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Biodegradable glucose and glucosamine grafted polyacrylamide/graphite composites for the removal of acid violet 17 from an aqueous solution

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Abstract: In this work, the structural characterization and adsorption behavior of glucose and glucosamine grafted polyacrylamide/graphite composites (denoted as Gu-g-PAM/graphite and GA-g-PAM/graphite) were investigated. The grafted polymers were characterized by using Fourier transform infrared (FT-IR) spectroscopy, ^1H nuclear magnetic resonance (NMR), ^{13}C NMR and N_2 sorption studies. The adsorption behavior of grafted polymers was compared by varying parameters such as pH, initial dye concentration, agitation time, adsorbent dose and temperature. The results showed that GA-g-PAM/graphite composite was an effective adsorbent for the uptake of acid violet 17 (Av-17) from an aqueous solution. The superior adsorption behavior was attributed to the presence of $-\text{NH}_2$ and $-\text{OH}$ groups in GA-g-PAM/graphite. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherms were used to describe the adsorption isotherm. The adsorption isotherm of the adsorbents fitted well with the Langmuir model with the maximum adsorption capacity (q_0) of 78.13 mg/g for GA-g-PAM/graphite. The efficiency of adsorption with time was described using pseudo first-order, pseudo second-order and intra particle diffusion kinetic models. The kinetic study revealed that the adsorption equilibrium was attained within 50 min. The thermodynamic analysis stated that the adsorption of dye is spontaneous, physical and endothermic in nature. Desorption results revealed that all the adsorbents exhibit excellent stability and remarkable regeneration ability.

Keywords: acid violet 17; adsorption; glucosamine; graphite; polyacrylamide.

1 Introduction

Acidic dyes with triphenylmethane groups are one of the most popular colors of dyes used on cotton, paper, leather, wool, silk and nylon. Acidic dyes are usually cheap, can be easily applied and they yield bright colors. Most of the dyes are hard to degrade by biological processes alone (1). Indeed, the presence of triphenylmethane dye of as little as 10–20 mg/l in water is visible and affects water transparency, which may have an impact on photosynthesis in aquatic plants (2). Chemical methods such as membrane separation, coagulation, oxidation reaction, adsorption, activated sludge treatment, photolytic degradation and ion exchange have been utilized for the treatment of dyes in effluents (3). Among various methods, adsorption has been found to be a potential technique due to the efficiency, selectivity, low cost, simplicity and possibility of recycling (4).

Numerous materials as adsorbents have been used to remove acid violet 17 (Av-17) dye from aqueous solutions such as red mud (5), orange peel (6), bagasse charcoal (7), cotton fiber (8), etc. Among them, polymeric materials are of key interest. Nowadays, biodegradable polymers are used as adsorbents for water treatment as they are eco-friendly in nature. The efficiency of polymers could be enhanced through chemical grafting with parental polymers (9, 10). The synthetic polymers provide more functional groups, adsorption capacity, desirable porosity, large surface area as well as thermal and mechanical stability (11). The synthetic polymers are able to modify their surface properties for the desired applications because of the variety of their functional groups (12).

Glucose is a biomaterial which contains active hydroxyl groups whereas glucosamine is a monomer which contains active hydroxyl groups and an amine group. The functional groups of these compounds give them the ability to bind with other compounds and adsorption potential towards many classes of pollutants (13). These functional groups serve as good coordination and reaction sites for the adsorption of several groups of pollutants (14). The chemical modification of glucose

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and glucosamine by grafting with polymers such as polyacrylamide (PAM) (15), polyethylenimine (16), poly(acrylic acid) (17), poly(methylacrylate) (18), etc., could improve its selectivity and adsorption properties. In that biodegradable PAM is one of the efficient adsorbent due to their highly active amide group which adsorbs anionic dye from aqueous mediums (19). The PAM grafted copolymers could serve as efficient adsorbents due to the incorporation of more functional groups like -NH_2 and -OH groups in the matrix which increases the coordination between adsorbents and pollutants (14).

In addition, graphite is introduced into the polymer matrix as a support because its crystalline nature reduces the attritional loss during regeneration (20), prevents agglomeration of the copolymer (21) and protrudes the functional groups of copolymers for the uptake of dye. Hence, grafting glucose and glucosamine with PAM onto the graphite support could enhance the adsorption capacity, selectivity and adsorption properties of each component.

In the present study, an attempt was made to prepare eco-friendly biodegradable graft copolymers such as glucose grafted PAM/graphite and glucosamine grafted PAM/graphite composite as adsorbents. The effect of experimental parameters and dye adsorption mechanism is explained based on the chemical, structural and morphological characterization. The adsorption capacity of PAM/graphite composites were compared and discussed with other adsorbents used for the removal of Av-17 dye. The results showed glucosamine grafted PAM/graphite (GA-g-PAM/graphite) composite as an effective adsorbent for the expulsion of Av-17 from an aqueous medium.

2 Materials and methods

2.1 Materials

Acrylamide, glucose and glucosamine were purchased from SRL Chemicals (India). Ammonium persulphate (APS) was obtained from Spectrum Chemicals (India). Graphite powder of 250 μm (98% pure) was procured from Loba Chemicals (India). Analytical grade acetone and ethanol were supplied from S.D Fine Chemicals (India). All chemicals were used without further purification. A commercial acidic dye, Av-17 was used as a target molecule for adsorption study, which has the following characteristics: molecular formula: $\text{C}_{41}\text{H}_{44}\text{N}_3\text{NaO}_6\text{S}_2$, $\text{MW} = 761.93 \text{ g/mol}$, $\lambda_{\text{max}} = 545 \text{ nm}$.

