Adsorptive Removal of Drimarene Brilliant Blue by Thermo Stable, Eco-friendly Graphene Oxide Reinforced Polyvinyl Alcohols Hydrogels With High Reusability Potential

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Highlights

- Synthesis of Graphene Oxide (GO) nano-particles reinforced Polyvinyl alcohol composite Hydrogels
- Exploring the adsorption potential of synthesized composite material for the removal of Drimarene Brilliant Blue
- Excellent Regeneration and Reusability Potential

Abstract: In this study graphene oxide (GO) reinforced polyvinyl alcohol (PVA) composites hydrogels were synthesized and used as efficient adsorbents for Drimarene Brilliant Blue K-4BL. GO nanoparticles (NPs) were synthesized by modified Hummer's method. The composites were characterized by Fourier transform infrared spectroscopy (FT-IR), Thermo-gravimetric analysis (TGA), Scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results showed homogeneous dispersion of reinforcement in the synthesized composites. Moreover thermal stability of the composites was significantly enhanced by the addition of graphene oxide nanoparticles. The synthesized composites were used for the removal of Drimarene brilliant Blue from model waste water. The effect of

pH, content of GONPs and initial concentration of Drimarene Brilliant Blue K-4BL on the adsorption capacity of synthesized GO/PVA composites were investigated. The equilibrium isothermal data were studied by applying Langmuir and Freundlich isotherm models. Results demonstrated that the adsorption process is well described by the Langmuir adsorption isotherm. According to the Langmuir model, maximum adsorption capacity i.e. 32mg/g was obtained at 0.7% GO/PVA composite. From the kinetic study it was concluded that pseudo-second-order model is the best fitted. Synthesized composites showed excellent reusability (almost 95 %) for the adsorption of Drimarene Brilliant Blue K-4BL after four successive cycles of adsorption and desorption. Thus, the GO/PVA composites demonstrated a great potential in terms of cost effectiveness, efficiency and reusability for the removal of Drimarene Brilliant Blue K-4BL dye.

Graphical Abstract

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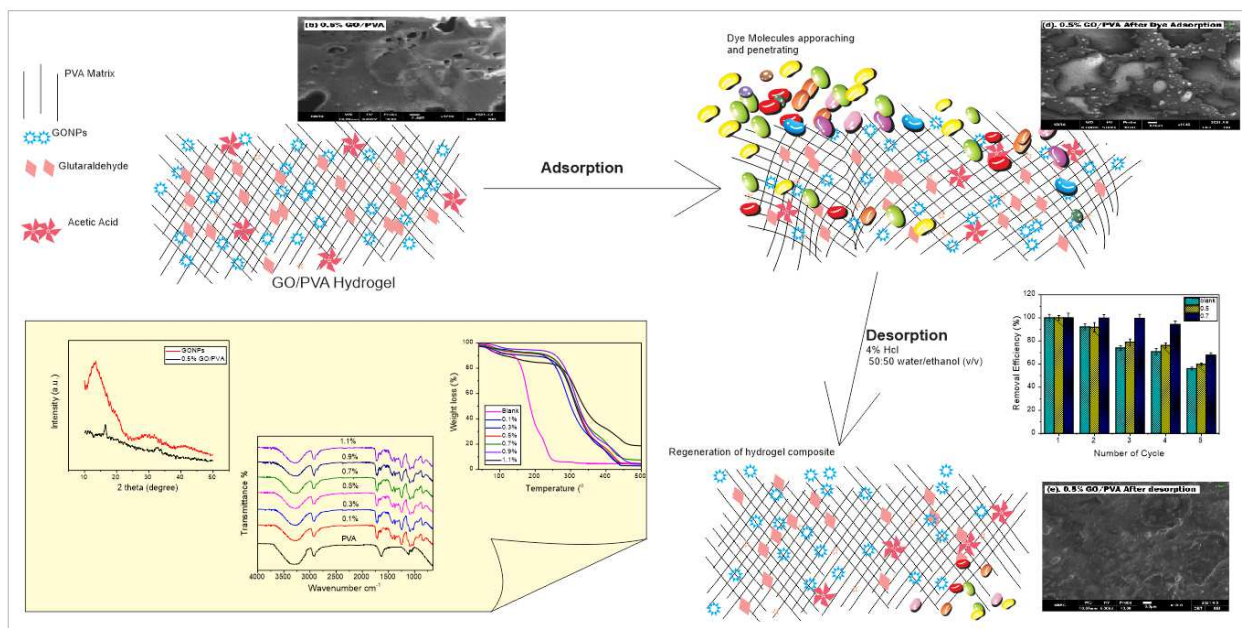
Keywords: Drimarene Brilliant Blue, GO/PVA Hydrogels, Adsorption – desorption, Reusability

Potential, Textile wastewater

Declarations:

Conflicts of interest/Competing interests

- The authors have no conflicts of interest to declare that are relevant to the content of this
  article.

90 **1. Introduction**

91   Watqer contaminants have been considered as one of the world's major health threats. Many

92   toxic pollutants and chemical compounds such as; oil pollutants from petrochemical industries,

93   heavy metals from metallurgical industries and dyes from textile industries, enter into the aquatic

94   systems [1, 2]. Among various pollutants, a considerable amount of dyes is discharged every day

95   into clean water bodies from textile industries during manufacturing and processing operations

96   [3]. Approximately 10 to 15% of dyes directly enter into wastewater which ultimately causes

97   serious hazards to aquatic and human life due to their high stability and complex molecular

98   structure [4].

99   Different types of dyes such as acidic, basic, direct, reactive and anthraquinone enter into

100   water bodies via textile sources [5]. Drimarene Blue is an anthraquinone cationic dye which is

101   the second highest textile dye after azo dye that is widely used in textile plants because of its

102   ease of operation, minimal energy consumption and a wide array of color shades. This cationic

103   dye is a considered a toxic substance that has not only adverse effects on the aquatic life, photo

104   planktons, and also contaminate the water leading towards the scarcity of clean water. Moreover,

105   it is not easily removed by simple treatment of wastewater, because of its inherent properties like

106   resistibility and stability towards oxidizing agents [5, 6]. Various methods have been developed

107   to remove dyes from wastewater e.g. floatation, reverse osmosis, adsorption, biological methods

108   and photo-catalytic degradation etc. Owing to its ease of operation, low-cost and high efficiency,

109   adsorption is considered the most versatile method for dye removal. Dye can be removed from

110   polluted wastewater with the help of various adsorbents such as nano-clay, synthetic polymers,

111   carbon-based materials, organic-inorganic composites [1, 7]. Carbon-based materials like

112   GONPs are the most promising adsorbents due to their high chemical stability, high surface area,

113   and excellent aqueous amphilicity [4]. These fascinating properties of graphene oxide are mainly

114   derived from its unique chemical structure composed of small sp^2 carbon domains, surrounded

115   by sp^3 carbon domains and oxygen-containing hydrophilic fundamental groups such as hydroxyl

116   and carboxyl [8]. GO is extensively used as nano-filler in the polymeric materials, dispersed

117   readily in the matrix of hydrogel and can efficiently develop strong interactions. Currently

118   different polymers such as polystyrene, polyurethane, polycarbonate, polyvinyl alcohol,

119   polypropylene, polyacrylamide reinforced with GONPs have been reported. PVA seems to be

120   one of the best candidate matrices for the incorporation of GONPs [9].

121   In GO reinforced polyvinyl alcohol functional groups present in GO act as active sites for

122   interfacial bonding with PVA to form a homogeneously dispersed GO/PVA composite [10].

123   Here in this study GO/PVA composites were synthesized by chemical cross-linking and tested

124   for the adsorption of cationic Drimarene Brilliant Blue K-4BL from model wastewater. The

125   effects of experimental parameters such as pH sensitivity, contents of GONPs on adsorption,

126   initial concentration of Drimarene Brilliant Blue K-4BL and time for the removal of dye were

127   studied to optimize the adsorption process.

