

Study of Tetracarboxyphenylporphyrin Covalently Bound to Silica in the Removal of Crystal Violet from Aqueous Solution

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Abstract

In this work, the Tetracarboxyphenylporphyrin Covalently Bound to Silica was used as adsorbent to remove Crystal Violet (CV) from aqueous solution. The immobilization of TCPP chromophores on SiO₂-NH₂ was performed by the sol-gel method. The bond formation was confirmed by the appearance of an amide bond at 1649 and 1539 cm⁻¹ in the FT-IR spectra. The SiO₂-NH₂-TCPP was used as adsorbent for removing Crystal Violet from aqueous solutions. The dye adsorption experiments were carried out by using batch procedure. UV-visible absorption spectroscopy was used to record the adsorption behavior. The pH effects, the contact time and the initial dye concentration were changed to obtain the best experimental conditions. The dye adsorption equilibrium was attained after 60 min of contact time.

Keywords: Tetracarboxyphenylporphyrin, TCPP, Silica, Adsorptive removal, Crystal violet

1. Introduction

It is very essential to remove crystal violet from industrial effluents before it is discarded into wastewater. Crystal Violet (CV), which is a typical cationic dye, has been widely applied in coloring paper, temporary hair colorant, dyeing cottons, and wools. Although not strongly hazardous, it can cause some harmful effects, such as heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans. Molecular structure of Crystal violet dye is shown at Fig1 and The physical and chemical characteristics of crystal violet is presented in table 1[1].

Conventional methods for the removal of crystal violet from waste water include physical-chemical and biological treatment technologies. Among them, adsorption has been found to be superior to other techniques for dye wastewater treatment in terms of cost, simplicity of design, ease of operation and insensitivity to toxic substances. Many adsorbents have been investigated, which include activated carbons, alginate, modified chitosan, functionalized polymeric resins and polymeric hydrogels [2].

Table1. The physical and chemical characteristics of crystal violet and Congo red dyes^a

Generic name	C.I. Basic Violet (10 BV 10)
Color index number	42555
Abbreviation	10 (BV10)
Molecular formula	C ₂₅ H ₃₀ N ₃ Cl
Purity (%)	80
Molecular weight	408
λ_{\max} (nm)	584
Chemical name (IUPAC)	Hexamethylpararosaniline chloride
Solubility in water	16 g/l (25 °C)
pH value	2.5–3.5 (10 g l ⁻¹ , H ₂ O, 20 °C)

^aThe data were obtained from the Merck Chemical Databases

Silica materials are one of the most extensively used adsorbents for trapping pollutants [3-4]. Recently, organic_inorganic hybrid adsorbents have been developed.

Many studies have focused on developing nanostructured materials, particularly ordered organic-inorganic hybrid materials. Silica materials can be readily modified with organic groups such as mercaptopropyl [5], propylamine [6], aminopropyl [7], imidazole[8], cyclam [9], to tune their characteristics for effective removal. In this context, Porphyrins have gained particular interest as a agent for dye removal.

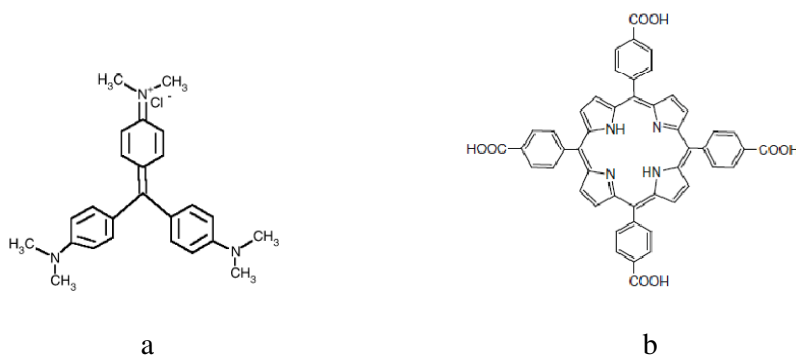


Fig.1. Molecular structure of a) Crystal violet dye, b) TCPP

Hence, current study was devoted to synthesize porphyrin-functionalized silica gel was used to investigate their applications as an adsorbent for the adsorption of crystal violet from aqueous solution. Molecular structure of Tetracarboxyphenylporphyrin is shown at figure 1. Effects of various experimental conditions such as pH, contact time and initial dye concentration, on the adsorption were evaluated. The results are promising for further application of porphyrin-functionalized silica gel as an efficient recyclable adsorbent for dye removal.