2.2 Preparation of glucose grafted PAM/graphite (Gu-g-PAM/graphite) and glucosamine grafted PAM/graphite (GA-g-PAM/graphite) composites

PAM/graphite composite was prepared as reported in an earlier work (22). Briefly, in a round bottom flask, 1.5 g of graphite and acrylamide monomer (0.01 mol) was dissolved in 10 ml of distilled water. The solution was heated at 75°C with constant stirring and then 0.01 g of APS was dissolved in 20 ml of distilled water was added drop wise. Then the reaction was continued for 8 h at the same temperature. Finally the reaction mixture was cooled, dispersed in acetone and the product thus obtained was dried, pulverized and sieved through a 125 μm sieve.

Synthesis of GA-g-PAM/graphite was done based on the literature (11, 23). Briefly, in a round bottom flask, 1.5 g of graphite and glucosamine (0.02 mol) was dissolved in distilled water. The solution was heated at 70°C with constant stirring. Then 0.01 g of APS was dissolved in 10 ml of distilled water which was added drop wise to the flask. The solution was pretreated with the initiator for 30 min with constant stirring and 0.01 mol of acrylamide monomer dissolved in 10 ml of distilled water was added drop wise. Then the reaction was continued for another 8 h at the same temperature. The reaction mixture was cooled, dispersed in acetone: ethanol mixture and the product was finally washed with acetone and dried at 60°C for 12 h, pulverized and sieved through a 125 μm sieve. To synthesis Gu-g-PAM/graphite, the same procedure was adopted, in which glucose was used instead of glucosamine.

A probable mechanism of graft copolymerization formation is based on the assumption that APS generates free radical sites on glucose and glucosamine. These free radicals react with acrylamide monomer and generate the graft copolymer (11). Figure 1 illustrates the synthetic route for the preparation of GA-g-PAM/graphite composite.

The percentage of grafting (% G) for the prepared compounds was calculated as (24):

$$\% \text{ G} = \frac{(\text{Wt. of the grafted product} - \text{Wt. of the glucosamine})}{\text{Wt. of the glucosamine}} \times 100 \quad [1]$$

The calculation revealed that the grafting percentage for Gu-g-PAM/graphite and GA-g-PAM/graphite was 69% and 71.2%, respectively.

Figure 1: Synthesis of GA-g-PAM on graphite support.

2.3 Characterization

Fourier transform infrared (FT-IR) spectra within the wave number range of $4000\text{--}500\text{ cm}^{-1}$ were obtained with a shimadzu IRPrestige-2 spectrometer (KBr pellets). For FT-IR study a little amount of potassium bromide salt and 5 mg of compound were taken to make a pellet. For nuclear magnetic resonance (NMR) study, the samples were prepared by dissolving 5 mg of compound in 5 ml of D_2O solvent. Then ^1H NMR and ^{13}C NMR spectrum was recorded on a JEOL model: ECX500, operating at 500 MHz in D_2O solvent. N_2 adsorption-desorption isotherms for the samples were measured at 77 K using a Quantachrome (Quadrasorb SI) adsorption analyzer. Before analysis, the samples (100 mg) were degassed for 8 h at 150°C . Prior to each adsorption measurement, the samples were degassed under vacuum at 473 K for 5 h.

The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method.

2.4 Adsorption experiments

A stock solution of 1000 mg/l of Av-17 dye was prepared. The molecular structure of Av-17 is shown in Figure 2. Batch adsorption experiments were carried out in a series

Figure 2: The molecular structure of acid violet 17.

of Erlenmeyer flasks containing 50 mg of PAM/graphite composites and 50 ml of Av-17 dye solutions of different concentrations (10–100 mg/l). The flasks were shaken in a temperature controlled orbital shaking incubator (REMI, RIS-24 BL) which was set at 170 rpm and was maintained at a temperature of 303 K for 100 min. For adsorption isotherms, dye solution of different concentration (10–100 mg/l) were incubated with adsorbent under agitation until equilibrium was achieved at three different temperatures namely 303 K, 313 K and 323 K. For kinetic studies, 50 mg of adsorbent was added to a 50 ml of 50 mg/l of dye at 303 K. An appropriate amount of dye solution was taken at designated times and the concentration of dye was detected by UV-Vis absorption spectroscopy. The effect of pH on adsorption was studied by adjusting the pH of solution from 2 to 11 using 0.01 M HCl and 0.01 M NaOH. The impact of initial dye concentration was investigated in the range of 25–100 mg/l. The effect of adsorbent dose was performed using 0.02–0.150 g of PAM/graphite composites keeping all the other parameters constant ($T = 303\text{ K}$, $\text{pH} = 7$, $t = 100\text{ min}$, dye = 50 ml of 50 mg/l).

The amount of dye adsorbed per gram of the composites was calculated by using the following equation [2]:

$$q_e = (C_o - C_e) \times V / W \quad [2]$$

where q_e is the amount of dye adsorbed mg/l by the adsorbent at equilibrium, C_o and C_e are the initial and equilibrium concentrations of dye solution mg/l, V is the volume of dye solution used (L) and W is the weight of adsorbent used (g).

