Removal of Toxic Crystal Violet dye from aqueous solution using water insoluble β–Cyclodextrin polymers

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Abstract: In this study, the different organic acids such as Tartaric Acid (TA), Citric Acid (CA), and Malic Acid (MA) were cross linked with β–Cyclodextrin (β-CD) to synthesize water insoluble β–Cyclodextrin polymers like CA/β-CD, TA/β-CD and MA/β-CD. The obtained polymers were characterized by different advanced analytical techniques such as FTIR, SEM and UV-Vis spectrophotometer. The adsorption technique was used to remove the ye Crystal Violet (CV) from aqueous solutions. The adsorption study was carried out in different conditions like pH, adsorbent mass, Dye concentration, temperature, contact time, adsorption isotherm, kinetics and thermodynamics. The adsorbent CA/β-CD shows highest adsorption of CV dye in all the conditions, because it contains high number of carboxyl groups. The negatively charged carboxyl ions of CA/β-CD attract positively charged CV dye electrostatically and removed CV from aqueous media with the efficiency of 94%. Therefore the results showed that the water insoluble polymers based on cyclodextrin could be used for the removal of dyes from aqueous media and could serve as alternatives for expensive adsorbents.

Keywords: Crystal Violet, β–Cyclodextrin, Citric Acid (CA), Tartaric Acid (TA) and Malic Acid (MA)

1.Introduction:

The water is very much essential for all the living systems like humans, animals and plants etc. but the quality of water is decreases every day due to pollution of fresh water from industries and human activities. One of the main water pollutant is dye which is used in large quantity by industry and released the same to water as industrial waste water. Therefore it is very much essential to increase the quality of water by decreasing water pollution. The water pollution was reduced by different process like photodegradation, adsorption and chemical reactions.

Crystal Violet is also known as gentian violet or methyl violet. Crystal violet or methyl violet is dye first synthesized at 1861. When CV dye dissolved in water it has blue-violet colour and shows the maximum absorbance at wavelength 590nm. The intensity of the dye colour varies with pH, the yellow colour forms due to positive charges on three nitrogen atoms and two of them are protonated. Among three two nitrogen atoms responsible for the green color. Crystal violet used in different applications like textile dye, dye paper, ink for printing, pen and printers. And also the CV used as coloring agent in fertilizers, leather and detergents.

Cyclodextrins are made up of large number of oligosaccharides containing six alpha cyclodextrins, seven beta cyclodextrins or eight gamma cyclodextrins anhydrous d-glucopyranose units. The scientist Cyclodextrins Villiers observed that the Cyclodextrins have special character, which have hydrophobic and glycosidic oxygens and protons of methane and they can able to form complexes with adsorbents [1-3]. The external surface of the Cyclodextrins is hydrophilic for the presence of hydroxyl groups present in the cavity. Different Cyclodextrins derivatives can be prepared by substituting the hydroxyl group, and these derivatives can used in different fields [4-8]. Adsorption technique was very efficient for the wastewater treatment and cyclodextrin-based polymers were used as adsorbent which are very cost effective [9, 10].

In this study β-Cyclodextrin (β-CD) was combine with different organic acids like tartaric acid (TA), Citric acid (CA) and Malic Acid (MA) which become water insoluble polymer and used for CV removal from aqueous solution. β-Cyclodextrin are porous, inexpensive materials with more surface area. β-Cyclodextrin are non toxic, highly compatible with high stability. The -OH groups of β-Cyclodextrin (β-CD) are responsible for the good combination of organic acids. The β-CD was used for the removal of crystal violet dye, the efficiency of the β-CD was increased by the process of functionalization with large area and large porosity. Therefore this is the first time that the β-Cyclodextrin and organic acids combination carried out and use for the removal of crystal violet from aqueous solution.

2.Materials and Methods:

The following chemicals were procured from SD fine (India) and used as it is. β-CD was 99+% pure, Citric Acid (CA) was 98+% pure, Tartaric Acid (TA) was 98+% pure, Malic Acid was 99+% pure, Crystal Violet (CV) was 95+% pure. The crystal violet solution was dissolve in distilled water for the production of 1000 mg L^{-1} concentration. Adjustment of P^H was undertaken using 0.1 M HCl and 0.1 M NaOH.

