Indian Journal of Chemical Technology
Vol. 28, November 2021, pp. 674-683

# Functionalized polyacrylamide/graphite composites - Biodegradable adsorbents for the removal of synthetic dye from aqueous solution

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*Received 10 August 2020; accepted 6 October 2021*

Eco friendly, biodegradable functionalized polyacrylamide/graphite composites have been used to adsorb synthetic dye from aqueous medium. The polymer composites have been synthesized and characterized with FT-IR, $^1$H and $^{13}$C NMR. The composite's adsorptive features have been analyzed using different parameters. The efficiency of adsorption process is determined using kinetic, equilibrium and thermodynamic analysis. The equilibrium uptake capacity was obtained from Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich models. The correlation coefficients indicate that the Langmuir model show satisfactory fit for the uptake of dye. The adsorption process follows pseudo second order in addition to intraparticle diffusion model with a good correlation coefficient. The thermodynamic parameters ΔG, ΔH and ΔS show that the adsorption process is spontaneous ($\Delta G < 0$), endothermic ($\Delta H > 0$) and had decreased entropy ($\Delta S > 0$). The equilibrium and kinetic experiments confirm that the temperature and *p*H play an important role i.e., the dye uptake increases with increased temperature and decreased *p*H. FTIR and desorption studies confirm the involvement of functional groups in adsorption mechanism.

**Keywords:** Isotherm, Kinetics, Reactive red M5B, Polyacrylamide, Thermodynamics

More than ten thousand diverse marketable pigments and dyes are available in market and more than $7\times10^5$ metric tons are produced throughout the world[1]. Among them, reactive dyes are extensively used in textile industry because of their wide variety of colour shades, brilliant colours, high wet fastness profiles, ease of application, being easily water soluble, covalent bonding with cellulose fibers and simple application technique[2]. About 50% of reactive dyes used in dyeing operations are released as effluents and hence colour removal from textile effluent is one of the major environmental concerns as the discharge of coloured wastewater into water bodies can trigger many significant problems, such as increasing toxicity, decreasing light penetration[3] and so on.

It is however difficult to treat dye containing wastewater as they are recalcitrant organic molecules, resistant to aerobic digestion, stable to light and oxidizing agents. Despite the existence of a wide range of wastewater treatment techniques, there is no single process capable of adequate mineralization of coloured effluents, mainly due to their complex nature[4]. Though many methods have been proposed for the expulsion of dye from aqueous medium viz., advanced oxidation, photocatalysis, precipitation, filtration, electrocoagulation and membrane process, etc., some of these methods have the limitations of being time consuming, costly, complex, and less sensitive[5]. However adsorption is one of the best methods for removing dyes due to their merits of simplicity, high effectiveness, reusability, cost effective and ease of process[6].

A considerable amount of work has been carried out regarding the expulsion of reactive dyes using various adsorbents viz., graphite oxide/chitosan composite[7], activated carbon from Pinus sp[8], starch/polyaniline composite[9], organozeolite modified CTAB[3], modified zeolite[2], tannery sludge[4] etc., Among them, the polymeric composites possess some specific characters over other adsorbents such as high porosity, high surface area, high affinity towards charged species, high stability with organic solvents, adoption to extreme experimental conditions, biodegradability and being nontoxic to the environment[5].

Polyacrylamide (PAM) with amide group is widely used as the active site of adsorbent to eliminate anionic dye from aqueous medium. They are stable and biodegradable in nature. PAM is a gel and hence swells. It was reported that swollen gels could be strengthened without decreasing their sorption ability via incorporation with the supporting materials[10]. Generally, carbon material is used in composites as a support; specifically graphite is widely used because of its reduced attritional loss during recycling. Graphite is introduced as a support into the polymer matrix as it is a viable and inexpensive reinforcing agent[7]. Though graphite particles are physically attached to the polymer network, they act as an active reinforcing agent and contribute significantly to the elastic modulus of gel.

Recently, it is reported that the adsorption capability of adsorbents could be enhanced by the modification of adsorbents via physical and chemical process[11]. Hence to improve the adsorption capacity of PAM/graphite composite, PAM surface is functionalized with biomaterials like glucose and glucosamine via grafting. Functionalized PAM copolymers could encompass the active sites of glucose and glucosamine to the aqueous solution. The amino and hydroxyl groups present in the grafted composites can serve as active/adsorption site for the adsorption of several groups of pollutants[12].