3 Results and discussion

3.1 Characterization of PAM/graphite composites

The FT-IR spectrum for bare GA-g-PAM/graphite is as shown in Figure 3 (curve A). It shows a peak at 3294 cm^{-1}

Figure 3: The FT-IR spectrum for bare GA-g-PAM/graphite before and after adsorption.

(A) Before adsorption and (B) after adsorption of dye.

due to the -OH group of glucosamine. The band observed at around 3363 cm^{-1} was due to C-H stretching and that around 1612 cm^{-1} and 1542 cm^{-1} were due to amide-I and amide-II bands in GA-g-PAM/graphite composite. The peaks at 1250 cm^{-1} , 1095 cm^{-1} and 1180 cm^{-1} corresponds to $-\text{CH}_2\text{OH}$, C-O-C linkage and C-N-C linkage, respectively, which confirms the grafting of glucosamine onto PAM/graphite (25).

The comparison of FT-IR spectra provides structural information confirming the Av-17 dye uptake by GA-g-PAM/graphite. The IR spectrum of GA-g-PAM/graphite after adsorption is represented in Figure 3 (curve B). The spectrum shows all the relevant peaks for adsorbent GA-g-PAM/graphite in addition to that of the Av-17 dye peaks. Absorbance peaks at 3356 cm^{-1} , 2931 cm^{-1} , 2273 cm^{-1} , 1581 cm^{-1} , 1411 cm^{-1} , 1373 cm^{-1} and 910 cm^{-1} were assigned

to aromatic -C-H stretching, $-\text{CH}_2$ stretching, tertiary amine salt, aromatic -C=C- stretching, C-N stretching of tertiary amine, -S=O and -S-O stretching (2), respectively. Thus the spectrum confirms the uptake of Av-17 by GA-g-PAM/graphite.

^1H NMR spectra of GA-g-PAM/graphite represented in Figure 4 further confirmed the structure of the formed product. A signal at 4.96 ppm was due to H-1 of the glucosamine unit, where as the H-2 proton of the ring resonates at 3.31 ppm. The resonance of H-3–H-6 protons of the glucosamine unit appeared in the middle of the spectrum (δ 3.84–3.93) forming a group of broad, overlapping signals. The proton signal at 5.45 ppm was due to -NH proton of glucosamine. Additionally, peaks at 2.99–3.04 ppm and 3.48–3.53 ppm were due to the ethylene protons of PAM (26). Gu-g-PAM/graphite showed a doublet at 4.52–4.54 ppm for H-1 and a multiplet at 3.37–3.43 ppm for H3-H6 protons of glucose. Additionally, a doublet at 2.09–2.11 ppm was due to primary -OH of glucose. Amide -NH₂ protons are indicated by a doublet at 5.11–5.12 ppm. A triplet and a multiplet were observed at 3.11–3.35 ppm due to $-\text{CH}_2-\text{CH}_2-$ protons of PAM.

Figure 5 represents the ^{13}C NMR spectrum of GA-g-PAM/graphite composite, which contains additional peaks in comparison to the ^{13}C NMR spectrum of the bare PAM/graphite composite. The distinct peaks at δ = 93.16, δ = 89.58, δ = 72.03, δ = 72.43 and at δ = 89.58 ppm were attributed to the carbon atoms C-1, C-2, C-3, C-4 and C-5 of glucosamine, respectively. The carbon atom of $-\text{CH}_2\text{OH}$ gave a peak at 76.59 ppm. The peak at δ = 178.26 ppm was due to the amide carbonyl carbon, while ethylene carbon

Figure 4: ^1H NMR spectrum of GA-g-PAM/graphite composite.

Figure 5: ^{13}C NMR spectrum of GA-g-PAM/graphite composite.

atoms ($-\text{CH}_2-\text{CH}_2-$ groups) appeared at $\delta=54.74$ ppm and at $\delta=57.18$, respectively. The ^{13}C NMR spectrum of Gu-g-PAM/graphite gave a distinct peak at $\delta=96.31$ ppm for anomeric carbon atom (C-1). The C-2 carbon resonates at $\delta=92.49$ ppm. The peaks at $\delta=73.15$, 74.53 ppm were due to carbon atoms (C-3, C-4) connected by $-\text{OH}$ groups. The C-5 carbon atom was confirmed by a peak at 76.15 ppm, while carbon atom of $-\text{CH}_2\text{OH}$ by a peak at 71.83 ppm. Further the peak at $\delta=179.88$ ppm was due to amide carbonyl carbon. Peaks at $\delta=60.98$ ppm and at $\delta=69.99$ ppm

could be assigned to two carbon atoms ($-\text{CH}_2-\text{CH}_2-$ groups) of PAM (11).

The porosity and the specific surface area of the as prepared PAM/graphite composites were characterized by N_2 adsorption/desorption isotherms as shown in Figure 6A. All the three composites exhibited the combined characteristics of type-II and type-IV isotherms (27). The BET surface area, pore volume and pore diameter of the composites were calculated based on the BJH theory and the values are listed in Table 1. It was observed that the

Figure 6: N_2 adsorption-desorption isotherm.

(A) BET surface area of the composites (B) BJH pore size distribution of the composites.

Table 1: Textural parameters of the PAM/graphite, Gu-g-PAM/graphite and GA-g-PAM/graphite composite sample.