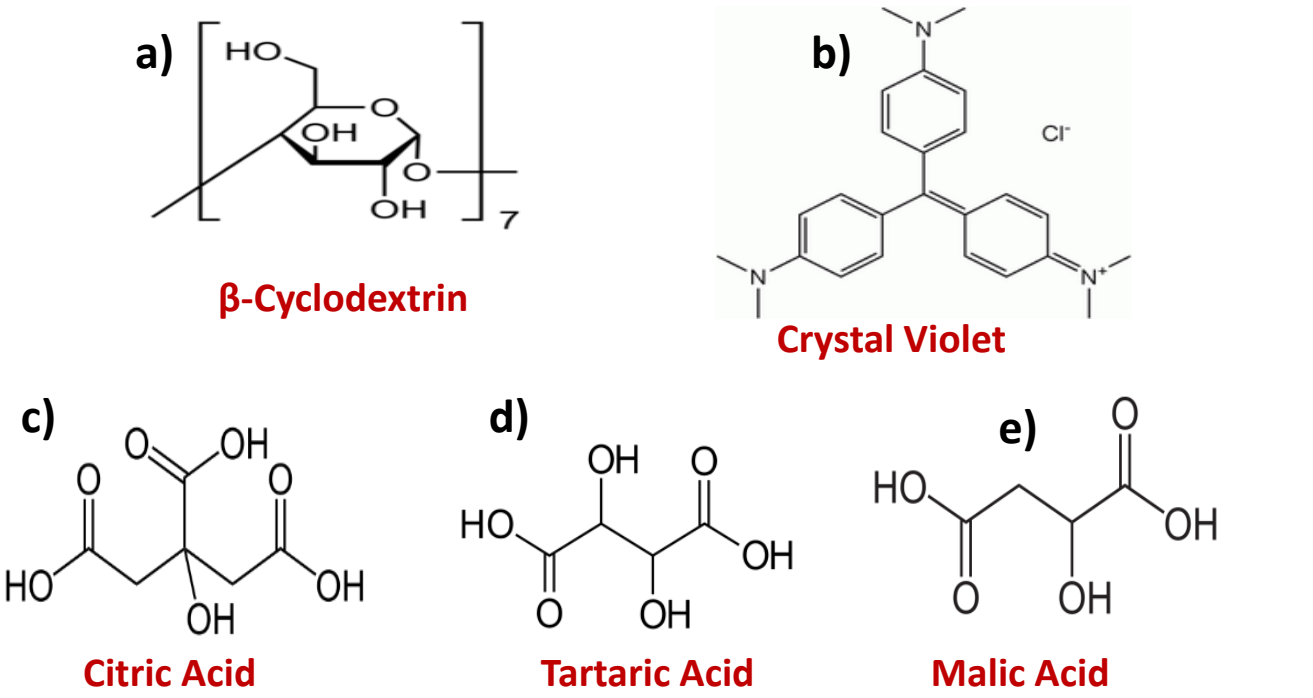

Figure1: Structural formula of (a) β-Cyclodextrin (β-CD), (b) Crystal Violet (CV), (c) Citric Acid (CA), (d) Tartaric Acid (TA) and (e) Malic Acid.

3.Synthesis of Beta-Cyclodextrin (β-CD) based water insoluble polymers:

3.1.Synthesis of Citric acid Beta-Cyclodextrin (CA/β-CD) water insoluble polymer:

In a typical synthesis, 135 mL of distilled water was taken in a 800 mL beaker, then 3 g of anhydrous Citric acid, 6 g of β-CD and 1.5 g of KH_2PO_4 were added and stirred the mixture to get homogeneous solution. Then the above said beaker kept in an oven to dry at the temperature of 140 ^oC for the period of 4 hours without stir. The product (7.02 g, 66.86% yield) obtained was cooled down to room temperature, soak with above 500 ml distilled water for nearly 5 times, filtered and dried at 50 ^oC. The final product was characterized with different advanced analytical techniques.

3.2. Synthesis of Malic acid Beta-Cyclodextrin (MA/β-CD) water insoluble polymer:

In a typical synthesis, Copolymerisation of Beta Cyclodextrin and Malic acid was done successfully. In details, in a solution of 3.82g Malic acid (28 mmol) and 3.6g $Na_2HPO_4.12H_2O$ (10 mmol) in 10ml of distilled water and 6g of CD (4.75 mmol) was added and heated for the duration of one hour at the temperature 110 ^oC. The mixture of powder was taken in petridish and dried at 180 ^oC for the duration of 120 min. The product was weighed, powdered and subsequently characterized.

3.3. Synthesis of tartaric acid Beta-Cyclodextrin (TA/β-CD) water insoluble polymer:

In a typical synthesis, 2.34g DL-Tartaric acid, 6 g of β-CD, 0.75 g of KH_2PO_4 and 135 mL of ultrapure water were mixed in an 800 mL beaker and stirred to achieve homogeneity. Then the above said beaker kept in an oven to dry at the temperature of 140 ^oC for the period of 3.5 hours without stir. The product obtained was cooled down to room temperature, soak with above 500 ml distilled water for nearly 5 times, filtered and dried at 50 ^oC. The final product was characterized with different advanced analytical techniques.

4. Adsorption experiments

The aqueous solution of crystal violet with the concentration of 10-50 mgL^{-1} was used for the study of adsorption process. The 20 mL of a dye solution (10 mgL^{-1}) was taken in a 100 mL of conical flask and 10-120 mg of CA/β-CD, TA/β-CD and MA/β-CD, were added. The above solution was kept in an incubator and shaked for the duration of 1 hour. In this study the different properties like adsorbent dosage, pH effect, initial dye concentration, effect of temperature and contact time. The supernatant solution was taken and analyzed using UV-vis spectrophotometer.

The removal efficiency R(%) of crystal violet dye analyzed using equation 1

$$R=\frac{C_o-C_e}{C_o} X\ 100\% \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where C_o is initial and C_e (mgL^{-1}) is final concentration of CV solutions, respectively.

The adsorbed dye concentration q_e (mgg^{-1}) at equilibrium can calculated by equation 2

$$q_e=\frac{C_o-C_e}{M} X\ V \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where C_o initial concentration at time (t = 0) and C_t (mgL^{-1}) is the concentrations of dye at any time during the test (t), respectively.

5.Characterization techniques:

5.1.Surface Morphology analysis:

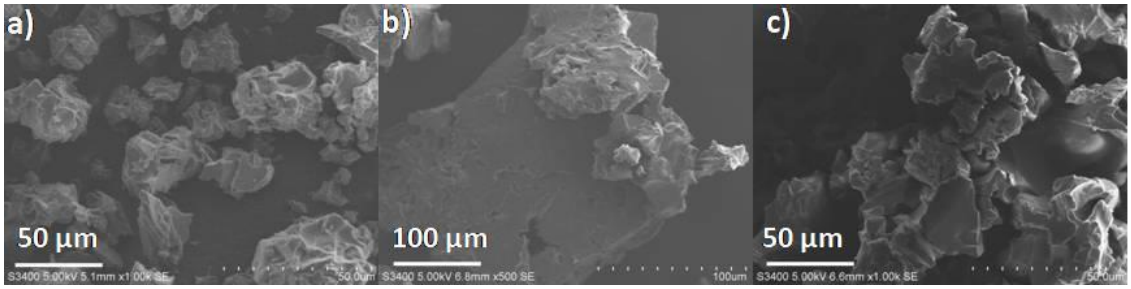

Figure 2: Scanning Electron Microscope images of (a) CA/β-CD and (b, c) CA/β-CD after CV dye adsorption in different magnifications.

The analysis of CA/β-CD surface morphology before and after adsorption was carried out by scanning Electron Microscope and showed in figure 2. Analysis was done for the samples with different

magnifications with different areas. Figure 2(a) shows the surface morphology of CA/β-CD in the range of 50 µm structure. Figure 2(b, c) shows the surface morphology of CA/β-CD after adsorption in the range of 100 µm and 50 µm structure, and it was observed that the material has some porous like structures also in its surface, which was useful for the adsorption experiments.