Objective of our work was to develop simple, biodegradable and environmentally benign adsorbent for the removal of synthetic dye reactive red M5B (RRM5B) from aqueous solution. Glucose and glucosamine grafted PAM/graphite composites (Gu-g-PAM/graphite and GA-g-PAM/graphite) as adsorbents were utilized. It was observed that grafted polymers show noticeably improved adsorption capacities for RRM5B dye when compared to the bare PAM/graphite. The effects of various parameters, namely, contact time, initial concentration, solution *p*H, and temperature were investigated. Adsorption isotherms, thermodynamics and kinetics of the adsorption process were also systematically analyzed.

## Experimental Section

### Materials

A commercial RR-M5B dye was used as a target molecule, which has the following characteristics: Molecular formula: $C_{19}H_{10}Cl_2N_6Na_2O_7S_2$, MW = 615.34 g/mol, $\lambda_{max} = 538$ nm.

### Preparation of Gu-g-PAM/Graphite and GA-g-PAM/graphite composites

Functionalized PAM/graphite composites such as Gu-g-PAM/graphite and GA-g-PAM/graphite composites were synthesized by the same technique as reported in earlier study. The synthesis of Gu-g-PAM/graphite is as follows. Graphite (1.5 g) and glucose (0.02 mole) dissolved in 10 mL of distilled water was taken in a round bottom flask. Then ammonium persulphate (0.01 g) dissolved in 10 mL of distilled water was added slowly with constant stirring at 70°C. Thereupon 10 mL of acrylamide (0.01 mole) was added to the flask and the reaction was continued for 8 h. Then the reaction mixture was cooled, dispersed in acetone: ethanol mixture, dried, pulverized and sieved through a 125 µm sieve. The same procedure was followed for the synthesis of GA-g-PAM/graphite composite[13].

### Characterization

Fourier transform infrared (FT-IR) spectrum within the wave number range of 4000 - 500 $cm^{-1}$ were obtained with a Shimadzu IR Prestiage-2 spectrometer (KBr pellets). $^{1}H$ and $^{13}C$ NMR spectrum was recorded in $D_2O$ solvent using a JEOL; model: ECX500 operating at 500 MHz.

### Adsorption studies

The adsorption ability of composites was evaluated by using RR-M5B dye. Adsorption experiments were conducted in a temperature controlled orbital shaker (REMI, RIS-24 BL) set at 170 rpm. The studies were performed by varying the experimental parameters like temperature, solution *p*H, contact time, adsorbate concentration and adsorbent dose. The effect of temperature change was performed at three temperatures: 303, 313 and 323 K. To explore the effect of *p*H on adsorption, the solution's *p*H was varied from 2 to 11 using 0.1 N NaOH and 0.1 N HCl. For kinetic studies, the samples were withdrawn at the predetermined time intervals and the concentration of dye solution was determined. The concentration of adsorbate dye varied from 10 to 100 mg/L and the dose of adsorbent varied from 0.01 to 0.120 mg.

The percentage of dye removal and the amount of dye adsorbed per gram of the composites was calculated as

$$\text{Removal }(\%) = (C_i - C_e) / C_i \quad \ldots(1)$$

$$q_e = (C_i - C_e) \times V/W \quad \ldots(2)$$

where $C_i$ and $C_e$ are the initial and equilibrium dye concentration (mg/L) respectively, $q_e$ is the amount of dye adsorbed (mg/g) by the adsorbent at equilibrium, V the volume of dye solution (L) and W the weight of polymer composite used (g).

## Results and Discussions

### Characterization of adsorbents

The FT-IR spectrum of Gu-g-PAM/graphite composite exhibited further peaks in addition to bare PAM/graphite peaks. Figure 1 depicts the FT-IR spectrum of Gu-g-PAM/graphite. In Gu-g/PAM spectrum, the peak at 3176 $cm^{-1}$ owing to -OH groups of glucose. The band at around 2930 - 3300 $cm^{-1}$ was attributed to C-H stretching of grafted composite. The peaks around 1616, 1600 and 1539 $cm^{-1}$ represent the presence of amide-I, amide-II, and amide-III bands in grafted composite respectively. The peak due to $-CH_2OH$ of glucose appeared at 1317 $cm^{-1}$. The peak at 1010 $cm^{-1}$ attributed to C-O-C linkage of glucose. Similar spectrum is obtained for GA-g-PAM/graphite also. In addition, GA-g-PAM/graphite shown peak at 1182 $cm^{-1}$ corresponds to C-N-C linkage of glucosamine.

$^1$H NMR spectra of Gu-g-PAM/graphite show a doublet at 4.52 - 4.54 ppm for H1 and multiplet at 3.37- 3.43 ppm due to H3-H6 protons of glucose. In addition, it gave doublet at 2.09 - 2.11 ppm due to primary -OH of glucose. Amide $-NH_2$ protons resonates at 5.11-5.12 ppm. Ethylene protons of polyacrylamide showed a triplet and multiplet at 3.11-3.35 ppm. Similar spectrum is obtained for GA-g-PAM/graphite. In addition, proton signal at 5.45 ppm was observed for -NH proton of glucosamine[14].