2. Results and Discussion

2.1. Characterization of the adsorbent

The immobilization of TCPP chromophores on SiO₂-NH₂ was performed by the sol-gel method. Silica gel immobilizing Tetracarboxyphenylporphyrin (TCPP) chromophore was prepared by the reactions of 3-aminopropyl silica gel (SiO₂-NH₂) with the TCPP. The 3-aminopropyl silica gel (SiO₂-NH₂) was selected as the carrier because of its ability to immobilize the functional groups through a covalent bond. Micrometer-sized SiO₂-NH₂ beads were prepared by reacting silica gel with 3-aminopropyl(triethoxy)silane (H₂N(CH₂)₃Si(OEt)₃). Reaction of SiO₂-NH₂ with TCPP is shown in figure 2.

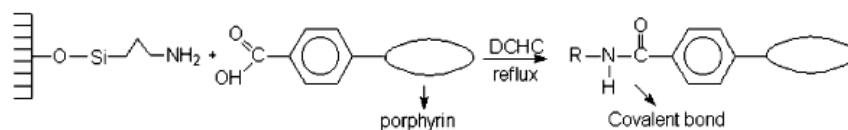


Fig.2. Reaction of SiO₂-NH₂ with TCPP

scanning electron microscopy (SEM) images of $\text{SiO}_2\text{-NH}_2$ and $\text{SiO}_2\text{-NH}_2\text{-TCPP}$ are displayed in figure 3.

The incorporation of TCPP on silica was confirmed by Fourier-Transform infrared (FT-IR) spectroscopy (Fig.4). In the FT-IR spectrum of $\text{SiO}_2\text{-NH}_2$, the peaks around 1633 cm^{-1} were assigned to asymmetric NH_2 stretching ($\nu_{\text{as}}\text{NH}_2$) and NH_2 deformation (δNH_2)[10], and that broad peak at 3300 cm^{-1} could be attributed to the overlap between secondary amine (NH) stretching (νNH) and symmetric NH_2 stretching ($\nu_{\text{s}}\text{NH}_2$). The FT-IR spectrum of $\text{SiO}_2\text{-NH}_2\text{-TCPP}$ revealed peaks at 1713 and 1527 cm^{-1} . These peaks were assigned to the C=O stretching vibration of TCPP and the NH_2 deformation (δNH_2) of the amide group, respectively. The amide group is formed when the carboxyl acid group of TCPP reacts with the amino group on $\text{SiO}_2\text{-NH}_2$. OH stretching of the carboxyl acid group of TCPP (3645 cm^{-1}), and CH_2 stretching (2862 and 2941 cm^{-1}) were also observed in this spectrum.