Adsorbent	Specific surface area (m ² /g)	Pore volume ml/g	Pore size (Å)
PAM/graphite	5.788	0.008	17.507
Gu-g-PAM/graphite	3.24	0.0056	16.136
GA-g-PAM/graphite	2.93	0.006	16.242

composites have a low surface area of 5.79 m²/g for PAM/graphite, 3.24 m²/g for Gu-g-PAM/graphite and 2.93 m²/g for GA-g-PAM/graphite. The pore volume and pore size of the PAM/graphite were found to be 0.008 ml/g and 17.507 Å, respectively, revealing that even after grafting with glucose and glucosamine there was no significant change in the pore volume and pore size for the grafted composites. This clearly indicates that the textural properties were not changed much by grafting. Furthermore, the corresponding pore size distribution curves were calculated by the BJH method and are shown in Figure 6B. For all materials, the maximum number of pore was in the range of 15–20 Å.

Even though the composites have a low surface area, the adsorption of Av-17 dye was high. This clearly indicates that the surface area does not play a vital role for adsorption, but the functional groups (-OH and -NH₂) present in the composites play a major contribution for the uptake of Av-17 dye from the solution.

3.2 Optimization of adsorption parameters

The immense effect of various parameters such as the temperature of the solution, pH, equilibrium time of adsorption, concentration of the dye and the adsorbent dose was optimized for the uptake of Av-17.

3.2.1 Effect of initial dye concentration

The amount of dye removal increases from 21.17 mg/g to 58.37 mg/g for PAM/graphite, from 22.99 mg/g to 63.10 mg/g for Gu-g-PAM/graphite and from 23.13 mg/g to 75.52 mg/g for GA-g-PAM/graphite, when the initial concentration of dye increased from 25 mg/l to 100 mg/l. This was due to the fact that availability of dye species was greater at a higher concentration as a result, it enhances the interaction between the dye and adsorbent. The effect of change in the initial concentration of the dye is represented in Figure 7.

Figure 7: Effect of initial dye concentration on the removal of dye.

3.2.2 Effect of contact time

Av-17 dye adsorption efficiency with time is demonstrated in Figure 8 for graphite, PAM, GA-g-PAM, PAM/graphite, Gu-g-PAM/graphite and GA-g-PAM/graphite composites. Pure PAM and GA-g-PAM without graphite are gels in nature and because of this the active sites are not well exposed to the pollutant resulting in less adsorption capacity. After the introduction of graphite into the PAM as a support and a reinforcing agent the composites revealed high adsorption capacity when compared to bare PAM and GA-g-PAM. The adsorption of Av-17 onto the composites was rapid at the initial stages until 50 min of contact time, thereafter; the adsorption rate became practically constant. It is obvious that at initial stages, a large number of vacant active sites are available for adsorption which gradually decreases with time. No change in the dye uptake was observed with further increase in time up to 100 min.

The intensifying of adsorption and consequently the attainment of equilibrium might be due to the limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of synthesized PAM/graphite composites (28). The Av-17 dye uptake increased from 49.52% to 61.90% for PAM/graphite with the adsorption capacity (q_e) of 28.47 mg/g, from 57.14% to 71.43% for Gu-g-PAM/graphite with q_e of 40.30 mg/g, from 79.05%

Figure 8: Adsorption efficiency of PAM/graphite composites with time.

to 90.28% for GA-g-PAM/graphite composite with q_e of 46.69 mg/g at contact time variation from 30 to 100 min. The optimum contact time for the removal of Av-17 was found to be 60 min.

3.2.3 Effect of temperature

The impact of temperature on adsorption was studied in the range of 303–323 K at 50 mg/l dye concentration. The dye molecules acquire sufficient energy to undergo interaction with active sites of the adsorbent with the increase in temperature, indicating that adsorption is endothermic in nature. When the temperature is increased, the amount (q_e) of dye removal increases from 28.47 mg/g to 31.43 mg/g for PAM/graphite, from 40.30 mg/g to 42.67 mg/g for Gu-g-PAM/graphite and from 46.69 mg/g to 47.87 mg/g for GA-g-PAM/graphite composites.

3.2.4 Effect of adsorbent dose

The effect of adsorbent dosage on the removal of Av-17 was studied for an initial dye concentration of 50 mg/l by

varying the dosage from 0.02 g to 0.150 g, keeping all other parameters constant ($T=303$ K, $pH=7$). For GA-g-PAM/graphite, the percentage of dye removal increases from 50.47% to 90.48% with an increase in adsorbent dosage. But the quantity of (q_e) of dye uptake increases from 39.71 mg/g to 46.69 mg/g with the decrease of adsorbent dosage. This is due to the fact that all the active sites of adsorbents could be effectively utilized under low adsorbent dosage. Thus, further experiments were carried out using 0.05 g adsorbent in order to optimize other adsorption parameters. Figure 9 depicts the effect of adsorbent dose on the removal of dye from aqueous solution.

3.2.5 Effect of pH on adsorption

The effect of pH on the adsorption of Av-17 was analyzed at different pH values ranging from 2 to 12. pH of the dye solution and was adjusted using 0.01 M hydrochloric acid and 0.01 M sodium hydroxide. The influence of pH on the dye uptake could be explained on the basis of pH zero point charge (pH_{zpc}) (29, 30). It was found to be 3.2 for PAM/graphite, 3.8 for Gu-g-PAM/graphite and 3.9 for GA-g-PAM/graphite composites, implying that at acidic pH, the electrostatic attraction increases between the polymer composites and the dye which results in higher adsorption capacity. The fact is explained by equations [2] and [3] and the Figure 10

Figure 9: The effect of adsorbent dose for the removal of Av-17 dye.