$^{13}$C NMR spectrum of Gu-g-PAM shows. Distinct peak at $\delta = 96.31$ ppm is due to anomeric carbon atom (C1). The peaks at $\delta = 92.49$, $\delta = 73.15$, $\delta = 74.53$ and $\delta = 76.15$ ppm were due to the carbon atoms of C2, C3, C4 and C5 of glucose respectively. The carbon atom of $-CH_2OH$ gave a peak at 71.83 ppm. The peak at $\delta = 179.88$ ppm was due to carbonyl carbon. Peaks at $\delta = 60.98$ and $\delta = 69.99$ ppm could be assigned to ethylene carbon atoms ($-CH_2-CH_2-$ groups) of polyacrylamide[15]. The same results were observed for GA-g-PAM/graphite[14].

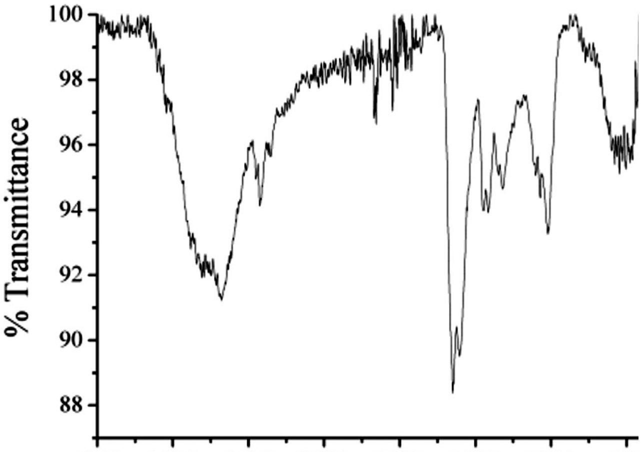

Fig. 1 — FT-IR Spectrum (a) Gu-g-PAM/graphite

### Optimization of adsorption parameters

The effect of various factors like temperature, time of adsorption, concentration of adsorbate, *p*H of dye solution and the dose of adsorbent was optimized for the uptake of RR-M5B by polymer composites.

### Effect of initial dye concentration

The effect of dye concentration was analyzed in the concentration range of (10 to 100 mg/L) with 0.05 g of composite in 50 mL solution for 100 min at 303 K. The result reveals that when the initial concentration of dye increases from 10 to 100 mg/L, the adsorption capacity increases from 6.27 to 41.78 mg/g, 7.05 to 55.03 mg/g and 8.53 to 60.92 mg/g for PAM/graphite, Gu-g-PAM/graphite and GA-g-PAM/graphite respectively is depicted in Figure 2a (supporting information). Whereas the removal percentage decreases because at higher concentration, steric repulsion between the solute molecules slow down the adsorption process, resulting in the decreased removal rate[12].

### Effect of contact time

The effect of contact time on adsorption was analyzed by using 50 ml of 50 mg/L RR M5B dye with 0.05 g of composite. The contact time varied from 0 to 100 min and it was found that adsorption of RR-M5B is rapid during the first 30 min and gradually increased until 80 min of contact time, thereafter, the adsorption rate became practically constant. This is obvious that at the initial stages of adsorption, the availability of adsorption sites on PAM/graphite composites is more. Adsorption capacity of polymer composites with time is depicted in Figure 2b (supporting information). The RR-M5B dye uptake was increased from 18.42 to 50 % for PAM/graphite with adsorption capacity ($q_e$) of 24.35 mg/g, from 28.94 to 63.16 % for Gu-g-PAM/graphite with $q_e$ of 33.01 mg/g, from 34.21 to 71.05 % for GA-g-PAM/graphite with ($q_e$) of 37.43 mg/g with contact time variation from 10 to 100 min. Therefore, 100 min shaking time was fixed as the optimum contact time for further studies.

### Effect of adsorbent dose

The adsorbent dose was varied from 0.02 g to 0.120 g with 50 mL of 50 mg/L dye concentration, keeping other parameters constant. Adsorbent dose

(0.05 g) shows prevailing removal of dye, while higher adsorbent doses also show slightly enhanced removal but not much variation. For GA-g-PAM/graphite the percentage of dye removal increased from 15.67 to 74.82 % and the quantity ($q_e$) of dye uptake increased from 8.25 to 38.21 mg/g with increase in adsorbent dosage. Hence, 0.05 g of adsorbent dose was finalized as an optimum dosage for further experiments.