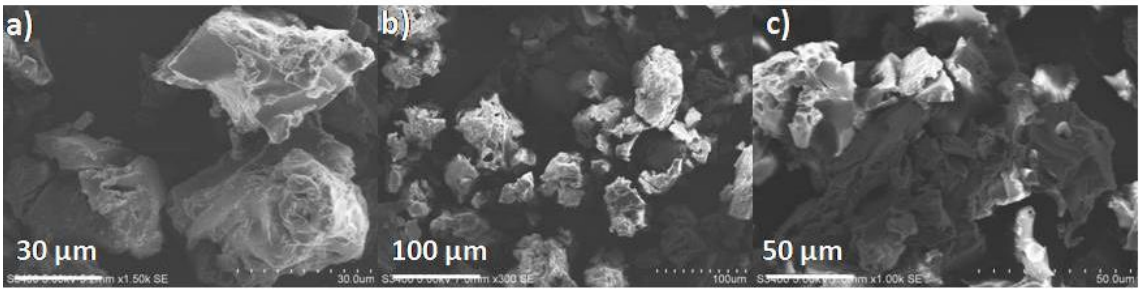

Figure 3: Scanning Electron Microscope images of (a) TA/β-CD and (b, c) TA/β-CD after CV dye adsorption in different magnifications.

The analysis of TA/β-CD surface morphology before and after adsorption was carried out by scanning Electron Microscope and showed in figure 3. Analysis was done for the samples with different magnifications with different areas. Figure 3(a) shows the surface morphology of TA/β-CD in the range of 30 µm in different area of sample and observed that the TA/β-CD has porous like structure in it's morphology. Figure 3(b, c) shows the surface morphology of tartaric acid in the range of 100 µm and 50 µm with some more porous structure in it's structure. It was observed from SEM images that the material has some porous like structures also in its surface, which was useful for the adsorption experiments.

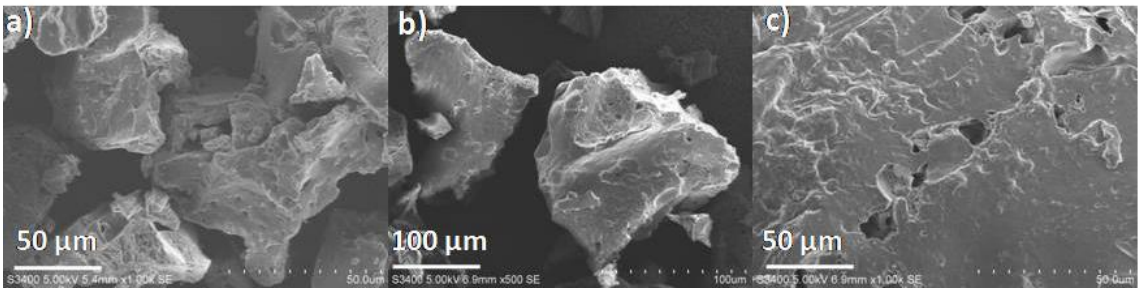

Figure 4: Scanning Electron Microscope images of (a) MA/β-CD and (b, c) MA/β-CD after CV dye adsorption in different magnifications

The analysis of MA/β-CD surface morphology before and after adsorption was carried out by scanning Electron Microscope and showed in figure 4. Analysis was done for the samples with different magnifications with different areas. Figure 4(a) shows the surface morphology of MA/β-CD in the range of 50 µm with porous like structure. Figure 4(b) and 4(c) shows the surface morphology of MA/β-CD in the range of 100 and 50 µm with the surface adsorbed by Crystal violet dye containing different numbers of

hole in it's structure. It was observed from SEM images that the material has some porous like structures also in its surface, which was useful for the adsorption experiments.

5.2.Functional Group Analysis:

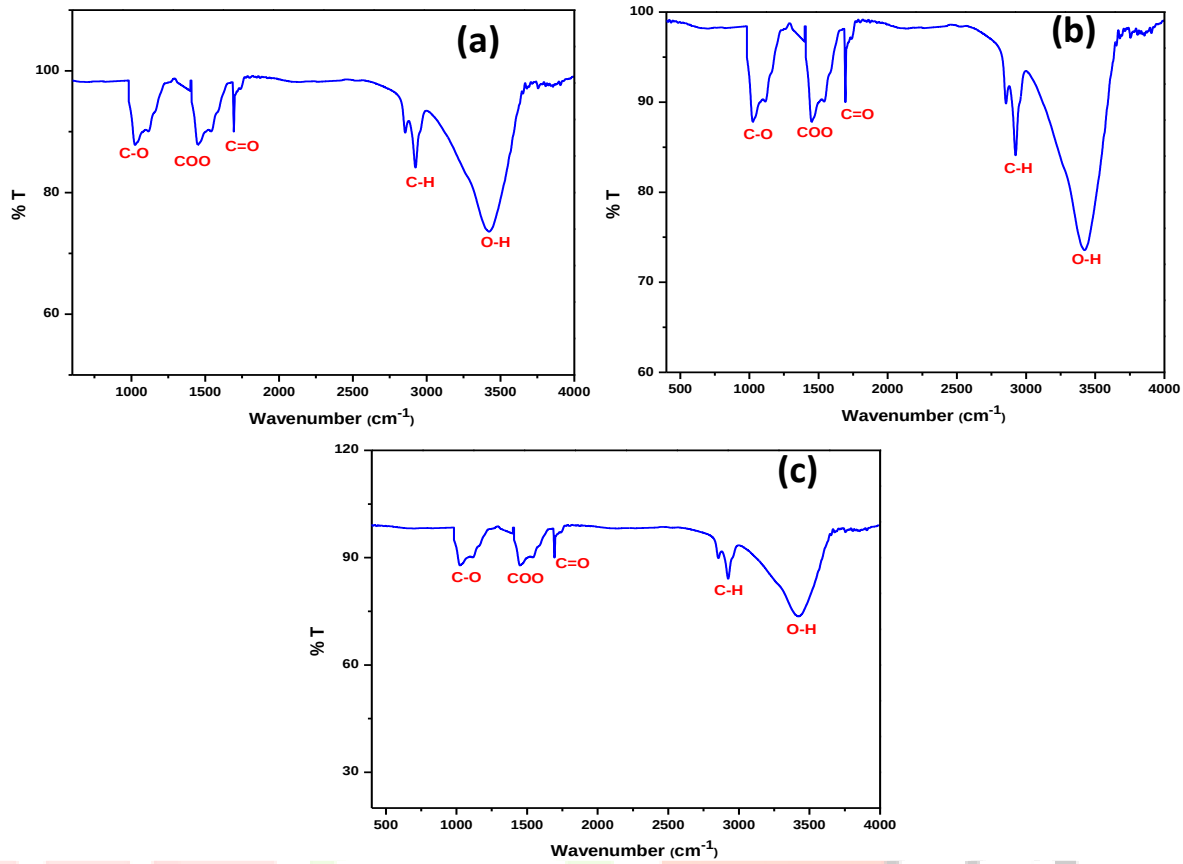

Figure 5: FTIR spectra of (a) CA/β-CD water insoluble polymer (b) TA/β-CD water insoluble polymer and (c) MA/β-CD water insoluble polymer after adsorption of CV dye