128   **2. Materials and Methods**

129   **2.1 Material**

130   Polyvinyl alcohol (PVA, weight-averaged molecular weight 75,000–78,000, 99% hydrolyzed),

131   Graphite powder (99.8%, average particle size 46 µm), concentrated sulfuric acid (98%), sodium

132   nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), 30% H_2O_2 solution, hydrochloric acid

133   (Sigma Aldrich, St. Louis, MO, USA) were used without further purification during the synthesis

134   of targeted composites. Deionized water was used throughout research work. The cationic dye

135   used in adsorption process was Drimarene Brilliant Blue K-4BL with the chemical formula:

136    $C_{19}H_{14}ClCuN_7O_8S_2$, molar mass: 631.49 g/mol, and molecular composition C-36.14%, H-2.23%,

137   Cl-5.61%, Cu-10.06%, N-15.53%, O-20.27% and S-10.15%.

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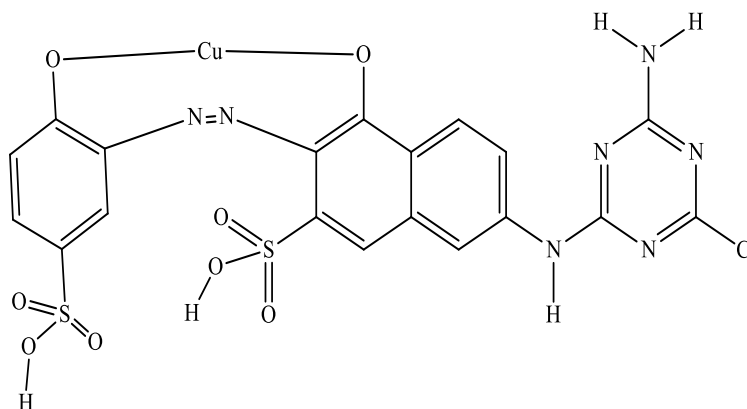
139   **Figure 1.** Chemical Structure of Drimarene Brilliant Blue K-4BL

140   **2.2 Synthesis of Graphene oxide**

141   Modified Hummer's method reported by Costa et al.[11] was followed to prepare the graphene-

142   oxide nanoparticles. Sulfuric acid (69 mL) was cooled at -4°C then added 1.5g of graphite

143   powder and 1.5g sodium nitrate ($NaNO_3$) in it. The mixture was stirred in an ice bath. After that,

144   9 g $KMnO_4$ was gradually added to the mixture. Then the ice bath was removed and the mixture

145   was allowed to warm at room temperature (25°C) and stirred for 1 h. After that, 100mL

146   deionized water was added, and continued the stirring for about 30 min at 90°C. Then distilled

147   water was added to the mixture. 30% hydrogen peroxide (10mL) was slowly added to one drop

148   per second. The yellow colors appeared by the addition of H_2O_2 into the solution and continued

149   the stirring of solution for 20 min. The solution was washed several times until the pH was about

150   7. Centrifugation of filtrate was done at 12,000 rpm for 5 minutes to collect graphene oxide

151   particles. Graphene oxide particles were dried in a vacuum oven overnight. Finally, the dried

152   graphene oxide particles/sheet was grinded to obtain graphene oxide nanoparticles.

2.3 Synthesis of pure PVA hydrogel film

Polyvinyl alcohol (5 wt %) was dissolved in distilled water at 80°C with constant stirring for about 2hr. The solution was allowed to cool at room temperature and glutaraldehyde (20% w/v in water) was added as crosslinking agent at a final glutaraldehyde concentration of 0.4%. Acetic acid was used as a catalyst (1.5mL). The solution was homogenized with continuous stirring for 30 min, and then poured into the mold and dried in the oven after letting the viscous solution stay at room temperature for 72 hr followed by drying at 45°C in vacuum oven. A smooth transparent 0.1mm thick film was formed [12].

2.4 Synthesis Graphene oxide/Polyvinyl alcohol (GO/PVA) composites

Graphene-oxide reinforced polyvinyl-alcohol composite hydrogels were synthesized following the method repoted by Han et al.[12] with some modifications.

Briefly, PVA 5 wt. % was dissolved in distilled water (10mL). Dispersion of GONPs (5mL) with different wt. % was transferred into the PVA matrix after sonication. Reaction mixture was stirred at 80ºC for two 2 hr. The solution was allowed to cool at room temperature followed by addition of glutaraldehyde (final concentration 0.4%) and acetic acid (1.5mL) as crosslinking agent and catalyst respectively. The mixture was again sonicated at 40ºC for 15 min to form a homogeneous suspension. Finally, the solution was transferred into the mold and dried in the oven at 45 ºC after letting it stay at room temperature for 72 hr.

Table 1. Medium compositions for the synthesis of GO/PVA composites

Sample Code	PVA(g)	1st Stage water (mL)	Glutaraldehyde (%)	Acetic Acid (mL)	GONPs (%)
0.1% GO/PVA	5	10	0.4	1.5	0.1

0.3% GO/PVA	5	10	0.4	1.5	0.3
0.5% GO/PVA	5	10	0.4	1.5	0.5
0.7% GO/PVA	5	10	0.4	1.5	0.7
0.9% GO/PVA	5	10	0.4	1.5	0.9
1.1% GO/PVA	5	10	0.4	1.5	1.1

172

2.5 Fourier Transform Infrared Spectroscopy (FT-IR)

174 Usually, in composites both matrix and reinforcement contain different types of inorganic and
175 organically derived functional groups such as hydroxyl, amino group, carboxyl and many more.
176 So the confirmations of these functional groups are recorded by Fourier transforms infrared
177 spectroscopy (FT-IR) spectroscopy. The spectra of samples (GO/PVA) were recorded on the FT-
178 IR spectrometer in the range of 4000-650 cm^{-1} using transmission mode.

2.6 Scanning electron microscope (SEM)

180 Surface morphology of synthesized composites, and the samples before and adsorption was
181 analyzed by Scanning Electron Micropscopy.

2.7 X-ray Diffraction (XRD)

183 The XRD of synthesized graphene oxide Nano-particles obtained by using D8 Advance, Bruker
184 with Cu-Kα radiation λ= 0.15406 nm source. These radiations were generated at a tube voltage
185 of 40 kV and 40 mA current. The diffraction peaks were recorded over a range of 2theta angles
186 from 0° to 60°. By using Bragg's equation ($\lambda = 2d\sin\Theta$) d-spacing was calculated in nanometer
187 [13].

2.8 Thermogravimetric Analysis (TGA)

Thermal stability of the pure PVA and GO/PVA composites was performed using simultaneous DSC-TGA Q600 thermal analyzer by TA Instruments. The heating rate was set at 10°C/min from room temperature to 500°C under N_2 atmosphere.

2.9 Adsorption of Drimarene Brilliant Blue K-4BL

2.9.1 Adsorption Kinetics

For kinetic study, dye adsorption experiments were performed via batch method by immersing 23mg of GO/PVA composites in 10mL of Drimarene Blue dye solution with various concentrations such as 50ppm, 100ppm, 150ppm, 200ppm, 250ppm and 300ppm at room temperature. Approximately, 15mL small glass vials were used for immersion of adsorbents in 10mL dye solutions and were shaken at 100rpm on orbital shaker. Kinetic study of adsorbent is a time based experiment, so absorbance of Drimarene blue dye solution were measured at regular time intervals with the help of UV Vis spectrophotometer at λ_{max}= 590nm. The readings were taken after 30 min of time intervals by withdrawing 0.5mL of dye solution. Before and after the adsorption, adsorption capacity of GO/PVA composites at time (q_t mg/g) were measured based on the changes of Drimarene blue dye concentration, according to the following equation:

$$q_t = (C_0 - C_t) \times V / W$$

Where, C_0 and C_t (mg/L) are the concentration of Drimarene Blue solution at the initial time and time t (min) respectively. V (L) is the volume of Drimarene Blue dye solution and W (g) is the mass of dried composites [14].

2.9.2 Effects of pH on GO/PVA composites

209   Drimarene Blue adsorption capacity by adsorbent was affected by pH values. GO/PVA

210   composites were soaked in 200 mg/L dye solution at different pH values (2, 4, 6, 8, and 10) and

211   adsorption experiments were done for 6hr to reach equilibrium.

2.9.3 Effects of initial Drimarene Brilliant Blue K-4BL concentration

213   The influence of initial Drimarene Brilliant Blue K-4BL concentration on the GO/PVA

214   composites was investigated. Different concentrations of dye solutions such as 50ppm, 100ppm,

215   150ppm, 200ppm, 250ppm and 300ppm were used and calculated adsorption capacities with

216   different composition of synthesized composites.