Figure 10: Effect of pH on the removal dye by the PAM/graphite composites.

depicts the effect of pH on the adsorption capacity of composites. However, at pH above 4, the surface charge of polymer composites become negative, which hinders the adsorption due to repulsion between dye and adsorbent resulting in low adsorption capacity. The adsorption capacity (q_e) decreases from 30.48 to 11.56 mg/g for PAM/graphite, 40.54–20.43 mg/g for Gu-g-PAM/graphite and 48.82–26.35 mg/g for GA-g-PAM/graphite composite with an increase of pH from 2 to 12. An appreciable amount of adsorption in the pH range of 4–12 reveals strong involvement of physical forces such as hydrogen bonding and Van der Waals forces in the adsorption process (31):

where R is the alkyl group of the composites.

3.2.6 Adsorption mechanism

The adsorption of Av-17 dye is affected by various factors like temperature, pH, equilibrium time, concentration of the dye and the adsorbent dose. Thus, from the experimental results, the ascertained optimum conditions for the maximum Av-17 dye adsorption were 50 mg/l dye

concentration with 0.05 g/50 ml adsorbent dose at pH-3 for a time of 60 min. The possible adsorption mechanism between the Av-17 and GA-g-PAM/graphite composite is described in Figure 11.

The hydroxyl group at C2 of Gu-g-PAM/graphite is replaced by $-\text{NH}_2$ group in GA-g-PAM/graphite. The adsorption capacity, q_e for GA-g-PAM/graphite and Gu-g-PAM/graphite were found to be 48.82 mg/g and 42.31 mg/g, respectively. More amino groups present in GA-g-PAM/graphite enhance the adsorption efficiency of GA-g-PAM/graphite than Gu-g-PAM/graphite. The $-\text{NH}_2$ in GA-g-PAM/graphite gives more q_e than the $-\text{OH}$ in Gu-g-PAM/graphite. The enhanced adsorption capacity of GA-g-PAM/graphite composite was attributed to the increased electrostatic interaction between sulfonate groups (negatively charged) of dye and amino groups (positively charged) of GA-g-PAM/graphite than hydroxyl groups present in the Gu-g-PAM/graphite, indicating that amino group has strong interaction with dye when compared hydroxyl groups (14). Thus the incorporation of more amino groups plays a vital role in the adsorption process. Apart from electrostatic interaction, van der Waals forces and hydrogen bonding between functional groups of dye and GA-g-PAM/graphite composite also influences the adsorption process. Graphite used as a support for the dispersion of grafted copolymers, decreases the aggregation of copolymers, resulting in the exposure of more active sites which interacts with the pollutant enhancing adsorption.

Figure 11: Adsorption mechanism between Av-17 and GA-g-PAM/graphite composite.

Table 2: Kinetic parameters for the adsorption of Av-17 by the composites.

Adsorbent	Concentration (mg/l)	Pseudo-first order			Pseudo-second order				Intra particle diffusion		
		$K_1 \cdot 10^{-2}$ (min^{-1})	q_e (mg g^{-1})	r_1^2	$K_2 \cdot 10^{-3}$ ($\text{g mg}^{-1} \text{min}^{-1}$)	q_e^a (mg g^{-1})	q_e^b (mg g^{-1})	r_2^2	K_t ($\text{g mg}^{-1} \text{min}^{-1/2}$)	C	r_3^2
PAM/graphite	25	6.285	28.214	0.9680	6.007	21.17	25.91	0.9982	2.5535	5.549	0.9664
	50	6.722	14.170	0.9306	5.573	34.39	36.32	0.9952	3.4583	8.638	0.9268
	75	5.909	41.839	0.9536	4.348	44.01	46.51	0.9949	4.4855	10.022	0.9643
	100	6.174	60.833	0.9233	3.367	58.37	62.85	0.9943	7.6424	12.545	0.9719
Gu-g-PAM/graphite	25	5.711	30.151	0.9360	1.984	22.40	23.31	0.9916	2.1352	5.040	0.9333
	50	6.932	54.815	0.9512	1.719	40.3	43.29	0.9816	6.4110	7.804	0.9864
	75	5.919	41.841	0.9536	1.594	46.38	45.98	0.9970	3.9529	8.122	0.9952
	100	6.333	64.565	0.9312	1.440	63.10	61.73	0.9947	6.9945	16.433	0.9964
GA-g-PAM/graphite	25	7.264	28.914	0.9800	11.658	23.13	23.74	0.9985	3.8698	2.797	0.9335
	50	8.164	59.234	0.9664	5.152	47.87	45.35	0.9951	6.9616	4.027	0.9472
	75	6.812	63.155	0.9844	3.449	64.71	61.50	0.9945	8.3403	6.206	0.9437
	100	7.022	71.077	0.9883	2.363	75.52	79.74	0.9998	9.1210	10.779	0.9558

^aExperimental.^bCalculated.