The functional group analysis of CA/β-CD was characterized by FTIR analysis and it is as shown in figure 5a. It was observed that the absorption at 3800 to 3200 cm^{-1} corresponds to the –OH groups, 2900 cm^{-1} corresponds to the –CH groups, 1750 cm^{-1} corresponds to the C=O groups of citric acid. Further the sharp absorption at 1400 cm^{-1} corresponds to the COOH group and 1090-1200 cm^{-1} corresponds to the C-O groups of citric acid and beta-cyclodextrin. The functional group analysis of TA/β-CD was characterized by FTIR analysis and it is as shown in figure 5b. It was observed that the absorption at 3750 to 3150 cm^{-1} corresponds to the –OH groups, 2850 cm^{-1} corresponds to the –CH groups, 1760 cm^{-1} corresponds to the C=O groups of tartaric acid. Further the sharp absorption of IR radiation at wave number region 1460 cm^{-1} corresponds to the COOH group, 1100-1250 cm^{-1} corresponds to the C-O groups of tartaric acid and beta-cyclodextrin. The functional group analysis of MA/β-CD was characterized by FTIR analysis and it is as shown in figure 7. It was observed that the absorption at 3850 to 3170 cm^{-1} corresponds to the –OH groups, 2870 cm^{-1} corresponds to the –CH groups, 1780 cm^{-1} corresponds to the C=O groups. Further the sharp

absorption at 1440 cm^{-1} corresponds to the COOH group 1180-1230 cm^{-1} corresponds to the C-O groups of malic acid and beta-cyclodextrin.

6.Results and Discussion:

6.1.Crystal Violet (CV) Removal studies by adsorption:

6.1.1.Effect of adsorbents:

The CA/β-CD has 94% removal efficiency which is shown in figure 6. The dye removal efficiency of is high due to high surface carboxyl groups. The more adsorption of crystal violet dye on CA/β-CD material due to positive charge which leads to high electrostatic attraction [11]. Number of carboxyl groups are more in CA/β-CD due to high electrostatic attraction.

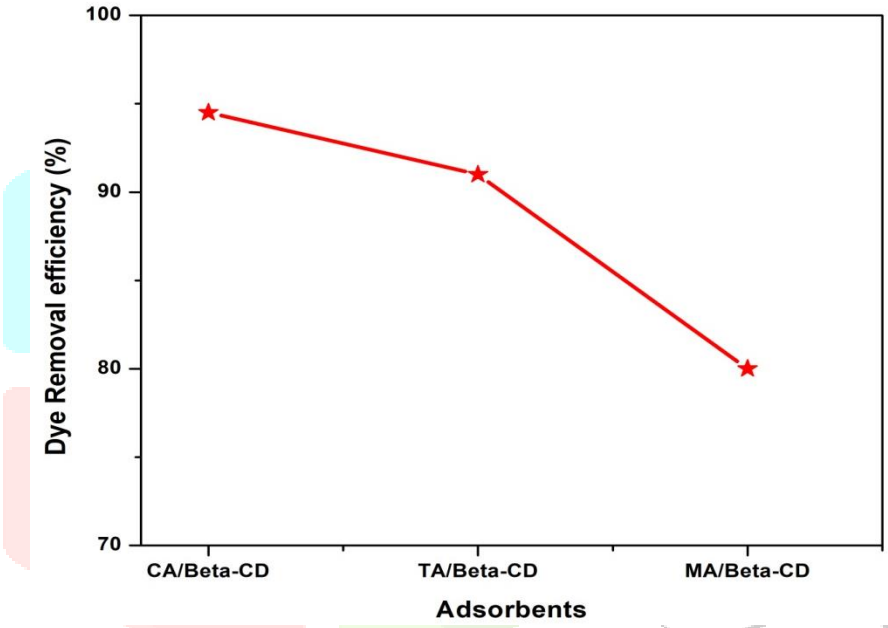

Figure 6. Effect of Adsorbent dosage on dye removal efficiency

6.1.2.Effect of pH

In this experiment, we used various pH range solutions. Different pH was adjusted using HCl (0.1 N) and NaOH (0.1 N) solutions. 100 mg of adsorbent was added to each flask containing 20 ml of CV dye solution and shaken until equilibrium conditions were reached. Similarly, the color intensity of the CV solution decreased sharply when the pH was below 4 and above 7. This large decrease in absorbance and color indicates instability when the CV is below pH 4 and above pH 7. The effect of pH value is shown in Table 1.

Table 1: Effect of pH on CV removal efficiency of adsorbents.

pH	Removal efficiency (%)		
	CA/β-CD	TA/β-CD	MA/β-CD
4	85.45	82.64	75.75
5	85.62	85.65	77.32
6	90.36	88.24	78.65
7	94.44	91.45	80.54

The values in Table (1) show that all adsorbents have better removal efficiency at pH 7. In particular, CA / βCD has a high removal efficiency of 94.44% at pH 7, and MA / βCD has a low removal efficiency of only 80.54% at pH 7.

6.1.3. Effect of adsorbent mass.

Figure 7 shows the efficiency of dye removal associated with different doses of adsorbent (10-120 mg). The efficiency of dye removal was slightly increased at doses of 10-90 mg for all materials. The effect of reduced removal efficiency is the rapid aggregation of βCD above 90 mg. Therefore, an optimized dose of 90 mg was used for further experiments.