2.9.4 Adsorption Isotherms

218   Adsorption isotherms were determined by using Langmuir and Freundlich isotherms models.

219   Relationship between the amount of dye adsorbed by the adsorbent and the concentration of dye

220   remaining in the solution has been described by adsorption isotherms. The Langmuir model

221   describes maximum adsorption of the dye molecules on the surface of composites while the

222   Freundlich model is applicable in the case of low concentration of adsorbate. The adsorption

223   capacity of composites was calculated by following equation:

$$q_e = (C_0 - C_e) \times V / W$$

225   Where, C_0 is the initial concentration of dyes as mg/L and C_e is the equilibrium concentration of

226   the dye as mg/L. V (L) is the volume of Drimarene Blue dye solution and W (g) is the mass of

227   dried composites.

2.10 Regeneration and Reusability of prepared composites

229   Regeneration and reusability of GO/PVA adsorbent was studied for five successive cycles of

230   adsorption and desorption. The adsorption-desorption of Drimarene Brilliant Blue K-4BL

231   molecule from GO/PVA composites was analyzed. Desorption of the Drimarene Brilliant Blue

232   K-4BL dye molecules was performed in 4% HCl 50:50 water/ethanol (v/v) solution and

233   desorbed composites were washed with distilled water. Five successive cycles of dye-desorption

234   were performed. The dye removal % was calculated by following equation:

235    $$\text{Removal of dye \%} = (C_0 - C_e) \times 100 / C_0$$

236   Where C_0 is the initial concentration of dye and C_e is the dye concentration at equilibrium [15].

237   **3. Results and discussion**

238   **3.1 FT-IR spectroscopic analysis of pure PVA and GO/PVA Composites**.

239   Pure PVA and GO/PVA composites were characterized by FTIR within the range of 4000-

240   650cm^{-1} as presented in Figure 2. For pure PVA, peak at 3312 cm^{-1} can be ascribed to O-H

241   stretching vibration of hydroxyl group. Asymmetric stretch of C-H occurs at 2920 cm^{-1} and

242   symmetric starching of C-H occurs at 2852 cm^{-1}. The peaks at 1632 cm^{-1}, 1088 cm^{-1}suggest the

243   stretch vibrations of C=O and C-O bonds respectively.

244   GO reinforced PVA composites have shown the presence of an intense O-H stretching vibrations

245   between 3100-3500 cm^{-1}. However, the peak of the O-H group in pure PVA was observed at

246   3312 cm^{-1}. As shown in Figure 2, when the content of GO increased in PVA polymer matrix,

247   extra peaks were observed below 1500 cm^{-1}, representing the different functional groups in GO.

248   The appearance of peaks at 2920 cm^{-1} and 2852 cm^{-1}represents C-H asymmetric vibrations and

249   C-H symmetric vibration respectively. FTIR peak at 1716 cm^{-1} corresponds to stretching

250   vibration of C=O ester groups formed between O-H groups of PVA and carboxylic acid groups

251   of GONPs. The peak at 1088 cm^{-1} is ascribed to C-O groups in GO/PVA composite. IR band at

252   1423 cm^{-1} may be shown for skeletal vibration of the unoxidized graphite domains. The IR band

253   at 1716 cm^{-1} corresponding to C=O group of GO shifted to higher wave number. The shift of

254   band presenting OH and C=O group suggest development of a strong intermolecular and intra-

255   molecular hydrogen bonding between GONPs and PVA polymer matrix.

256   Appearance of these peaks also suggests that GONPs covalently and physically bonded (H-

257   bonding) with PVA chain successfully. In this study though GO/PVA composites are different

258   but FTIR spectra of all these compositions have almost similar trend, which is shown in Figure 2.

259   These results are in concordance to Rathod et al. (2014) [16].

260   Proposed scheme for the development of cross links in the GO/PVA is given in the Figure 2b.
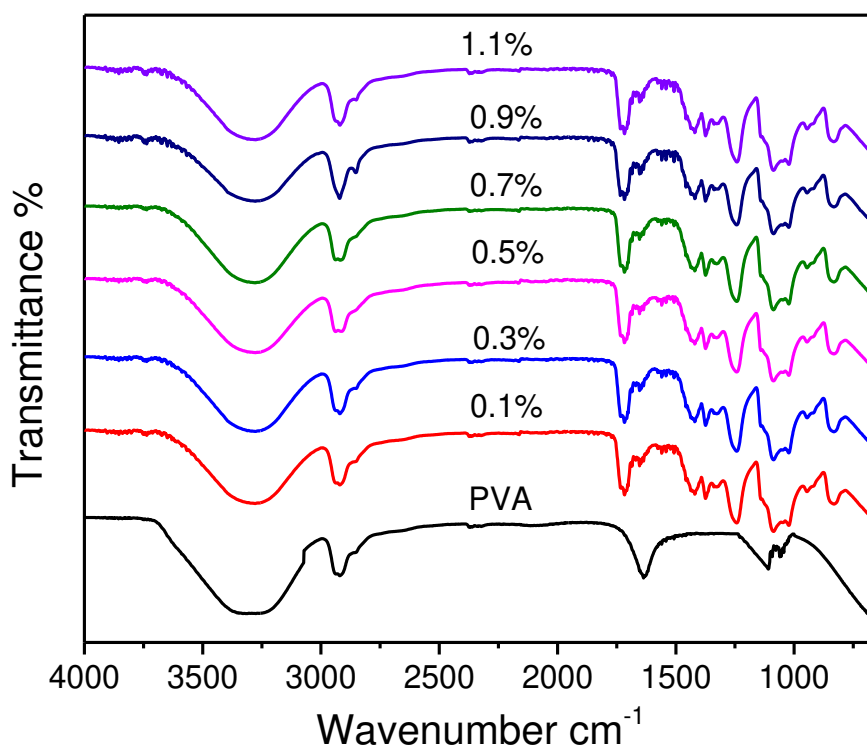
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262   **Figure 2a.** FTIR spectra of PVA and GO/PVA composites

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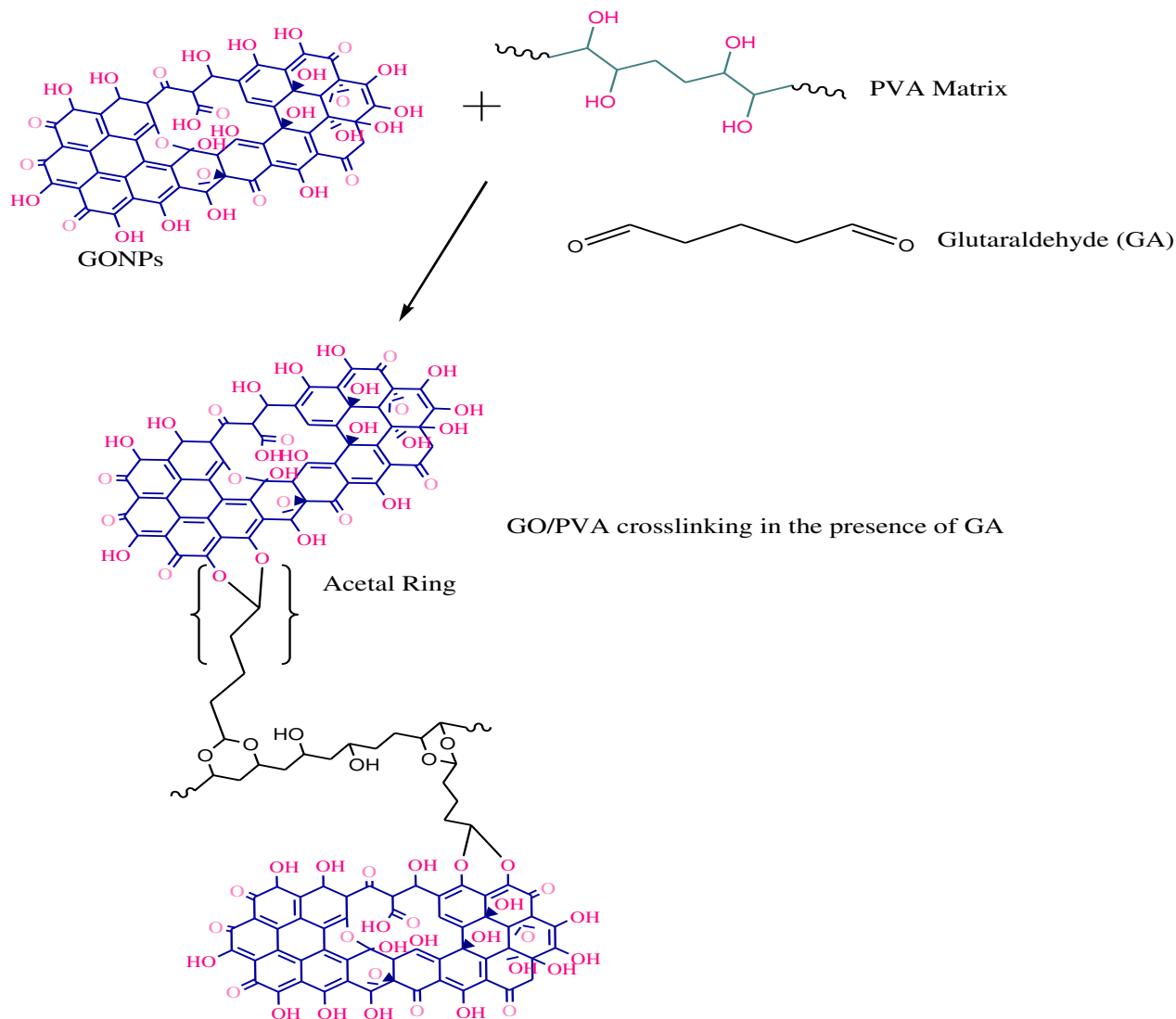
Figure 2b. Proposed scheme for the possible interaction between GO and PVA