**Effect of *p*H on adsorption**

Effect of *p*H on the adsorption of RR-M5B by the composites was analyzed in the *p*H range of 2 to 11. The zero point charge ($pH_{zpc}$) of the adsorbents were determined to investigate the surface behaviour for the adsorption of RR-M5B[16]. The $pH_{zpc}$ of PAM/graphite, Gu-g-PAM/graphite and GA-g-PAM/graphite composites were found to be 3.2, 3.8, and 3.9 respectively.

With increasing *p*H, the adsorption capacity of PAM/graphite composites exhibits downward trend. Marginal decrease in adsorption capacity has been observed with the *p*H change from 2 to 7. Such results could be explained by the fact that, at $pH < 4$ the surface charge of adsorbents are positive while the $-SO_3$ groups of dye molecules are negative or neutralized ($-SO_3H$). Since the *p*Ka of sulphonic acid is 1.9, the electrostatic attraction between the polymer composites and dye was more which results in higher adsorption capacity. At alkaline *p*H, a considerable decrease in adsorption takes place due to deprotonation of amino groups. Moreover, competition between excess $OH^-$ and dye anions increases, which results in lower adsorption capacity. Figure 2c, supporting information shows the effect of *p*H on the removal RR-M5B by the PAM/graphite composites. The adsorption capacity ($q_e$) decreased from 33.01 to 2.09 mg/g, 38.91 to 6.51 mg/g and 44.80 to 10.92 mg/g for PAM/graphite, Gu-g-PAM/graphite and GA-g-PAM/graphite composite respectively with an increase of *p*H.

**Effect of temperature**

The impact of temperature on adsorption was determined in the range of 303 to 323 K at 50 mg/L dye concentration. It was seen that the rate and amount of adsorbed RR-M5B significantly improved by raising temperature. This is due to the fact that dye molecules acquire sufficient energy to interact with the active sites of the adsorbent with rise of temperature and it also indicates that adsorption is endothermic in nature. The adsorption capacity ($q_e$) increased from 25.65 to 31.54 mg/g, 33.01 to 35.96 mg/g and 37.43 to 41.85 mg/g for PAM/graphite, Gu-g-PAM/graphite and GA-g-PAM/graphite respectively with the rise of temperature.

Thus from the experimental results, conditions optimized to achieve maximum adsorption efficiency were $pH = 2$; time = 80 min; dye concentration 50 mg/L; adsorbent dose = 0.05 g/50 ml; temperature = 303 K.

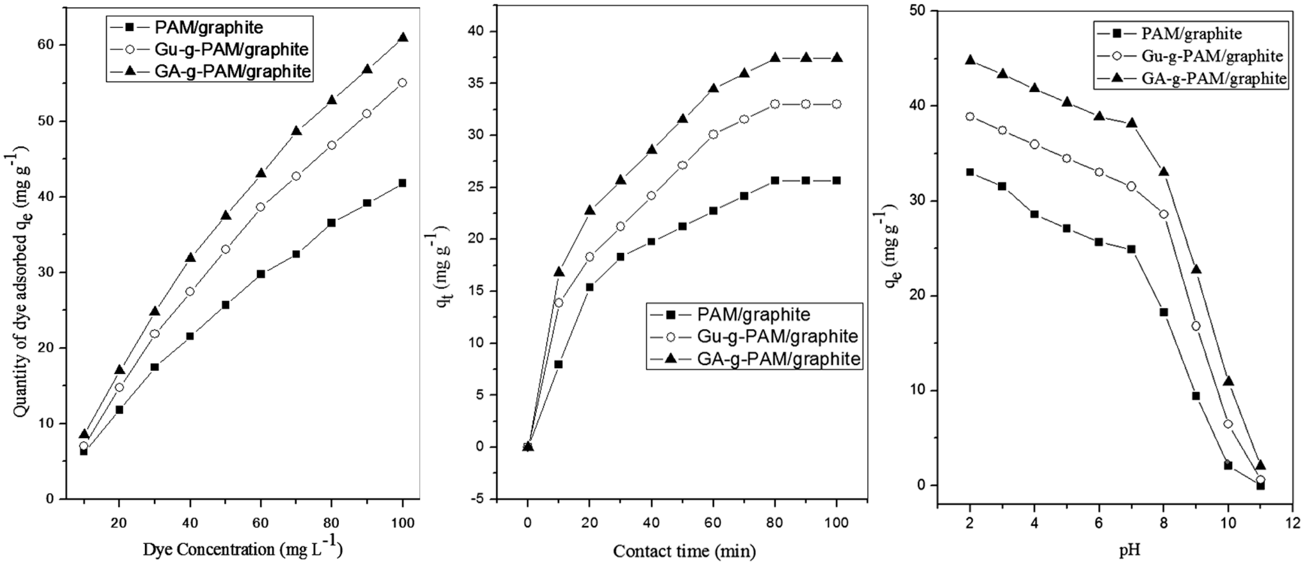

Fig. 2(a-c) — (a) Effect of initial dye concentration on the removal of dye, (b) Adsorption efficiency of PAM/graphite composites with time and (c) Effect of *p*H on the removal RR-M5B by the PAM/graphite composites.