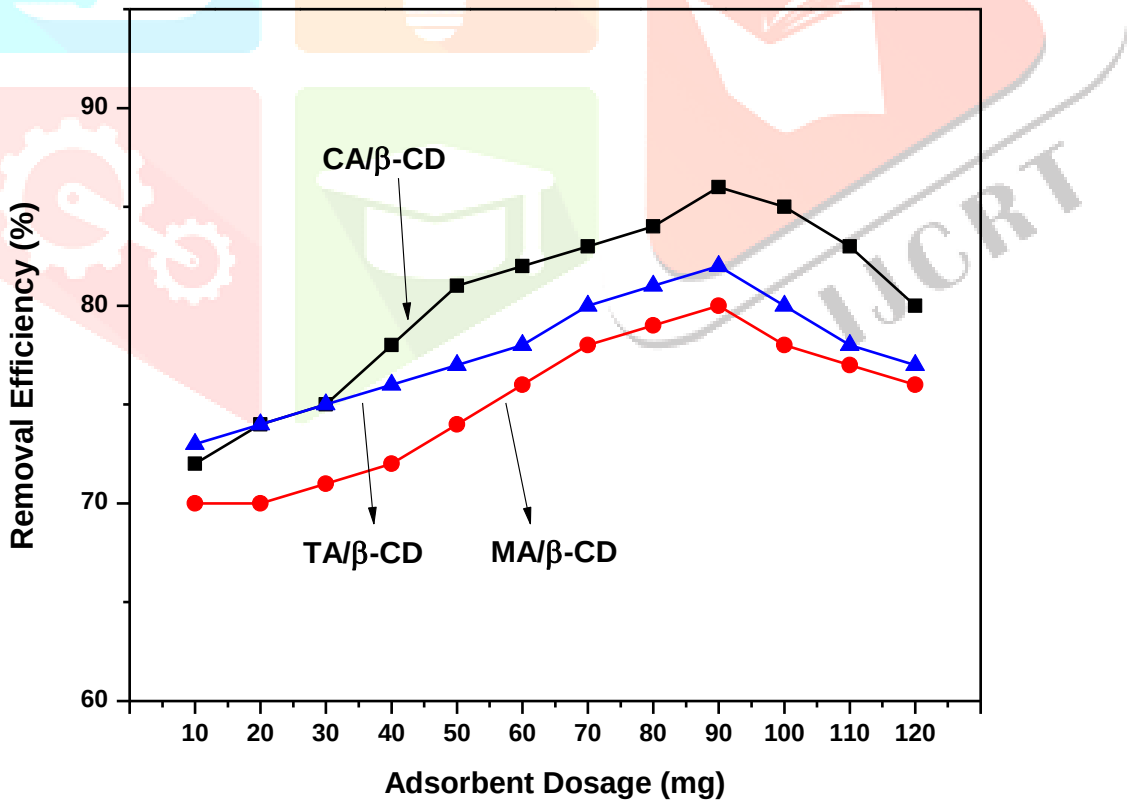

Figure 7: Effect of adsorbent dosage on the Removal efficiency for CV.

6.1.4.Effect of initial dye concentration.

The different concentrations of CV dye were 0, 10, 20, 30, 40, and 50 mg / L. During the experiment, 90 mg of adsorbent was added to 20 ml of different concentrations of CV dye solution and held in the shaker for 1 hour until adsorption equilibrium was reached. The solution was then centrifuged and the supernatant was analyzed with a UV-Vis absorption spectrophotometer. The efficiency of adsorbent removal decreases with increasing dye concentration (Fig. 8). The removal efficiency of all the adsorbents CA / βCD, TA / βCD and MA / βCD produced was high at a dye concentration of 10 mg /L. Also, as the dye concentration increases from 20 to 50 mg / L, the removal efficiency decreases. Decreased removal efficiency due to the unavailability of the adsorbent surface at high dye concentrations for dye adsorption.

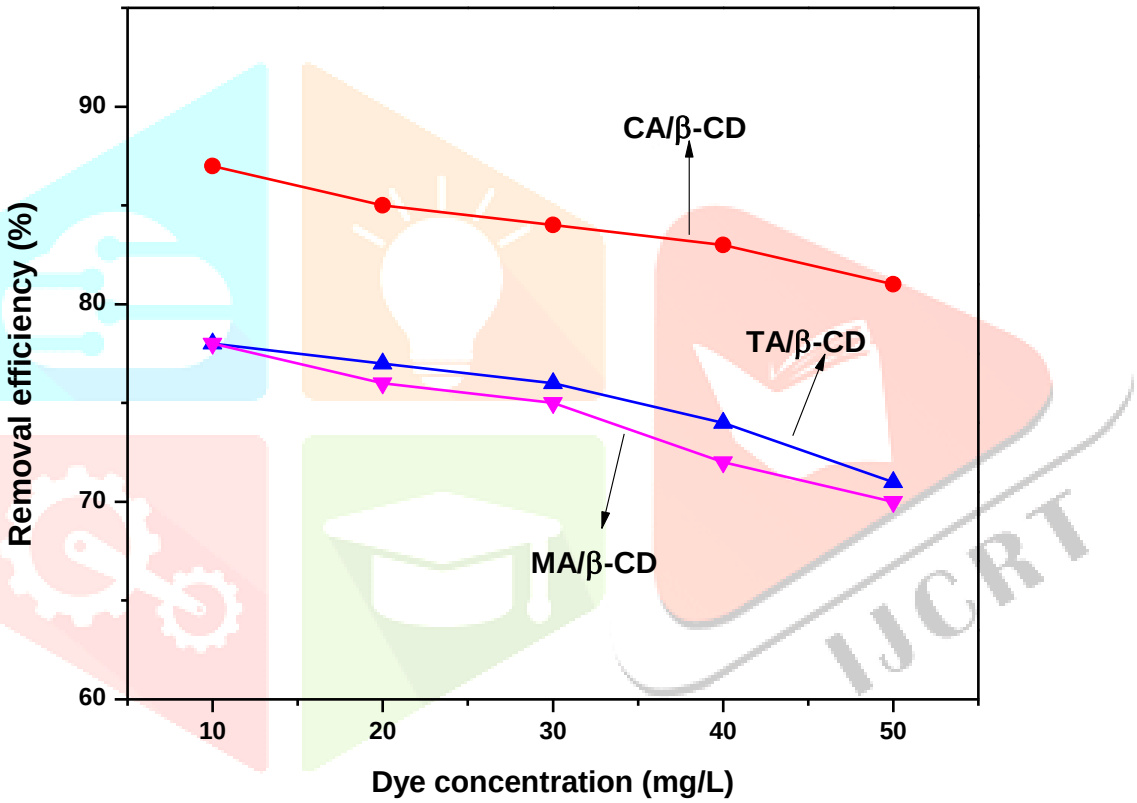

Figure 8: Effect of CV concentration on the removal efficiency.