3.2 X-ray diffraction (XRD) study

Graphene oxides NPs and 0.5% GO/PVA composites were characterized by XRD. The sample was in powder and solid form. As shown in Figure 2 GO NPs exhibits diffraction at $2\Theta = 13.6°$. By using Bragg's equation ($\lambda = 2d\sin\Theta$), d-spacing calculated which was 0.65nm or 6.5A°. According to result of d-spacing GO suggests the presence of oxygen containing groups like hydroxyl, carboxyl and epoxide in the layer of GONPs. XRD pattern of 0.5% GO/PVA

272 composites was showed at 2 Θ = 16.5°, the characteristic peak of GONPs was found disappeared

273 at 2Θ = 13.6°, which was mainly due to the disappearance of the ordered and periodic structure

274 of GO in the PVA matrix, also suggesting the well exfoliation and uniformly dispersed of

275 GONPs in PVA matrix [17].
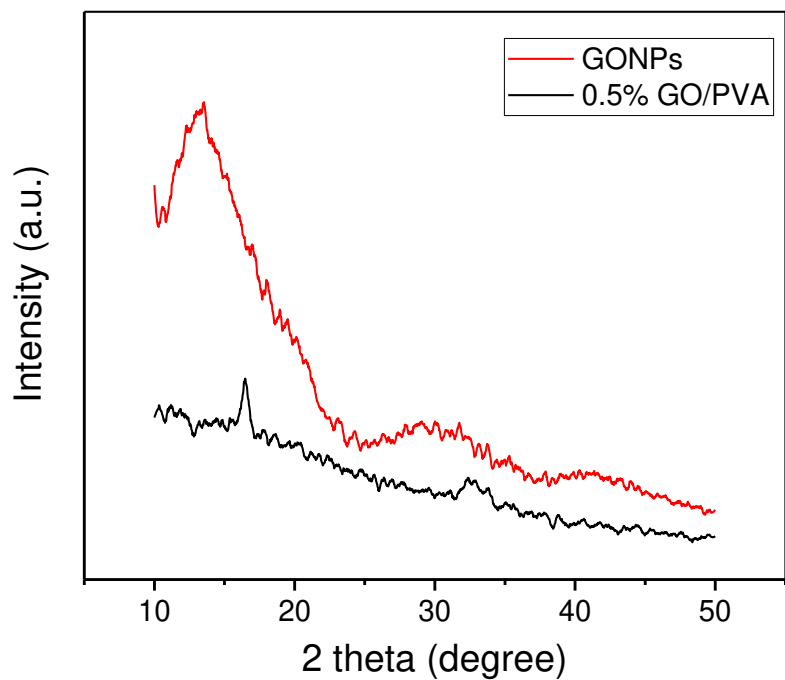
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277 **Figure 3.** X-Ray Diffraction profiles of GO NPs and 0.5% GO/PVA composites XRD patterns

278 of GONPs and 0.5% GO/PVA composites

279 **3.3 Scanning Electron Microscopic (SEM) studies**

280 **3.3.1 SEM studies before adsorption**

281 Morphological analysis of GO reinforced polyvinyl-alcohol composites was done by SEM.

282 Results illustrated that, amount GO NPs plays a key role for altering the surface morphology of

283 prepared composites. More benefits were achieved by the better dispersion of graphene oxide

NPs in polyvinyl-alcohol matrix. Figure 4 (a) illustrates, the plane, homogeneous and smooth

structure with the distribution of some bulges of pure PVA matrix. Figure 4 (b) showed the

uniform dispersion of graphene oxide nanoparticles and when compared with pure PVA films,

the surface of composite showed porous and rough morphology as represented by the Fig 4b and

4c for the composite samples with 0.5 and 0.7% reinforcement respectively. More content of GO

into the matrix makes the cross linking points and increased the porous structure of graphene

oxide reinforced polyvinyl-alcohol composites. Figure 4(c) represented 0.7% GO/PVA

composites displayed high surface area due to the porous and rougher structure which was

responsible to high adsorption capacity for Drimarene Brilliant Blue K-4BL dye.

3.3.2 SEM studies of composites after dye adsorption

After the adsorption of Drimarene Brilliant Blue K-4BL dye, morphological surface of GO/PVA

composites were transferred into homogenous and smooth structure. It is indicating that, dye

molecules were penetrated into the porous sites of composites and porous areas completely

filled. Some areas on the composites have shown (Figure 4 d) the coagulation which might be

ascribed to the clusters of dye molecules adsorbed onto the surface of GO/PVA composites.

3.3.3 SEM studies of composites after desorption

Finally, dye desorbed composites were characterized by SEM. It can be seen in Figure 4 (e) the

porous structure was appeared after the desorption of dye, might be suggested that maximum dye

molecules desorbed from the surface of composites.

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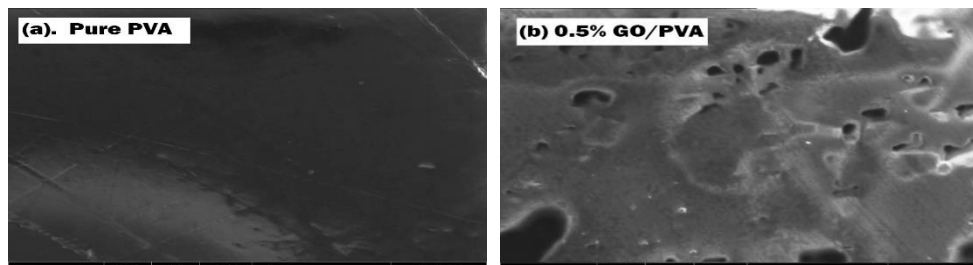
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Figure 4. SEM images of GO/PVA composites (a) Pure PVA, (b) 0.5% GO/PVA (c) 0.7%

GO/PVA, (d) 0.5% GO/PVA After dye adsorption, (e) 0.5% GO/PVA after desorption.

3.4 Thermogravimetric Analysis (TGA)

Thermal characterization of PVA and GO/PVA composite hydrogels was studied via TGA. The

weight loss of pure PVA categorized in two steps, firstly decomposition of hydroxyl groups

within 200-300°C, could remain 90% of its initial weight. In the second step, carbon chains were

decomposing in 300-400°C only 30.4% of its initial weight remained. 10% weight remained,

when temperature reached up to 500°C. So the major decomposition temperature of pure PVA

was analyzed at 350ºC as shown in Figure 5.

324   Thermal decomposition of GO/PVA composites as shown Figure 5 the weight loss would be

325   characterized in two steps. In the first step, hydroxyl, carboxyl and/or epoxide groups were

326   decomposed at 100-250°°C, and could remain 5% of its total weight loss. In the second step,

327   carbon containing chains were decomposed in 250-450ºC with only 65% of its total weight loss.