3.2.7 Adsorption kinetics

Kinetic models were employed to correlate the experimental adsorption data. It is one of the important characteristics that define the efficiency of adsorption with time. To investigate the adsorption process pseudo first-order, pseudo second-order and intra particle diffusion models were used. The pseudo first order kinetic model is expressed as (32).

$$\log (q_e - q_t) = \log C_e - k_1 t / 2.303 \quad [5]$$

As q_e and q_t (mg/g) are adsorption capacities at equilibrium and at time t (h), respectively. k_1 (min^{-1}) represents the first-order rate constant. The experimental (q_e , exp) and calculated (q_e , cal) values and correlation coefficients related to Lagergren's plots of composites are listed in Table 2. However, the experimental data deviated considerably from the calculated data. The low correlation coefficients r^2 reveals poor agreement with pseudo first-order kinetics.

The pseudo second-order kinetic plot for the adsorption of Av-17 can be written as (33)

$$t/q_t = 1/k_2 q_e^2 + 1/q_e \times t \quad [6]$$

where k_2 is the second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). The plot t/q_t vs. t is linear for all initial dye concentrations. The value of k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) decreases with the increase of dye concentration from 25 to 100 mg/l which suggests a decrease in the available vacant sites of an adsorbent for adsorption (34). From Table 2, it is evident that the higher value of correlation coefficients $0.9816 < r^2 < 0.9998$

implies better fitness of this model. Also, the experimental $q_{e,\text{exp}}$ value is in good agreement with calculated $q_{e,\text{cal}}$ value which suggests that adsorption of Av-17 onto the composites follows pseudo second-order kinetics. Figure 12 represents the pseudo second-order kinetic model for the adsorbent GA-g-PAM/graphite composite.

The kinetic data were also evaluated using the Weber and Morris intra particle diffusion equation and expressed as (35, 36):

Figure 12: Pseudo second-order kinetics for the GA-g-PAM/graphite.

$$q_t = k_t \times t^{1/2} + C \quad [7]$$

where q_t is the amount of dye adsorbed (mg/g) at time t (min), k_t is the intra particle diffusion rate constant ($\text{g mg}^{-1} \text{min}^{-1/2}$) and C is a constant. If the plot q_t vs. $t^{1/2}$ is linear and passes through the origin (0, 0), then the intra particle diffusion step can be considered as the rate controlling step. If the plots are multilinear, then there will be two or more rate determining steps involved in the adsorption process (36). The intra particle diffusion model fit and the parameters are represented in Figure 13 and Table 2. It shows the deviation of lines from the origin suggesting the involvement of an intraparticle diffusion process (37) and it was not the sole rate determining process (38). From Figure 13, the intraparticle diffusion plot shows three linear regions in the adsorption of Av-17 onto PAM/graphite composites, which indicated the involvement of several steps in adsorption. The initial linear region described the boundary layer diffusion of Av-17 dye, whereas the second stage can be attributed to the gradual adsorption where the intraparticle diffusion of dye molecules through the pores of composites occurs. The third region is the final equilibrium stage where the intraparticle diffusion process becomes slow due to the decreased concentration of Av-17 in the aqueous solution and decreased adsorption sites

(39). The observed multilinearity also confirms that intraparticle diffusion is not the only rate determining step (40). Similar results were reported for the removal of pb(II) by mansonia wood dust (41) and by PAM zirconium (IV) iodate (37). The results of our study reveals that the intra particle diffusion also has some contribution (42). The r^2 values from 0.9268 to 0.9964 implies the applicability of intra particle diffusion (43).

The values of intercept give an idea about the thickness of the boundary layer, i.e. as the intercept increases the resistance to the external mass transfer increases (34). As seen in Table 2, the C values increased from 5.55 to 12.54 mg/l for PAM/graphite, 5.04–16.43 mg/l for Gu-g-PAM/graphite and 2.79–10.78 mg/l for GA-g-PAM/graphite at 303 K. Furthermore, based on the correlation coefficient (r^2) values the dye adsorption fitted with pseudo second-order kinetic model followed by intra particle diffusion model.

3.2.8 Adsorption isotherms

Adsorption isotherm was studied by adding 0.05 g of adsorbents to the 50 ml of 50 mg/l of the dye solution at temperatures 303 K, 313 K and 323 K until equilibrium is established. In this study, Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherms were used to describe the adsorption isotherm and equilibrium data. The Langmuir isotherm is used in the form of equation [8]. According to the Langmuir isotherm, all adsorbent sites are equivalent, adsorption occurs at a specific homogeneous site within the adsorbent and there are no interactions between adsorbate molecules (44):

$$C_e / q_e = 1 / Q_{\max} K_L + C_e / Q_{\max} \quad [8]$$

where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g). C_e is the concentration at equilibrium (mg/l) and $Q_{\max}$ is the maximum adsorption capacity of the adsorbent (mg/g). K_L is the Langmuir adsorption constant (l/mg). The maximum adsorption capacity $Q_{\max}$ increases with an increase of solution temperatures from 303 K to 323 K. It clearly indicates that the adsorption of Av-17 dye by the composites is an endothermic process. Table 3 summarizes various isotherm parameters at different temperatures along with the isotherm constants. Figure 14 represents the Langmuir isotherm's fit for the adsorbent GA-g-PAM/graphite composite.

To determine the favorability of adsorption process the dimensionless separation factor " R_L " is calculated as follows

Figure 13: Intra particle diffusion model for GA-g-PAM/graphite composite.