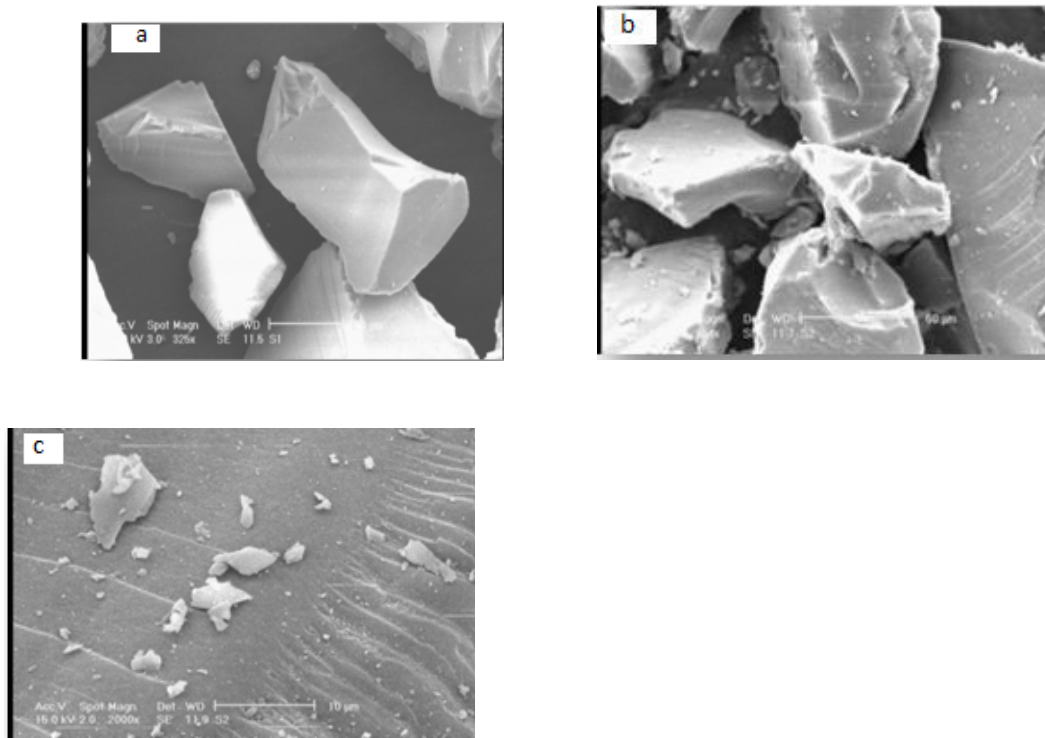


Fig3. SEM images of a) $\text{SiO}_2\text{-NH}_2$ ($\times 325$), b) $\text{SiO}_2\text{-NH}_2\text{-TCPP}$ ($\times 450$) and c) $\text{SiO}_2\text{-NH}_2\text{-TCPP}$ ($\times 2000$)