### Adsorption isotherms

To measure the adsorption capacity of PAM/graphite composites four isotherm models were applied to the experimental data, including Langmuir, Freundlich, Dubinin – Radushkevich (D-R) and Temkin isotherm. The adsorption isotherm was studied until equilibrium is established using 0.05 g of adsorbents in the 50 ml of 50 mg/L of the dye solution at temperature 303, 313 and 323 K.

#### *Langmuir Isotherm Model*

Langmuir isotherm assumes that adsorption is limited to the formation of monolayer coverage of adsorbate on homogeneous adsorbent surface [17] and is expressed as

$$C_e/q_e = 1/K_L q_o + C_e/q_o \quad \ldots(3)$$

As $C_e$, $q_e$, $K_L$ and $q_o$ are the concentrations of dye solution at equilibrium (mg/L), equilibrium adsorbed rate of dye over composites (mg/g), Langmuir constant (L/mg) and monolayer capacity (mg/g) respectively. The values $K_L$ and $q_o$ are obtained from the plot $C_e/q_e$ versus $C_e$ and the parameters are listed in Table 1. The values of $K_L$ decreased with increasing temperature, indicating that the dye and composites had higher affinity and relatively higher adsorption energy at lower temperature. The $q_o$ increased with increase of temperature indicating that adsorption of RR-M5B is an endothermic process. Figure 3 (supporting information) represents the Langmuir isotherm fit for GA-g-PAM/graphite.

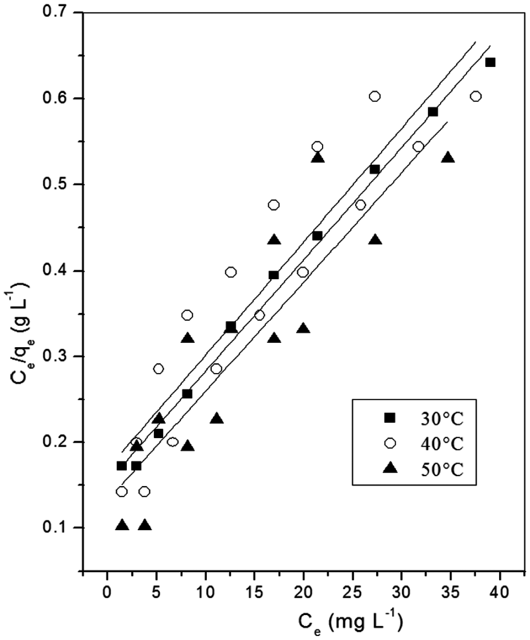

Fig. 3 — Langmuir isotherm for the adsorption of RR-M5B on GA-g-PAM/graphite composite.

Table 1 — Summary of various isotherm parameters for the adsorption of RR-M5B at 303 K, 313 K and 323 K.