6.1.5.Effect of temperature

As shown in Fig. 9, the effect of temperature on the efficiency of CV removal by the adsorbent was investigated by changing the temperature from 30 to 60 ° C. The electrostatic attraction between the adsorbent and the adsorbent tends to weaken at high temperatures, so the dye removal efficiency decreases as the temperature rises from 30 ° C to 60 ° C.

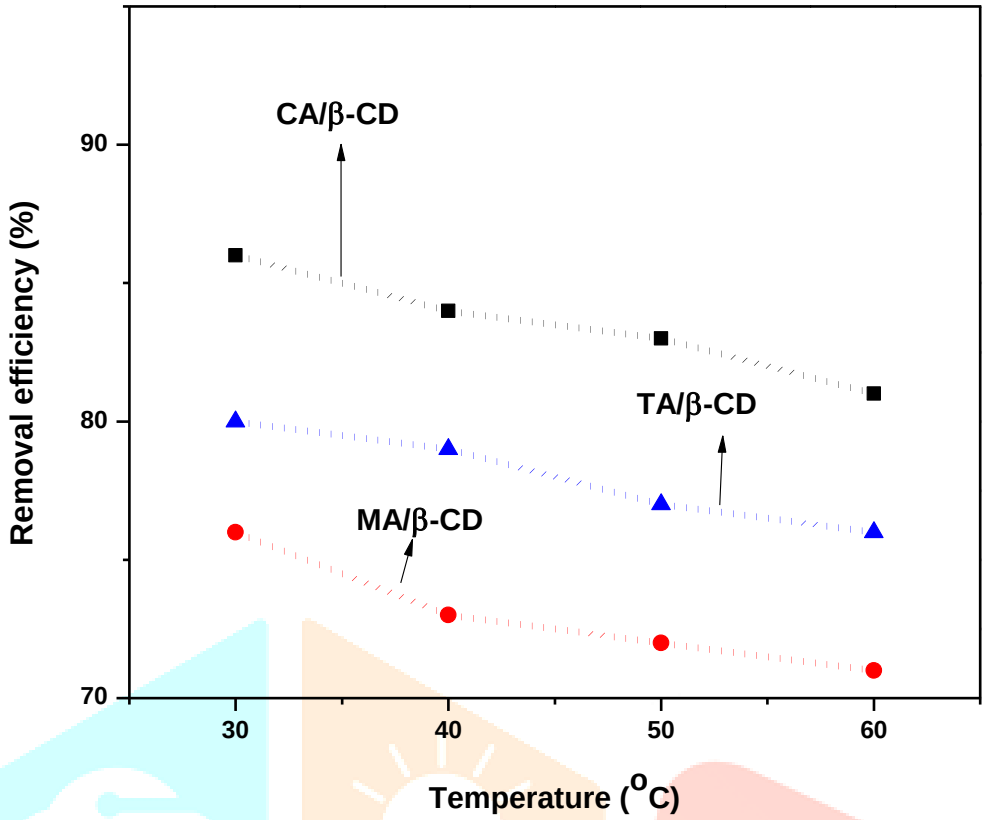

Figure 9: Effect of temperature on the removal efficiency.

6.1.6. Effect of contact time.

Figure 10 shows the efficiency of CV removal as a function of time and the amount of CV adsorbed on the adsorbent. 80 or 78% dye with 90 minutes contact time. The CV adsorption process was significantly faster due to the availability of active centers and the large surface area of the adsorbent. In addition, there is no gravitational force between the adsorbent and the adsorbent, so saturation was reached in 120 minutes of contact time.

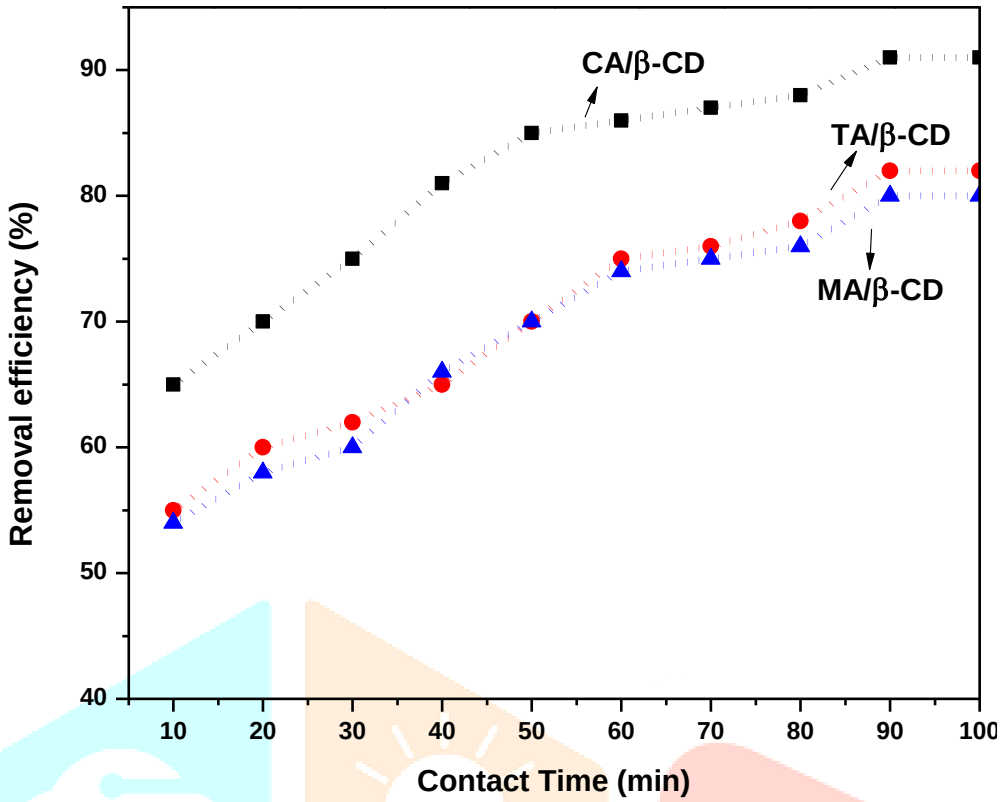

Figure 10: Effect of contact time on the removal efficiency.