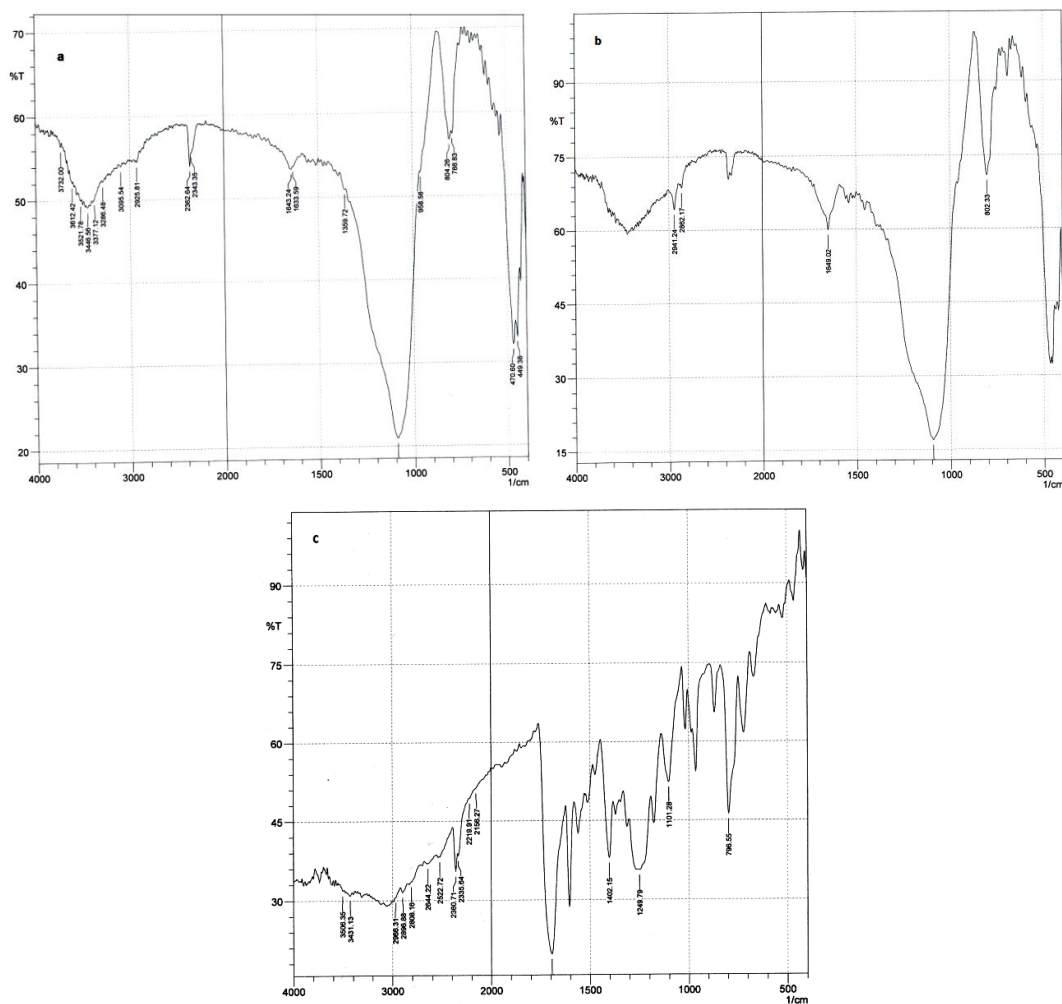


Fig4. FT-IR spectra of a) SiO₂-NH₂, b) SiO₂-NH₂-TCPP, c) TCPP

The presence of TCPP on SiO₂-NH₂ was also confirmed by UV-vis spectroscopy (Fig. 5). The TCPP spectrum showed Soret band (417 nm) and four weak Q-bands. SiO₂-NH₂-TCPP showed absorption bands at 414 nm (Soret band) and at 514, 548, 591, and 647 nm. This result suggests that TCPP was functionalized onto SiO₂-NH₂ (as characterized by a blue shift of the Soret band associated with a significant amount of TCPP) during the preparation process. When TCPP was functionalized onto SiO₂-NH₂, the polarity in the vicinity of TCPP increases, as evidenced by the shifts of the absorption bands towards a higher energy [11].

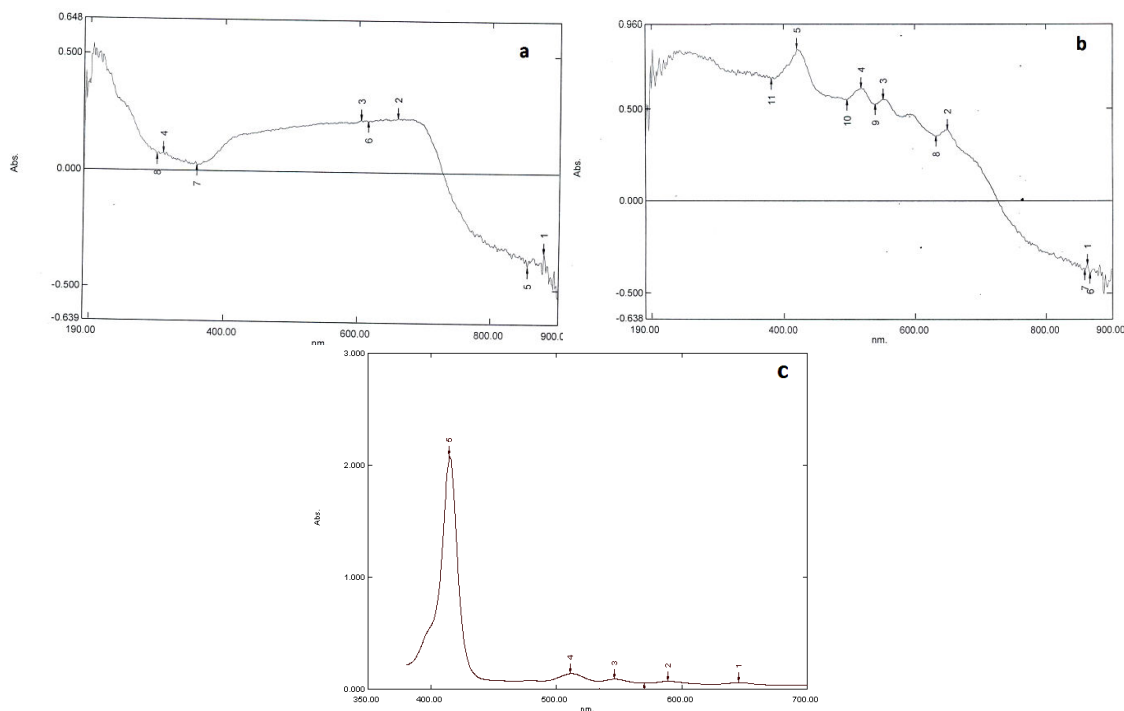


Fig5. Solid UV-vis spectra of a) $\text{SiO}_2\text{-NH}_2$, b) $\text{SiO}_2\text{-NH}_2\text{-TCPP}$ and c) UV-vis of TCPP in DMF

2.2. Sorption studies

An accurate weighed quantity of the dye was dissolved in double-distilled water to prepare a stock solution. The solutions for adsorption tests were prepared from the stock solution to the desired concentrations by successive dilutions. After taking the measurements by UV-vis spectroscopy, a curve was made to calculate the concentration of each experiment.

The percent removal of dye from solution was calculated by the following equation:

$$\% \text{removal} = \frac{C_0 - C_i}{C_0} \times 100$$

Where C_0 is the initial concentration of dye and C_i is the final concentration of dye.