Table 3: Summary of various isotherm parameters for the adsorption of Av-17 at 303 K, 313 K and 323 K.

Adsorbent	T (K)	Langmuir isotherm				Freundlich isotherm			Dubinin-Radushkevich isotherm			
		q_0 (mg/g)	b (l/mg)	r^2	R_L	K_f	n	r^2	q_0 (mg/g)	β (mol ² kJ ⁻²)	E (kJ mol ⁻¹)	r^2
PAM/graphite	303	40.16	9.20	0.9891	0.0022	6.981	2.375	0.8598	30.44	2.247	0.472	0.9774
	313	40.98	7.48	0.9933	0.0027	8.257	2.545	0.8750	31.37	1.331	0.613	0.8814
	323	41.32	4.79	0.9925	0.0042	14.051	3.877	0.9231	31.47	2.867	0.418	0.7542
Gu-g-PAM/graphite	303	56.18	3.30	0.9595	0.0060	23.618	4.628	0.9089	42.86	4.605	0.330	0.5560
	313	56.50	2.73	0.9659	0.0073	26.205	5.035	0.9212	44.59	4.620	0.329	0.6109
	323	58.14	2.63	0.9541	0.0076	28.418	5.418	0.8311	51.78	9.818	0.226	0.5898
GA-g-PAM/graphite	303	76.10	1.14	0.9941	0.0172	53.951	10.501	0.9361	56.05	1.338	0.611	0.4430
	313	77.52	0.88	0.9956	0.0221	56.624	10.689	0.9583	48.43	9.479	0.230	0.1090
	323	78.13	0.58	0.9950	0.0335	57.137	11.748	0.9538	47.23	3.782	0.364	0.1229

Figure 14: The Langmuir isotherm for the adsorption of Av-17 on GA-g-PAM/graphite composite.

$$R_L = 1 / (1 + K_L C_0) \quad [9]$$

where K_L is a Langmuir adsorption constant. The obtained R_L value was found to be close enough to zero, which clearly states that the adsorption process is favorable for all the adsorbents (45).

The adsorption capacity of GA-g-PAM/graphite is compared with other adsorbents used for the removal of Av-17 dye from aqueous medium. GA-g-PAM/graphite exhibited higher adsorption capacity over other adsorbents. This higher adsorption capacity is obtained within 50 min of contact time for 50 ml of 50 mg/l of dye solution

using 0.05 g of adsorbent. Whereas for other adsorbents to obtain the same adsorption capacity, higher adsorbent dose and more contact time are needed (5–7, 46–48). The adsorption capacity of various adsorbents are compared with PAM/graphite composites and listed in Table 4.

The Freundlich isotherm model is used to describe a heterogeneous system and is expressed by the following equation [10]

$$\log q_e = \log k_f + 1/n \log C_e \quad [10]$$

where k and n are Freundlich constants related to adsorption capacity and intensity of the adsorption. The value of Freundlich constant k_f and n increases with increase in temperature from 303 K to 323 K indicating that adsorption is favorable at a higher temperature (43). However, the k_f values of bare PAM/graphite composite is lower than glucose grafted and glucosamine grafted PAM/graphite composites, which specifies that grafting increases the adsorption capacity (3).

D-R isotherm states the nature of the adsorption process and the model is represented as

$$\ln q_e = \ln q_0 - \beta \epsilon^2 \quad [11]$$

Table 4: Comparison of adsorption capacities of various adsorbents for the uptake of Av-17 from aqueous medium.

Adsorbents	q_0 (mg/g)	References
Red mud	1.37	(5)
Penicillium	4.32	(47)
Coir pith	8.06	(48)
Banana pith	13.10	(46)
Orange peel	19.88	(6)
Bagasse charcoal	38.32	(7)
PAM/graphite	40.16	Present study
Gu-g-PAM/graphite	56.18	Present study
GA-g-PAM/graphite	76.10	Present study

where q_e is the amount of dye adsorbed per unit dosage of the adsorbent (mg/g), q_d the monolayer capacity and β is the activity coefficient related to mean sorption energy and ε is the Polanyi potential expressed as

$$\varepsilon = RT \ln (1 + 1/C_e) \quad [12]$$

The mean sorption energy, E (kJ/mol) is determined by

$$E = 1/(2\beta)^{1/2} \quad [13]$$

If E lies between 0 and 8 kJ/mol, the adsorption is physisorption and if it is between 9 and 16 kJ/mol then the adsorption is chemisorption. In the present study, we observed a low mean sorption energy which clearly indicates that adsorption of Av-17 onto the composites is due to physisorption between the dye and the adsorbent (34).

By comparing Langmuir, Freundlich and D-R isotherm models' results, presented in Table 3, it is concluded that the Langmuir isotherm model is the suitable model for the adsorption process and the Langmuir plot, C_e/q_e vs. C_e at different temperatures is found to be linear.

3.2.9 Adsorption thermodynamics

The experimental data obtained by the effect of temperature were analyzed under optimized conditions. It was observed that adsorption of Av-17 onto PAM/graphite, Gu-g-PAM/graphite, GA-g-PAM/graphite composites increased with the increase of temperature from 303 K to 323 K. Thermodynamic parameters associated with adsorption were determined by using equations [14] and [15] (49):

$$\ln K = \Delta S/R - \Delta H/RT \quad [14]$$

$$\Delta G = -RT \ln K \quad [15]$$

where ΔG is change in Gibbs free energy (J/mol) R is the universal gas constant (8.314 (J/K mol) T is the temperature (K), ΔH is change in enthalpy (J/mol), K equilibrium constant, ΔS change in entropy (J/K mol).