328   85% of total weight had lost when temperature reached up to 500ºC. Results of GO/PVA

329   composites indicated, thermal stability of these composites was enhanced by the addition of GO

330   reinforcement into polyvinyl alcohol matrix; Slighter but gradual increase has been observed in

331   the thermal stability of all the compositions of GO/PVA composites [18].
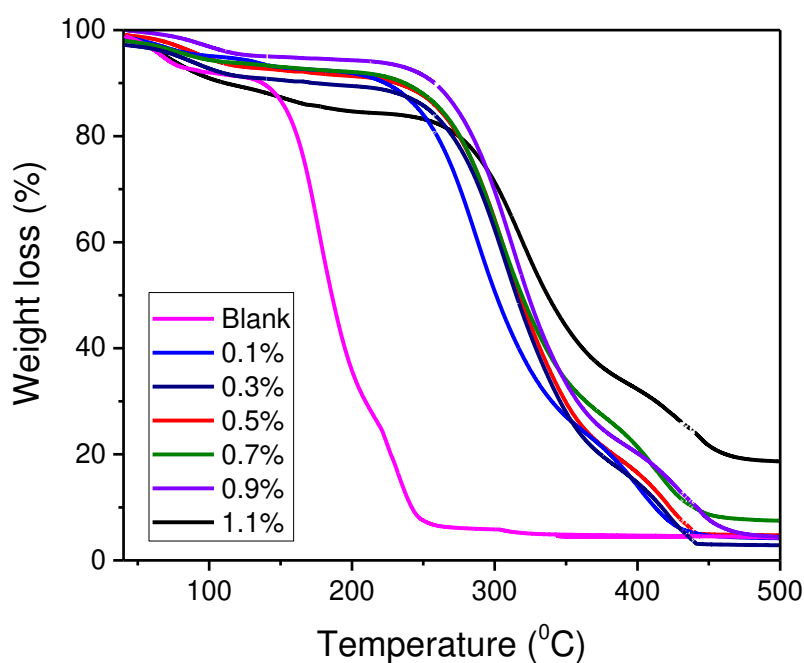
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333   **Figure 5.** TGA plots of pure PVA and GO/PVA composites

334   **3.5 Adsorption of Drimarene Brilliant Blue K-4BL dye**

335   **3.5.1 Adsorption Kinetics**

336   In this study adsorption kinetics was investigated at room temperature by using by using 200ppm

337   concentration of the solution at pH 8. Drimarene Brilliant Blue K-4BL, a cationic dye, was

338   selected to investigate adsorption efficiency of GO reinforced polyvinyl alcohol composites.

339   Chemical structure of Drimarene Brilliant Blue K-4BL dye shows cationic group like (N^+, S^+)

340   and benzene rings; making the GO reinforced composites more compatible for the adsorption of

341   dye through $\pi - \pi$ stacking and electrostatic interactions [19].

342   Initially the adsorption capacity rapidly increased because adsorbate molecules adsorbed on the

343   accessible site of the adsorbent quickly. With the passage of time adsorption capacity decreases

344   due to limited surface adsorption and repulsive forces between Drimarene Brilliant Blue K-4BL

345   dyes molecules in liquid and solid phase [20].

346   For further investigation of adsorption mechanism, experimental data was calculated by using

347   pseudo first order and pseudo second order linear equations of two kinetic models are given

348   below:

349   Pseudo first order kinetic equation $= \ln (q_e - q_t) = \ln q_e - k_1 t$

350   Pseudo second order kinetic equation $= t/q_t = t / k_2 q_e^2 + t / q_e$

351   Where q_e is quantity of Drimarene Blue adsorbed (mg/g) at equilibrium, q_t is quantity of

352   adsorbed dye at time (min). k_1 (min^{-1}) is constant of pseudo first order, and k_2(min^{-1}) is constant

353   of pseudo second order. Different parameters for these two models were calculated such as

354   calculated q_e, correlation coefficient R^2 values and rate constants (k_1, k_2) also presented in Table

355   3 These parameters were calculated for all compositions with various concentrations of dye

356   solutions as mentioned above.

Parametric values of pseudo first order and pseudo second order shown in Table 2 It was

observed, all calculated (q_e) values of composites are close to experimental (q_e) obtained by

using pseudo second order equation, but q_e values, obtained from pseudo second order equation,

are substantially different from experimental q_e values. While R^2 values of the composites were

close to 0.999, resulting from the calculation of pseudo second order, these are greater than

values of pseudo first order model. Baseds on q_e and R^2 values, the best fitted model was a

pseudo second order model for explaining the adsorption mechanism as chemisorption of

Drimarene Brilliant Blue K-4BL dye onto GO/PVA composites [20].

Table 2. Kinetics parameters of Pseudo-first-order and Pseudo-second-order (dye concentration=
200ppm; pH=8)

Composites	$q_{e, exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
		R^2	$q_{e,cal}$ (mg/g)	k_1 min^{-1}	R^2	$q_{e,cal}$ (mg/g)	k_2 (mg/g min^{-1})
Pure PVA	55.4	0.739	94.0	-1.04E-05	0.110	543.4	4.29E-07
0.1%GO/PVA	55.5	0.928	79.7	-8.86E-06	0.012	-591.7	3.04E-07
0.3%GO/PVA	54.2	0.926	81.1	-9.28E-06	0.115	460.8	5.96E-07
0.5%GO/PVA	55.3	0.952	79.4	-9.20E-06	0.215	438.5	6.74E-07
0.7%GO/PVA	53.6	0.882	107.4	-1.34E-	0.120	325.7	1.38E-06

				05			
				-8.10E-			
0.9%GO/PVA	50.4	0.885	83.8	06	0.457	-121.6	5.19E-06
				-1.24E-			
1.1%GO/PVA	54.8	0.796	113.3	05	0.189	-244.4	0.189

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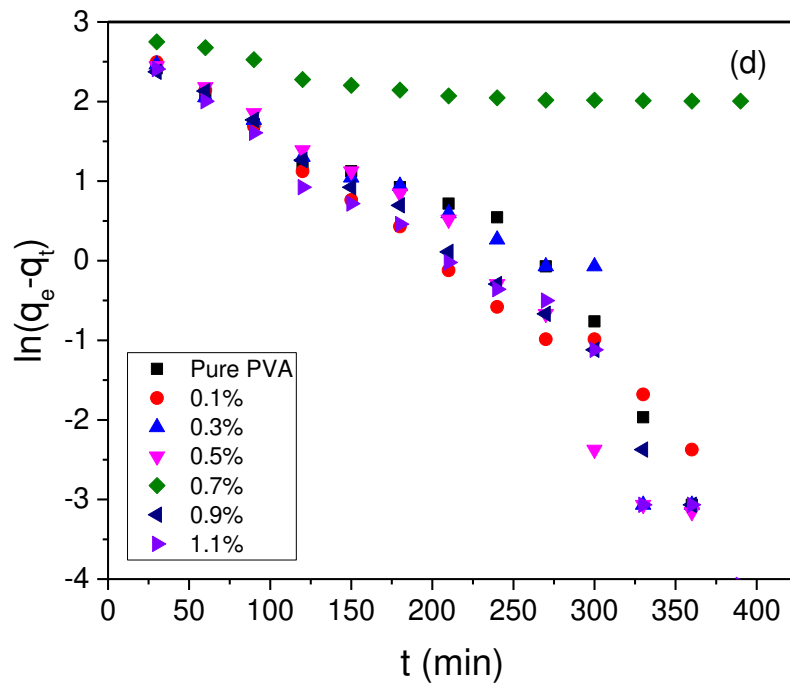
Figure 6. Pseudo-first-order kinetic plot for Drimarene Brilliant Blue K-4BL adsorption on PVA and GO/PVA composites at pH 8

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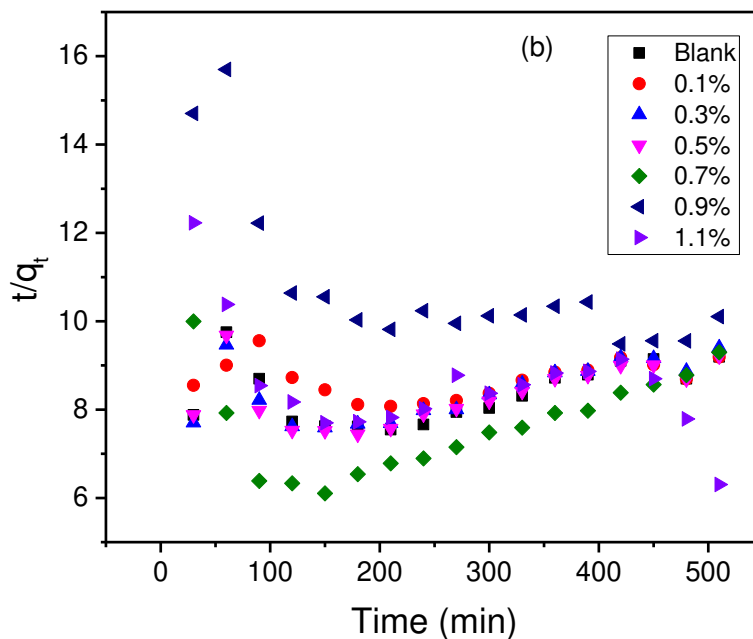
Figure 7. Pseudo-second-order kinetic plot for Drimarene Brilliant Blue K-4BL adsorption on PVA and GO/PVA composites at pH 8.