6.1.7.Adsorption isotherms:

The interaction between the dye (adsorbent) and the adsorbent can be determined by the adsorption isotherm, that is, Langmuir isotherms and Freundlich isotherms. The uniform or monolayer interaction of the adsorbent on the adsorbent refers to the Langmuir isotherm. Non-uniform or multi-layered interactions of the adsorbent on the adsorbent are Freundlich isotherms.

For Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \dots\dots\dots\dots\dots\dots\dots\dots (3)$$

Where qm (mgg^{-1}) denotes the maximum adsorption capacity of adsorbent and K_L (Lmg^{-1}) denotes Langmuir constant related to the affinity of binding sites and adsorption energy.

For Freundlich isotherm:

$$l_n q_e = l_n K_F + \frac{l_n C_e}{n} \dots\dots\dots\dots\dots (4)$$

Where K_F (mgg^{-1}) and n are the Freundlich constants of adsorption capacity and adsorption tendency respectively.

Figure 11(a, b), shows the adsorption isotherm of CV adsorbed on adsorbents and investigation with experimental data. The observation of higher correlation coefficients for CA/β-CD, TA/β-CD and MA/β-CD were well fitted with Freundlich isotherm. Therefore, CV adsorption on active sites of above adsorbents is a multilayer adsorption process.

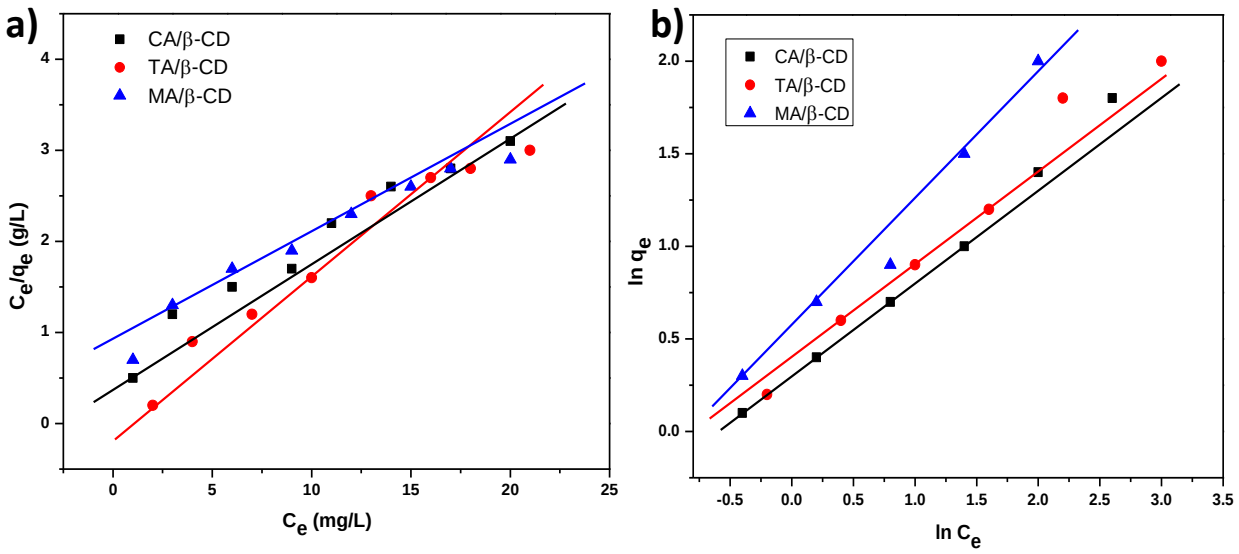

Figure 11: (a) Langmuir adsorption isotherm and (b) Freundlich adsorption isotherm of CA/β-CD, TA/β-CD and MA/β-CD for the adsorption of CV.

6.1.8.Adsorption Kinetic Study:

Batch Kinetic Studies:

Using the unit mass of adsorbent to determine the length of time that the adsorbent is removed from the aqueous solution is a very important parameter for the adsorbent process. The adsorbent concentration in the aqueous solution can be measured at a specific point in time, qt (mgg^{-1}) according to equation (5):

$$q_t = \frac{C_o - C_t}{M} X\ V \ldots\ldots\ldots\ldots\ldots (5)$$

Where C_t (mgL^{-1}) is a concentration of adsorbate in aqueous solution at a certain time t (h).

The following equations were used for fitting the adsorption kinetics:

For pseudo-first-order kinetic model,

$$\log(q_e - q_t) = log q_e - \frac{K_1}{2.303} t \ldots\ldots\ldots\ldots (6)$$

For pseudo-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \dots\dots\dots\dots\dots\dots (7)$$

For intra-particle diffusion:

$$q_t = K_{int} t^{\frac{1}{2}} + C \dots\dots\dots\dots\dots (8)$$

Where K_1 (min^{-1}) is rate constant of pseudo-first-order and K_2 ($g^{-1}mg^{-1}min^{-1}$) is the rate constant of pseudo-second-order adsorption kinetics, respectively.

Equilibrium adsorption capacity q_e and k_2 values were analyzed with axial intercept and gradient values (Fig. 12b). The linear lines explain the relationship between experimental and calculated values with the masses of various CVs and adsorbents.

The value of k_2 and the equilibrium adsorption capacity q_e were calculated using the intercept and slope of the graph (Figure 12b). The linearity of these graphs shows that the experimental and calculated q_e values at various initial CVs and adsorbent concentrations are in goodagreement. Therefore, the adsorption of CV follows a pseudo-secondary kinetics model.