The thermodynamic parameters calculated from the plot $\ln K$ vs. $1/T$ (Figure 15) are given in Table 5. From the Table 5, we could find that at all temperatures, ΔG is negative which suggests the spontaneous nature of adsorption and the values of ΔG become more negative with the rise of temperature manifest that lower temperature makes the adsorption easier (37, 50). The positive values of enthalpy and entropy changes imply the endothermic nature of adsorption and increased a degree of internal freedom of the system during adsorption, respectively (39, 51).

Figure 15: Thermodynamic study of the adsorption of Av-17 on GA-g-PAM/graphite.

The values of ΔH also give an idea about the type of adsorption. The enthalpy for physisorption is in the range of 2.1–20.9 kJ/mol, while the enthalpy for chemisorption is in the range of 80–200 kJ/mol. The enthalpy values for the adsorption of Av-17 onto composites falls in the range from 3.04 to 14.73 kJ/mol which clearly shows that adsorption between dye and adsorbents are physical in nature. The same result is also attained in D-R isotherm.

3.3 Desorption studies

To determine the reusability of the polymer composites as adsorbents and also to understand the mechanism of adsorption eight consecutive adsorption-desorption cycles were performed with 0.1 N HCl and 0.1 N NaOH as stripping solutions. Figure 16 shows simultaneous adsorption-desorption of dye onto GA-g-PAM/graphite. The composites loaded with dye were placed in 0.1 N NaOH as the stripping solution and stirred for 2 h at 303 K and final dye concentration is determined (52). The amount of dye desorbed from the loaded polymer composites increases with an increase of pH from 2 to 11 and there is no considerable change in desorption above pH 11 for all the adsorbents. The percentage of desorption observed at pH 11 was 87.63% for GA-g-PAM/graphite, 69.32% for Gu-g-PAM/graphite and 49.93% for PAM/graphite in the first cycle. The regeneration efficiency was decreased by

Table 5: Thermodynamic parameters for the adsorption of dye Av-17.

Adsorbent	C_0	K			ΔG (kJ/mol)			ΔH (kJ/mol)	ΔS (J K ⁻¹ mol ⁻¹)
		303 K	313 K	323 K	303 K	313 K	323 K		
PAM/graphite	60	0.94	1.05	1.19	-2.63	-3.59	-6.26	9.82	31.82
	80	0.66	0.73	0.79	-2.58	-3.22	-3.85	7.55	21.46
	100	0.55	0.59	0.62	-0.70	-0.98	-1.37	5.31	12.49
Gu-g-PAM/graphite	60	1.10	1.20	3.34	-2.76	-3.24	-8.68	6.28	35.71
	80	0.43	0.49	1.69	-1.08	-1.32	-4.25	3.55	18.42
	100	0.44	0.45	1.64	-1.10	-1.31	-4.23	3.04	16.77
GA-g-PAM/graphite	60	3.36	3.72	3.72	-8.47	-9.68	-9.99	14.73	77.04
	80	1.62	1.79	1.91	-4.07	-4.65	-5.14	12.05	53.28
	100	1.09	1.16	1.26	-2.76	-3.02	-3.38	6.66	31.03

Figure 16: Simultaneous adsorption-desorption cycles using GA-g-PAM/graphite.

4% in the first cycle and for further three cycles it revealed less than 7% decrease for GA-g-PAM/graphite. Furthermore, the regeneration efficiency was maintained at 78.65% for up to eight cycles. The regeneration studies showed that adsorption capacity q_e decreases from 48.82 to 42.04 mg/g for the adsorbent GA-g-PAM/graphite after three cycles of adsorption-desorption compared with original adsorption capacity. The effect of pH on desorption of Av-17 indicates that 0.1N NaOH with a pH range of 11 is a better reagent for all the adsorbents. The higher percentage of desorption will be helpful for the recycling of spent adsorbent and also indicates that physical forces play the predominate role in

the removal of dye. The amount of desorption was calculated by using the following equation (53).

$$\% \text{ Desorption} = \frac{(\text{Amount released to solution (mg/l)} \times 100)}{\text{Total adsorbed (mg/l)}}$$

4 Conclusion

Functionalized PAM/graphite composites were prepared as adsorbents by grafting with glucose and glucosamine for the removal of Av-17 dye. The structural characterization of the composites was done using techniques such as IR, ¹H NMR and ¹³C NMR and BET analysis. GA-g-PAM/graphite had shown excellent adsorption efficiency compared to graphite, PAM, GA-g-PAM, PAM/graphite and Gu-g-PAM/graphite. This is due to its functional groups (-NH₂ and -OH) and its effective interaction with dye molecules. The kinetic data were in good agreement with the pseudo second-order model. The equilibrium data were fitted well with the Langmuir isotherm. The thermodynamic study reveals that the adsorption of Av-17 was found to be endothermic and spontaneous in nature for all the composites. The adsorption capacity of adsorbents is found to be more at acidic pH for all the composites. The desorption studies indicate the reusability of the composites. The results showed that GA-g-PAM/graphite was a suitable material for removal of Av-17 dye from aqueous solution.

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