| Isotherm | Parameters | PAM/ graphite | | | Gu-g-PAM/ graphite | | | GA-g-PAM/ graphite | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | T(K) | 303 | 313 | 323 | 303 | 313 | 323 | 303 | 313 | 323 |
| Langmuir isotherm $Ce/qe = 1/K_L qo + Ce/qo$ | Qo (mg/g) | 39.94 | 47.62 | 50.48 | 71.23 | 72.83 | 75.59 | 76.80 | 77.04 | 78.19 |
| | $K_L$ (L/mg) | 21.78 | 14.01 | 13.71 | 22.96 | 15.55 | 11.33 | 11.79 | 10.11 | 5.80 |
| | $R_L$ | 0.0009 | 0.0014 | 0.0015 | 0.0009 | 0.0013 | 0.0018 | 0.0017 | 0.0020 | 0.0034 |
| | $r^2$ | 0.9977 | 0.99028 | 0.99395 | 0.97249 | 0.99537 | 0.99599 | 0.99793 | 0.99858 | 0.99412 |
| | SD | 0.0167 | 0.0441 | 0.0317 | 0.03126 | 0.01531 | 0.01544 | 0.00884 | 0.00725 | 0.01371 |
| Freundlich Isotherm $\log qe = \log k_f + 1/n \log Ce$ | $k_f$ | 2.826 | 5.908 | 6.221 | 4.276 | 5.604 | 9.561 | 8.613 | 9.578 | 23.60 |
| | n | 1.472 | 2.007 | 1.997 | 1.434 | 1.575 | 2.033 | 1.786 | 1.820 | 3.402 |
| | $r^2$ | 99894 | 0.98793 | 0.98931 | 0.99456 | 0.9458 | 0.96562 | 0.99615 | 0.98131 | 0.97409 |
| | SD | 0.0096 | 0.02883 | 0.02755 | 0.02341 | 0.07347 | 0.05415 | 0.01899 | 0.04241 | 0.01878 |
| Dubinin-Radushkevich isotherm | Qm (mg/g) | 29.57 | 30.90 | 32.69 | 44.27 | 44.03 | 42.69 | 43.82 | 46.73 | 52.32 |
| | K ($mol^2 K/J^2$) | 4.791 | 1.649 | 1.619 | 6.269 | 3.093 | 8.680 | 1.06 | 1.06 | 1.26 |
| $\ln qe = \ln Qm - K\varepsilon^2$<br>$\varepsilon = RT \ln(1+1/Ce)$ | E (KJ/mol) | 0.323 | 0.551 | 0.556 | 0.282 | 0.402 | 0.240 | 0.69 | 0.69 | 0.63 |
| | $r^2$ | 0.95048 | 0.89729 | 0.9491 | 0.95103 | 0.92262 | 0.89178 | 0.93788 | 0.96369 | 0.85783 |
| | SD | 0.15182 | 0.19367 | 0.13843 | 0.11063 | 0.20213 | 0.22124 | 0.17563 | 0.13611 | 0.12741 |
| Temkin Isotherm $qe = B \ln K_T + B \ln Ce$ | $K_T$ (L/mg) | 3.948 | 1.360 | 1.210 | 2.849 | 1.730 | 1.199 | 1.02 | 1.12 | 1.19 |
| | B | 10.709 | 11.033 | 13.268 | 13.513 | 16.581 | 17.423 | 13.98 | 15.93 | 16.21 |
| | SD | 0.9986 | 0.98786 | 0.98959 | 0.99856 | 0.98582 | 0.98671 | 0.99923 | 0.99183 | 0.97289 |
| | $r^2$ | 0.5084 | 1.44562 | 1.36425 | 0.68333 | 2.168 | 2.09886 | 0.54851 | 1.84105 | 2.20335 |

The essential characteristic feature of the Langmuir isotherm is expressed in terms of a dimensionless constant, which is defined as

$$R_L= 1/ 1+K_LC_o \qquad \ldots(4)$$

where, $K_L$ is the Langmuir constant related to the energy of adsorption (L/mg). The value of $R_L$ reveals the nature of adsorption which can be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$)[18]. The value of $R_L$ for RR-M5B ($0 < K_L < 1$) shows that the adsorption is favourable.

### *Freundlich isotherm model*

This model assumes that the binding strength gradually decreases with the increase of surface coverage of adsorbent[19] and represented as

$$\log q_e = \log k_f + 1/n \log C_e \qquad \ldots(5)$$

where, n and $k_f$ are Freundlich constants, indicating the favorableness of adsorption process and removal capacity of the adsorbent, respectively. As shown in Table 1, the value of $k_f$ increased with increase of temperature indicating that the adsorption is endothermic. Value of n greater than unity ($n > 1$) indicates the promising adsorption of RR-M5B onto polymer composites.

### *Dubinin-Radushkevich (D-R) isotherm*

D-R isotherm provides knowledge about the characteristics of adsorption process[20] and given as

$$\ln q_e = \ln Q_m – K\varepsilon^2 \qquad \ldots(6)$$

$$\varepsilon = RT \ln (1+1/C_e) \qquad \ldots(7)$$

Where, K is the D-R constant ($mol^2\ kJ^{-2}$) related to the sorption energy. The slope of the plot ln $q_e$ versus $\varepsilon^2$ gives K and the intercept yields adsorption capacity $Q_m$ ($mg\ g^{-1}$), $\varepsilon$ Polanyi potential ($J\ mol^{-1}$), R gas constant (8.314 J mol-1 K-1), T the absolute temperature and E mean sorption free energy ($kJ\ mol^{-1}$).

