,cal(mg/g)	K1(1/min)	R2
10	9.8	0.25	0.164	0.752

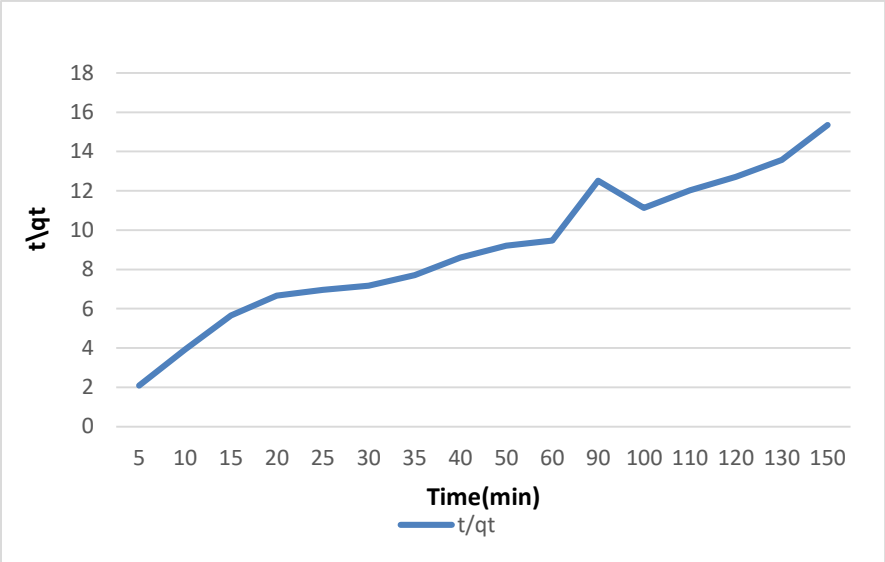

Fig. 14 PSEUDO 2nd Order

VI. Conclusion

FT-IR spectra show minute change in the surface properties of NCB after adsorption when compared to that of before adsorption. Adsorption is observed to increase with contact time. Initially the increase in adsorption is rapid because of lots of free sites for the adsorption. Adsorption decreases at later stages until the saturation is achieved due to saturation of active sites. The optimum contact time for equilibrium was found to be around 2 hours. Adsorption increases with increasing pH. The adsorption of cationic dye is majorly influenced by negative charges in the solution which is in turn influenced by the solution pH. At pH=4 there is more positive charge in the solution so less adsorption whereas at pH=10 there is more negative charges which increases adsorption of Crystal Violet. Maximum adsorption was found to happen at pH=10. When adsorbent dose increases adsorption increases due to the availability of free sites for adsorption. 100mg/100ml concentration of NCB is taken as the optimum adsorbate dose. As we increase adsorbate dose more than the optimum the increase in adsorption is very less and it becomes cost ineffective leading to loss of NCB. The correlation coefficient, R2 value and correspondence with experimental qe value favors pseudo 1st order and thus the adsorption is assumed to be pseudo-first order with k1 = -029 and R2= .973. Moreover the qe value calculated was also almost near to the experimental value.

VII. References

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