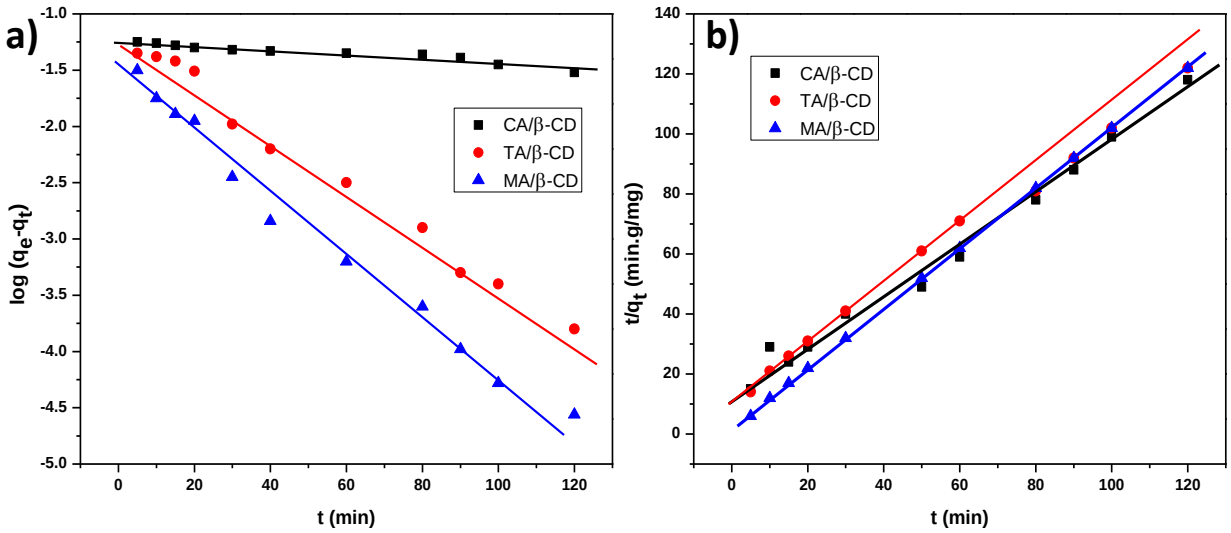

Figure 12: Adsorption kinetic of CV onto CA/β-CD, TA/β-CD and MA/β-CD: (a) Pseudo-first order kinetics, (b) Pseudo-second-order kinetics

6.2. Reusability studies

In addition, adsorbent recycling studies were conducted to evaluate real-time application. Desorption of CVs from the adsorbent was performed by treating them in a shaker with 10 ml of methanol for 30 minutes. The adsorbent was recovered from the mixed solution by centrifugation and drying at 80 ° C.

overnight. The recovered adsorbent was reused to remove CV and the efficiency was calculated using UV-vis spectroscopy (Figure 13). The efficiency of CV removal slowly declined with the number of recycles. In the current study, the adsorbent can be used for up to 5 cycles with a removal efficiency of 7090%. Therefore, adsorbents can be a potential, efficient and inexpensive material for removing CV from contaminated water in real time.

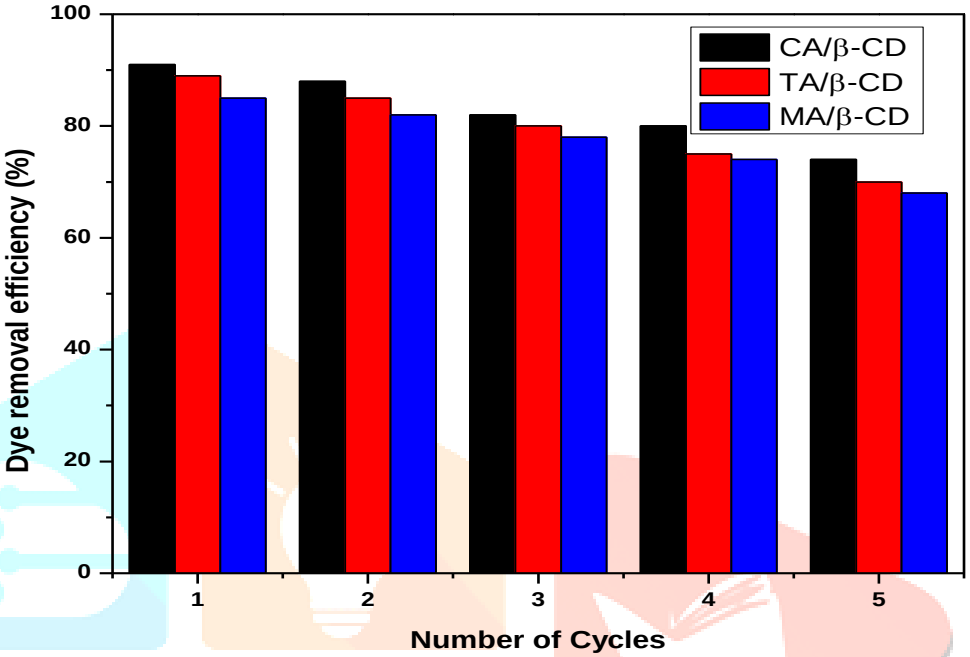

Figure 13: Reusability of adsorbents, CA/β-CD, TA/β-CD and MA/β-CD.

7. A possible mechanism of CV adsorption onto adsorbents:

The dye removal efficiency of the CA / βCD adsorbent was higher than that of TA / βCD and MA / βCD. Therefore, citric acid plays an important role in removing CV from aqueous solutions. CV removal from aqueous solution is 91% for CA / βCD, 80% for TA / βCD and 78% for MA / βCD. The maximum adsorption capacity was obtained by Langmuir isotherm modeling. This indicates that CA / βCD has a high adsorption capacity compared to other adsorbents. In addition, the removal process assumes that electrostatic attraction attracts the negative charge on the CA / βCD surface to the positive charge on the CV dye. However, citric acid has more carboxyl groups (negatively charged ions) that can attract positively charged CV dyes more efficiently. High removal efficiency and adsorption capacity of CA / βCD have been achieved compared to TA / βCD and MA / βCD. CV also contains tertiary amines. However, the modified CA / βCD contains more OH groups. Therefore, the designed adsorbent selectively removes cationic dyes.

Conclusion:

The different organic acids such as Citric Acid (CA), Tartaric Acid (TA) and Malic Acid (MA) were cross linked with β–Cyclodextrin to synthesize water insoluble β–Cyclodextrin (β-CD) polymers like CA/β-CD, TA/β-CD and MA/β-CD. The obtained polymers were characterized by different advanced analytical techniques. The synthesized polymers were used to remove CV dye from aqueous solutions through adsorption. The adsorption study was carried out in different conditions and optimized conditions were investigated for best adsorption of dyes at pH=7, adsorbent mass=90 mg, Dye concentration = 10 mg/L, temperature = 30 ºC, contact time 10 to 80 minute, adsorption isotherm is Freundlich isotherm, kinetics is pseudo second order and thermodynamics. The adsorbent CA/β-CD shows highest adsorption of CV dye in all the conditions, because it contains high number of carboxyl groups. The negatively charged carboxyl ions of CA/β-CD attract positively charged CV dye electrostatically and removed CV from aqueous media with the efficiency of 94%. Therefore the results showed that the water insoluble polymers based on cyclodextrin could be used for the removal of dyes from aqueous media and could serve as alternatives for expensive adsorbents.

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