3.5.2 Effect of pH on adsorption

Solutions at different pH play a significant role for Drimarene Brilliant Blue K-4BL adsorption process, which can activate functional groups of adsorbents to impart a specific surface charge [13]. Figure 8 showed the effect of pH solutions on adsorption. pH effects on the adsorption capacity of prepared composites were determined by changing pH such as 2, 4, 6, 8 and 10. It was found that the adsorption capacities of Drimarene Brilliant Blue K-4BL on the composites increased gradually with the increase of pH from 2 to 8. Drimarene Brilliant Blue K-4BL carrying ammonium and sulphur groups exist in cationic form in the wide range of pH. At low pH, protonation of hydroxyl and carboxylic groups makes the positively charged surface of the composites, which limits adsorption capacity of positively charged Drimarene Brilliant Blue K-

384 4BL due to repulsive forces. At maximum pH, adsorption capacities of composites were

385 increased due to deprotonation of –COOH and –OH groups furnish the composites with negative

386 charges, resulting in an enhanced electrostatic interaction of the composite with cationic dye

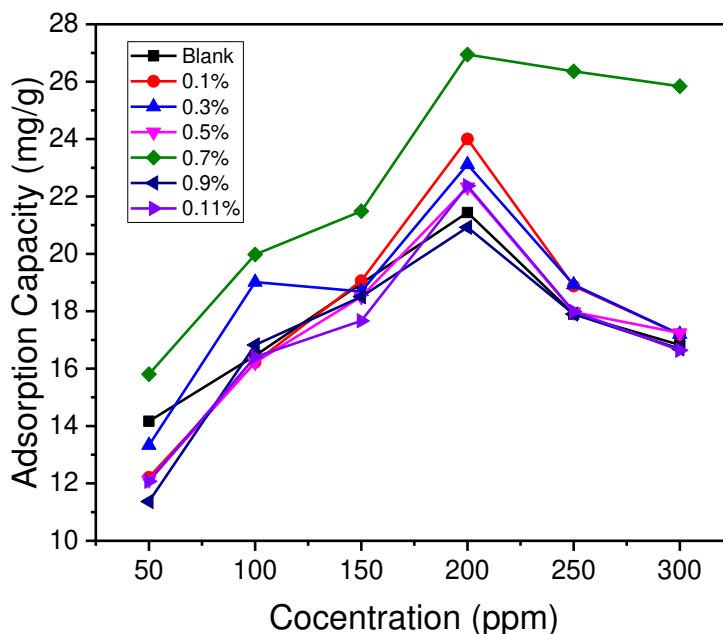387 Drimarene Brilliant Blue K-4BL.
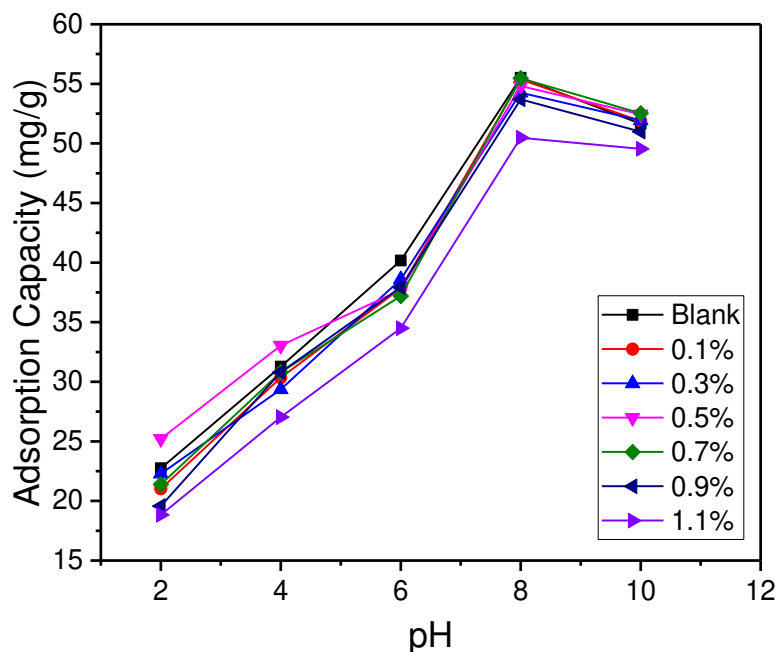
388

389 **Figure 8.** Effect of pH on the adsorption capacity of GO/PVA composites (Drimarene Brilliant

390 Blue K-4BL conc.: 200ppm, contact time 6 hrs, and T = 25ºC).

391 **3.5.3 Effect of initial concentration on adsorption**

392 The effect of initial Drimarene Brilliant Blue K-4BL concentration on the Drimarene Brilliant

393 Blue K-4BL adsorption ability of the synthesized GO/PVA composites was investigated.

394 Different initial concentrations of Drimarene Brilliant Blue K-4BL dye were used to analyze the

395 adsorption capacities. Figure 9 shows adsorption capacities enhanced by the increase of initial

396 Drimarene Brilliant Blue K-4BL concentration. Initial concentrations were used such as 50ppm,

397   100ppm, 150ppm, 200ppm, 250ppm and 300ppm. Higher Drimarene Brilliant Blue K-4BL

398   concentration might offer increased driving force to decrease the resistance for mass transfer

399   from solid to liquid phase of dye molecules [18].

400

401

402   **Figure 9.** Effect of concentration of Drimarene Brilliant Blue K-4BL on adsorption capacity of

403   GO/PVA composites (pH = 8, contact time = 6 hrs, and T = 25ºC).

404   **3.5.4 Effect of content of GO NPs on Drimarene Brilliant Blue K-4BL adsorption**

405   GONPs generated the effects with respect to the adsorption ability and removal capacity of

406   Drimarene Brilliant Blue K-4BL at dye concentration (200 mg/L). Different experiments were

407   performed with the various compositions of GO/PVA composites. Removal efficiency of

408   Drimarene Brilliant Blue K-4BL was increased with increment of GONPs reinforcement into the

409   PVA polymer up to 0.7% GO/PVA composites, which is because of large active sites available

410 for the adsorption process. Further increased the amount of GONPs from 0.9% to 1.1% GO/PVA

411 resulted in removal efficiency decreased because the active sites for adsorption were not present

412 by the saturation of GONPs in PVA polymers. Zamani *et al.* [2] also reported the similar results

413 in their literature.
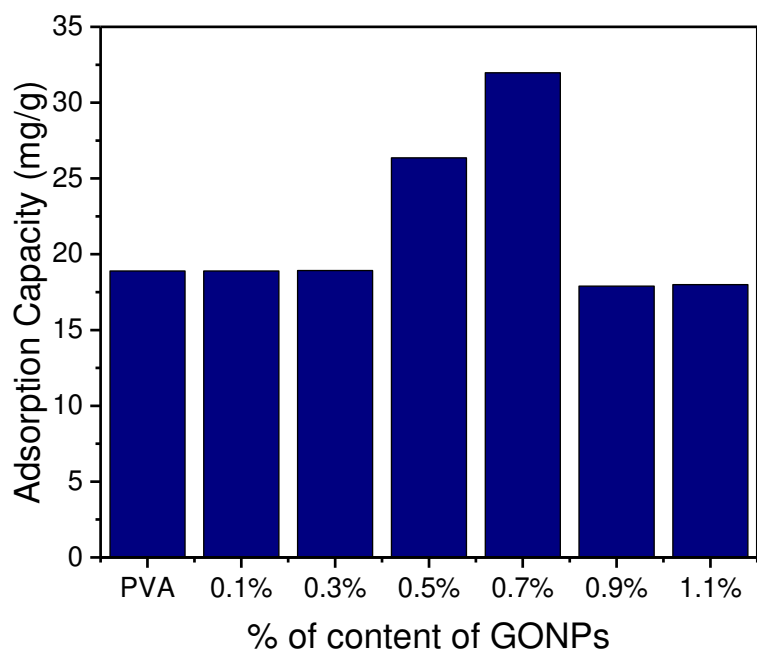
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415 **Figure 10**. Effect of content of GO NPs on Drimarene Brilliant Blue K-4BL adsorption