2.2.1. Effect of pH

The effect of pH in the range 5–9 on the removal of CV was investigated using 0.1 mol L^{-1} HCl or NaOH solutions for pH adjustment, with the initial CV concentrations fixed at 5 ppm. percent adsorption increased by raising of pH and reached maximum (59%) at pH 8 and then decreased at higher pHs. the following studies of CV were conducted at a fixed initial pH of 8.

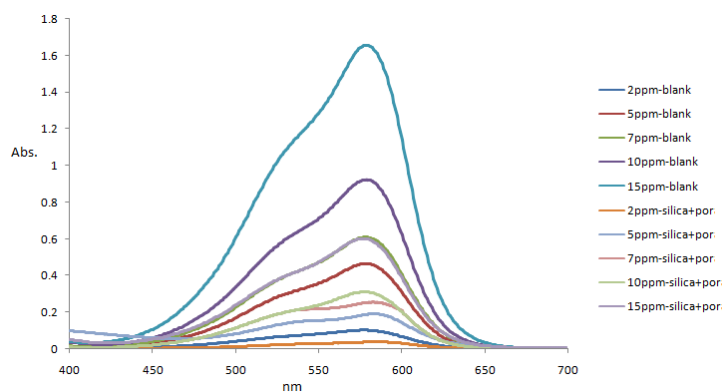
In case of basic dyes (crystal violet) at lower pH, the H^+ ions will compete with the dye cations causing in decrease in percent value. This can be observed from the higher and lower sorption capacity of crystal violet at higher and lower pH. Similar results were reported for the adsorption of crystal violet from aqueous solution on to jute fiber carbon [12].

2.2.2. Effect of contact time

The removal of crystal violet increases with time and attains saturation in about 60min by using optimum pH. Initially, the removal of crystal violet is rapid, but it gradually decreases with time until it reaches equilibrium. The crystal violet showed a fast rate of sorption during the first 25 min of the sorbate–sorbent and the rate of percent removal becomes almost insignificant dye to quick exhaustion of the adsorption sites. The rate of percent removal and adsorption capacity are higher in the beginning due to large surface area of the adsorbents available for the adsorption of the crystal violet.

2.2.3. Effect of initial dye concentration

Adsorption studies were carried out with different initial concentrations of CV ($2\text{--}15\text{ mgL}^{-1}$) at 25°C and pH 8. Figure 5 show visible absorption spectra of the CV solutions, before and after adsorption with $\text{SiO}_2\text{-NH}_2\text{-TCPP}$ and $\text{SiO}_2\text{-NH}_2$. Removal efficiency percents of CV in various concentrations by $\text{SiO}_2\text{-NH}_2\text{-TCPP}$ (Fig.6) show that the maximum adsorption is at the 10 ppm CV (66%).



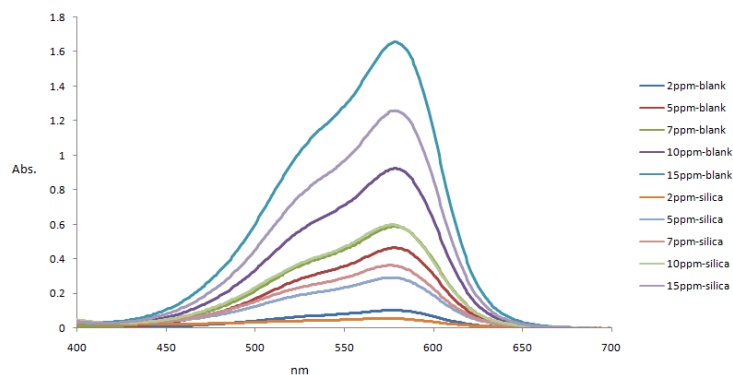


Fig6. Visible absorption spectra of the CV solutions, before and after adsorption with SiO₂-NH₂-TCPP (up) and SiO₂-NH₂ (down)

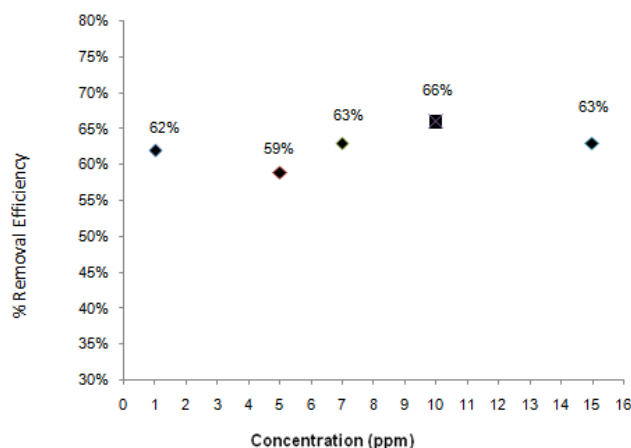


Fig7. Removal efficiency percents of CV in various concentrations. Conditions: 0.02 g SiO₂-NH₂-TCPP, 20mL of various concentrations of CV, agitation time of 60min.