The mean sorption energy, E (kJ/mol) is determined from K using[21]

$$E = 1/ (2K)^{1/2} \qquad \ldots(8)$$

As seen in Table 1, the E value is between 0.32 - 0.55, 0.24 - 0.40 and 0.60 - 0.69 ($kJ\ mol^{-1}$) for PAM/graphite, Gu-g-PAM/graphite and GA-g-PAM/graphite respectively which clearly indicates that adsorption of RR-M5B onto the composites is based on physisorption[22].

### *Tempkin Isotherm*

This model is expressed as

$$q_e = B \ln K_T + B \ln C_e \qquad \ldots(9)$$

Where, B = RT/b, B is the heat of adsorption, $K_T$ is the equilibrium binding constant ($L\ mg^{-1}$). The heat of adsorption for all the polymer composites increases with the increase of temperature revealing that adsorption is endothermic [23].

Among the four isotherms Langmuir model with higher $r^2$ values fits well the equilibrium data. This means that the adsorption takes place at specific homogeneous sites.

### **Adsorption kinetics**

The kinetic parameters are useful for the determination of rate – limiting and mass transfer step in adsorption process. To study adsorption kinetics pseudo first order, pseudo second order and intraparticle diffusion model were evaluated.

### **Pseudo first order kinetics**

The pseudo first order kinetics is defined as [24]

$$\log (q_e-q_t) = \log (q_e) – (k_1/2.303) \times t \qquad \ldots(10)$$

As $q_e$ and $q_t$ are the amount of dye adsorbed at equilibrium ($mg\ g^{-1}$) and at time t ($mg\ g^{-1}$) respectively. The pseudo first order rate constant $k_1$ ($min^{-1}$) is calculated from the plot log ($q_e$-$q_t$) versus t. The kinetic parameters are summarized in Table 2 and shows that the calculated equilibrium capacity $q_e$ is significantly different from the experimental $q_e$ revealing that the adsorption is not likely to be first order[22].

### *Pseudo second order kinetics*

The linear form of this model is

$$t/q_t = 1/k_2q_e^2 + 1/q_e \times t \qquad \ldots(11)$$

Where $q_e$ and $q_t$ are the amount of dye adsorbed at equilibrium ($mg\ g^{-1}$) and at time t ($mg\ g^{-1}$) respectively. $k_2$ is the second order rate constant ($g\ mg^{-1}\ min^{-1}$) calculated from the intercept of the plot $t/q_t$ versus t, a straight line with the slope of $1/q_e$. It was observed from Figure 4 (supporting information) that the calculated $q_e$ is nearly equal to experimental $q_e$. This suggests that RR-M5B adsorption follows pseudo second order kinetics.

The initial adsorption rate h ($mg\ g^{-1}\ min^{-1}$) at t = 0 is expressed as

$$h = k_2q_e^2 \qquad \ldots(12)$$

The plot t/qt versus t is linear for all initial dye concentrations. The value of $k_2$ ($g\ mg^{-1}\ min^{-1}$)

Table 2 — Kinetic parameters for the adsorption of RR-M5B onto the PAM/graphite, Gu-g-PAM/graphite and GA-g-PAM/graphite composites.

| Kinetic models | Parameters | PAM/ graphite | | | | Gu-g-PAM/ graphite | | | | GA-g-PAM/ graphite | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Conc (mg/L) | 25 | 50 | 75 | 100 | 25 | 50 | 75 | 100 | 25 | 50 | 75 | 100 |
| Pseudo first order $\log (q_e\text{-}q_t) = \log (q_e) - (k_1/2.303) \times t$ | $K_1$*$10^{-2}$ ($min^{-1}$) | 3.10 | 3.85 | 4.05 | 4.31 | 3.43 | 4.15 | 4.50 | 4.07 | 5.94 | 7.64 | 6.86 | 7.45 |
| | $q_e$ (mg $g^{-1}$) | 17.35 | 25.91 | 34.60 | 39.84 | 20.81 | 36.26 | 44.15 | 29.88 | 16.97 | 38.91 | 44.23 | 45.27 |
| | $r_1^2$ | 0.9520 | 0.9787 | 0.9522 | 0.9680 | 0.9568 | 0.9324 | 0.9615 | 0.9817 | 0.9302 | 0.9590 | 0.9581 | 0.9538 |
| Pseudo second order $t/q_t = 1/k_2qe^2 + 1/q_e \times t$ <br> $h = k_2qe^2$ | $K_2$ *$10^{-3}$ (g $mg^{-1}$ $min^{-1}$) | 1.37 | 1.97 | 0.99 | 0.85 | 0.90 | 0.47 | 0.40 | 0.32 | 1.72 | 1.05 | 1.55 | 0.78 |
| | $q_e^a$ (mg $g^{-1}$) | 15.38 | 25.65 | 40.55 | 58.22 | 18.32 | 33.01 | 44.76 | 55.03 | 22.74 | 37.43 | 47.71 | 60.92 |
| | $q_e^b$ (mg $g^{-1}$) | 17.17 | 24.99 | 43.12 | 56.43 | 19.50 | 35.97 | 43.52 | 53.16 | 21.60 | 35.96 | 50.35 | 62.03 |
| | $r_2^2$ | 0.9725 | 0.9916 | 0.9892 | 0.9957 | 0.9888 | 0.9881 | 0.9966 | 0.9993 | 0.9989 | 0.9986 | 0.9992 | 0.9998 |
| | h | 0.40 | 1.23 | 1.85 | 2.71 | 0.34 | 0.61 | 0.75 | 0.91 | 1.31 | 2.21 | 4.13 | 4.49 |
| Intra particle diffusion $q_t = k_t \times t^{1/2} + C$ | $K_t$ (g $mg^{-1}$ $min^{-1/2}$) | 1.97 | 2.78 | 3.41 | 4.28 | 2.25 | 3.40 | 4.14 | 3.28 | 2.389 | 4.118 | 5.068 | 6.703 |
| | C | 1.49 | 2.68 | 4.42 | 5.30 | 1.91 | 2.98 | 9.07 | 26.87 | 1.78 | 2.32 | 6.50 | 7.95 |
| | $r_3^2$ | 0.9939 | 0.9419 | 0.9964 | 0.9891 | 0.9868 | 0.9864 | 0.9858 | 0.9357 | 0.9730 | 0.9838 | 0.9249 | 0.9727 |