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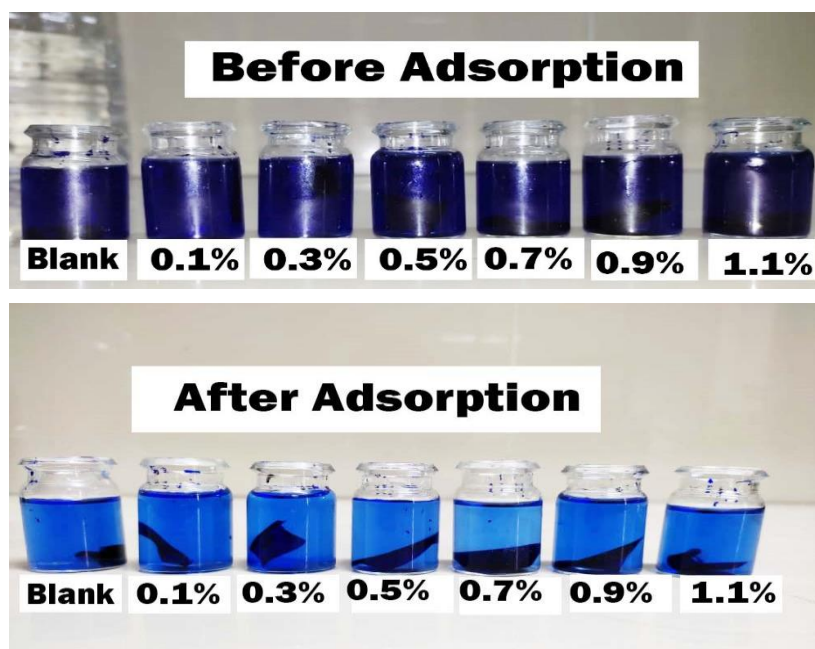
Figure 11. GO/PVA composites before and after adsorption of Drimarene Brilliant Blue K-4BL at 200ppm.

3.6 Adsorption Isotherms

Equilibrium data is important to analyze the mechanism of adsorption isotherms. It gives a relationship between concentration of dye and amount of dye adsorbed by adsorbent. They can give information about surface property, mechanism of adsorption and affinity of adsorbent for dye [20].

In this work, Langmuir isotherm model and Freundlich isotherm model were used to calculate Drimarene Brilliant Blue K-4BL dye adsorption isotherms parameter on the prepared GO/PVA composites. By the definition of the Langmuir model, maximum adsorption takes place on a homogeneous adsorbent surface to form a monolayer of adsorbates. The non-linear form of Langmuir equation as shown

$$C_e / q_e = C_e / q_{max} + 1 / k_2 q_{max}$$

Here C_e (mg/L) is dye concentration at equilibrium and q_e (mg/g) adsorption capacity at equilibrium. q_{max}(mg/g) theoretical adsorption capacity at maximum point. k_2 is Langmuir adsorption constant [18]. The Langmuir model can be explained by R_L. R_L is constant, which is dimensionless parameter of adsorption can have expressed as following;

$$R_L = 1 / 1 + K_L C_0$$

441   Here K_L is constant of the Langmuir model (L/mg) and C_0 is the highest initial concentration of

442   Drimarene Brilliant Blue K-4BL. The R_L representing nature of isotherm: adsorption is linear for

443    $R_L = 1$, unfavorable for $R_L > 1$, favorable for $0 < R_L < 1$; and if $R_L = 0$ then it shows the

444   irreversible condition [2].

445   According to Freundlich isotherm, maximum adsorption takes place to form a multilayer of

446   adsorbate on the heterogeneous adsorbent surfaces [18]. Equation of Freundlich model can be

447   represented in non-linear form as follows;

448    $$\ln q_e = \ln K_F + \ln C_e / n$$

449   Here, C_e (mg/L) is concentration of dye at equilibrium point and q_e (mg/g) is adsorption capacity

450   at equilibrium stage. 1/n is adsorption intensity and K_F is Freundlich constant.

451   Constant adsorption parameter can be expressed as '1/n' whose values vary from 0 to 1; Value of

452   1/n calculated from equation, if $1/n < 1$ then it can be suggested that adsorption capacity of

453   adsorbent is slow down at lower equilibrium concentration.

454   Equilibrium data of adsorption isotherms were obtained at room temperature. By comparing R^2

455   illustrated in Table 3 the isotherm data of prepared GO/PVA composites with the different

456   compositions were better fitted to Langmuir isotherm model than the Freundlich isotherm model.

457   According to the Langmuir model, maximum adsorption capacities of 0.1%, 0.3%, 0.5%, 0.7%,

458   0.9% and 1.1% GO/PVA composites were obtained 18.5 mg/g, 18.8 mg/g, 19.8 mg/g, 20 mg/g,

459   32 mg/g, 19.3 mg/g and 19.1 mg/g. So, 0.7% GO/PVA showed maximum adsorption capacity at

460   32 mg/g than others.

461   **Table 3.** Isotherm parameters for the adsorption of Drimarene Brilliant Blue K-4BL on

462   GO/PVA composites.

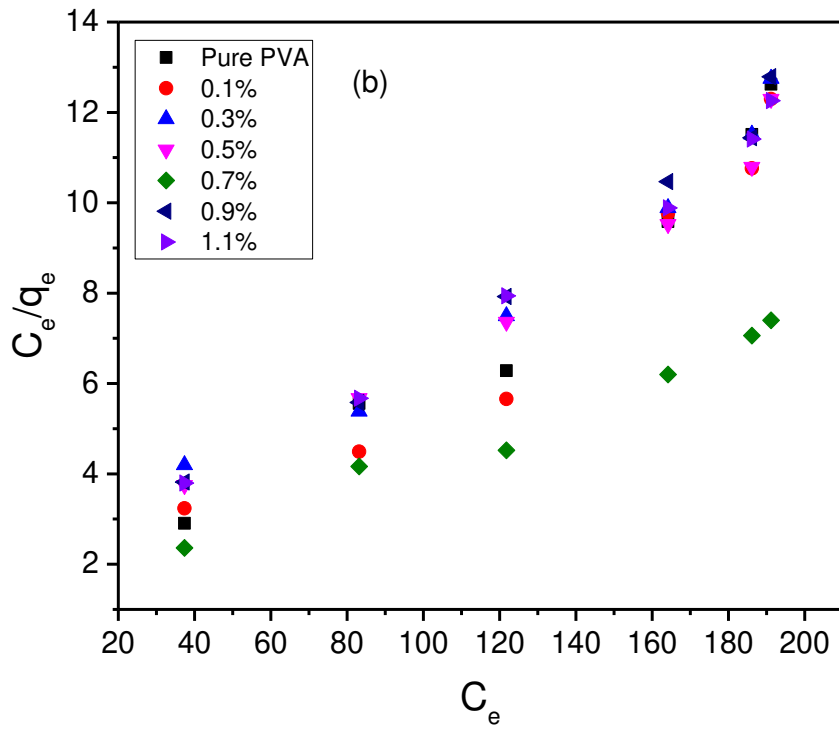| Composites	Langmuir				Freundlich		
	R^2	q_{max}	K_L	R_L	R^2	K_F	$1/n$
Pure PVA	0.948	18.5	0.197	0.019	0.282	8.696	0.14
0.1% GO/PVA	0.934	18.8	0.386	0.010	0.171	8.075	0.16
0.3% GO/PVA	0.961	19.8	0.042	0.085	0.470	4.532	0.26
0.5% GO/PVA	0.973	20.8	0.036	0.098	0.338	5.030	0.25
0.7% GO/PVA	0.970	32.0	0.025	0.133	0.874	4.900	0.32
0.9% GO/PVA	0.984	19.3	0.045	0.080	0.320	5.641	0.22
1.1% GO/PVA	0.947	19.1	0.044	0.082	0.296	3.023	0.37

463

464 As seen from the table, all the compositions of the GO/PVA composites have high correlation

465 coefficient (R^2) of the Langmuir model as compared to Freundlich. It is also confirmed the