3. Conclusion

In summary, the the Tetracarboxyphenylporphyrin Covalently Bound to Silica was used as adsorbent to remove Crystal Violet (CV) from aqueous solution.

Silica gel immobilizing Tetracarboxyphenylporphyrin (TCPP) chromophore was prepared by the reactions of 3-aminopropyl silica gel (SiO₂-NH₂) with the TCPP. The 3-aminopropyl silica gel (SiO₂-NH₂) was selected as the carrier because of its ability to immobilize the functional groups through a covalent bond. Micrometer-sized SiO₂-NH₂ beads were prepared by reacting silica gel with 3-aminopropyl(triethoxy)silane (H₂N(CH₂)₃Si(OEt)₃). The immobilization of TCPP chromophores on SiO₂-NH₂ was performed by the sol-gel method.

The bond formation was confirmed by the appearance of an amide bond at 1649 and 1539 cm^{-1} in the FT-IR spectra.

The $\text{SiO}_2\text{-NH}_2\text{-TCPP}$ was used as adsorbent for removing Crystal Violet from aqueous solutions. The UV-visible absorption spectroscopy was used to record the adsorption behavior. The pH effects, the contact time and the initial dye concentration were changed to obtain the best experimental conditions. At optimum pH 8, the dye adsorption equilibrium was attained after 60 min of contact time. The maximum adsorption was at the 10 ppm CV (66%). In comparison of $\text{SiO}_2\text{-NH}_2\text{-TCPP}$ with $\text{SiO}_2\text{-NH}_2$, The $\text{SiO}_2\text{-NH}_2\text{-TCPP}$ is better for removal of crystal violet.

4. Experimental

4.1. Preparation of adsorbents

4.1.1. Synthesis of Tetrakis(4-carboxyphenyl)porphyrin (TCPP)

Pyrrole (2.33 mmol) and 4-carboxybenzaldehyde (2.33 mmol) were dissolved in 100 ml propionic acid. And the mixture was refluxed for 4 h, and then this crude product was cool to room temperature. After cooling to room temperature, the mixture was added to 100 mL of methanol and chilled in an ice bath with stirring. The deep-purple crystals are filtered and washed with methanol and hot water. The resulting solid was dissolved in chloroform containing 2% acetone and purified by column chromatography over silica gel using chloroform as eluent [11].

4.1.2. Synthesis of tetrakis(4-carboxyphenyl) porphyrin-functionalized silica ($\text{SiO}_2\text{-NH}_2\text{-TCPP}$)

In a round bottom flask, 1.0 g of amino functionalized SBA-15 and 0.18 g dicyclohexylcarbodiimide (DCHC) were suspended in 50 ml of N,N-dimethylformamide (DMF). The 0.88 mmol of tetrakis(4-carboxyphenyl)porphyrin was dissolved in 5 ml of DMF and added drop wise to round bottom flask. The mixture was refluxed at 60 °C for 8 h. After cooling down to room temperature, the product was filtered and dried [11].

4.2. Adsorbate

The adsorption of CV from aqueous solution onto $\text{SiO}_2\text{-NH}_2\text{-TCPP}$ and $\text{SiO}_2\text{-NH}_2$ was performed using batch equilibrium technique. All the experiments were carried out at 25 °C. For the determination of adsorption isotherms, 20 ml of dye solution of known initial concentration was shaken with a certain amount of the adsorbent (0.02 g) on a shaker at 25

°C. The pH was adjusted to 8, either using HCl or NaOH. Initial dye concentrations were changed in the range of 2mgL^{-1} to 15mgL^{-1} . At various time intervals, samples were taken and allowed to settle and further centrifuged at 3000rpm for 10 min. The concentration of the residual dye was measured using UV-vis spectrophotometer at appropriate wavelength corresponding to the maximum absorption of CV (584 nm).

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