466 monolayer adsorption of Drimarene blue dye onto the composite surface as shown in Figures 12

467 and obtained data was summarized in Table 3.
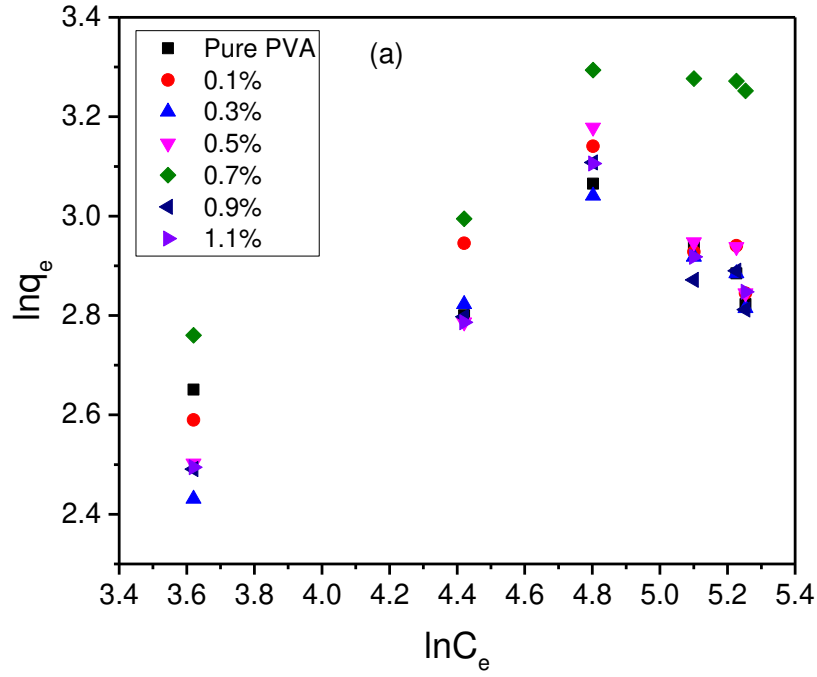
470 **Figure 12.** Adsorption isotherms of Drimarene Brilliant Blue K-4BL on GO/PVA composites at

471 25ºC (a) Freundlich isotherm (b) Langmuir isotherm .

472 Here, there is a comparison of adsorption capacities of blue dyes that have been shown by

473 different adsorbents.

474 **Table 4**: Comparison of adsorption capacities of dyes onto various adsorbents from literature

Adsorbent	Dye	Q_{max} (mg/g)	Reference
Poly(vinyl alcohol)/poly(acrylic acid /clay	Methylene Blue	28.80	[21]
PVA/GA/β-cyclodexrin	Methylene Blue	27.25	[21]
Poly(vinyl alcohol)/alginate/kaolin	Methylene Blue	30.80	[21]
Poly(vinyl alcohol)/bentonite clay	Methylene Blue	27.9	[21]
Natural Clay	Nile Blue	25	[22]
PVA/D – glucose/agar membrane	Methylene Blue	29	[23]
PDA/GO	Methyl Orange	30.0	[24]

| PVA/PAA/GO-COOH@PDA | Methylene Blue | 31.3 | [24] |
| GO/PVA | Drimarene Brilliant Blue K-4BL | 32 | This work |

475

3.7 Regeneration and reusability of prepared composites

477 As terms of efficiency and effectiveness, not only high adsorption capacity of adsorbent for dye

478 is demanded, but also good regeneration performance is expected. In this work, the aim is

479 production of low-cost materials [12]. As mentioned above, the maximum adsorption capacity of

480 dye by adsorbent occurs at pH 8. So, it was observed that dye desorbed at low pH. This result

481 suggests using an acidic media to regenerate the GO/PVA composite. For Drimarene Brilliant

482 Blue K-4BL solutions of C_0 = 200 mg/L pH 8 was chosen to perform the recycle experiment.

483 Different desorption experiments were tested. Drimarene Brilliant Blue K-4BL was fairly

484 removed in 0.1M HCl water solution, 0.1M HCl ethanol solution, 4% HCl water solution, 4%

485 HCl ethanol solution and 4% HCl with 50/50 of ethanol/water (V/V) solution, whereas the most

486 convenient desorption medium was 4% HCl with 50/50 of ethanol/water (V/V) mixture. This

487 suggests the tendency of Drimarene Brilliant Blue K-4BL to dissolve in 4% HCl water/ethanol

488 solution rather than adsorbing on GO/PVA composite through weak hydrogen bonding and van

489 der waals interactions. It is analyzed that electrostatically adsorbed cationic Drimarene Brilliant

490 Blue K-4BL on GO/PVA was exchanged with H^+ ions [25].

491 Five adsorption and desorption cycles were performed by immersing pure PVA, 0.5% GO/PVA

492 and 0.7% GO/PVA composites in 4% HCl water/ethanol solution. As shown in Figure 13,

493 removal efficiency of dye decreases slightly from almost 100% to 99.8%, 99.5%, 95%, and 67%

494 for 0.7% GO/PVA respectively after five cycles. According to the high regeneration, good

495 reusability and high adsorption capacity, the present GO/PVA composite can be considered as a

496 good candidate in the application for the removal of dye from contaminated water.
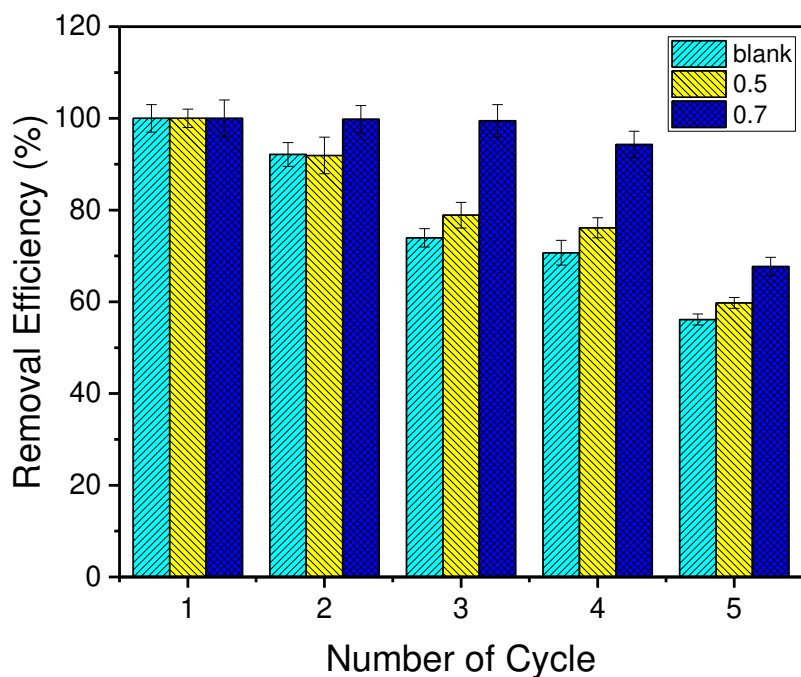
497

498 **Figure 13.** Reusability of PVA, 0.5% and 0.7% GO/PVA composites (dye conc. = 200ppm,

499 contact time = 6 hrs at 25ºC).

500 **3.8 Conclusion**

501 In this work, we have investigated the performance of GO/PVA composites for the removal of

502 Drimarene Brilliant Blue dye from model wastewater at different concentrations and pH.

503 GO/PVA composites with different compositions have been analyzed that offer higher

504 adsorption capacities than the pure PVA. Initial concentrations of Drimarene Brilliant Blue K-

505　4BL dye and pH of dye solutions significantly affected the adsorption process. Equilibrium and

506　kinetic studies suggested that modified Langmuir and pseudo second order models were best

507　fitted with the experimental data. Regeneration and reusability was also analyzed by performing

508　adsorption-desorption cycles. The results revealed that GO reinforced PVA composites can be

509　regenerated and reused for Drimarene Brilliant Blue K-4BL dye adsorption with almost 70%

510　removal efficiency after five cycles. This study has shown the effective sorption potential of

511　GO/PVA composites as these hydrogels are an upright choice for the removal of textile dyes and

512　are usable even after successive five cycles in media with pH near to neutral values; and most of

513　the textile effluents fall with this pH range. Hence no pre-treatment would be required before

514　using this composite for the removal of dye. Based on the whole discussion, GO/PVA

515　composites could be applied as an effective and reusable adsorbent for the treatment of textile

516　contaminated water.

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