a-experimental b-calculated

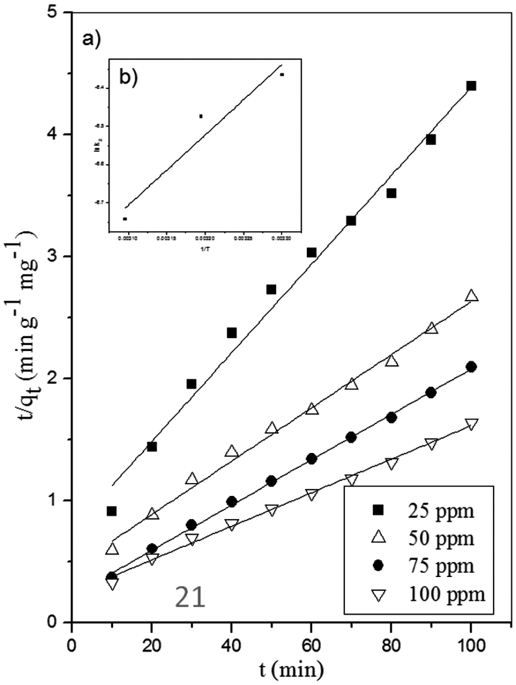

Fig. 4 — Pseudo second order kinetics for the GA-g-PAM/graphite.

decreases with increasing initial dye concentration from 25 to 100 mg/L suggesting a decrease of available vacant sites of adsorbent for adsorption while the initial adsorption rate h increases[25]. The activation energy for adsorption can be calculated using the values of $k_2$. The linear relationship between temperature and rate constant is represented as

$$\ln k_2 = \ln A - E_a/RT \qquad \ldots(13)$$

A (mg $mL^{-1}$ $min^{-1}$) is the Arrhenius factor, $E_a$ (J/mol) Arrhenius activation energy, R (J/K mol) gas constant and T (K) the temperature. The magnitude of $E_a$ for RR-M5B on PAM/graphite, Gu-g-PAM/graphite and GA-g-PAM/graphite were found to be 32.84, 8.92 and 15.29 KJ/mol respectively. The weak forces (5-40 KJ/mol) signifies the characteristic of physical adsorption while higher activation energy (40-800 KJ/mol) designates chemical adsorption[26]. Thus, the RR-M5B adsorption might be confirmed to physisorption, which fitted the results of Dubinin-Radushkevich (D-R) isotherm.

### Intra Particle Diffusion Model

The kinetics were also analyzed by intra particle diffusion model to gain insight into the diffusion mechanism involved during adsorption which is expressed as[27]

$$q_t = k_t \times t^{1/2} + C \qquad \ldots(14)$$

where, $q_t$ is the amount of dye adsorbed (mg/g) at time t (min), $k_t$ the intra particle diffusion rate constant (g mg $^{-1}$ min $^{-1/2}$) and C is a constant related to thickness of the boundary layer. If the regression of

$q_t$ versus $t^{1/2}$ is linear and passes through the origin, then the intra particle diffusion can be considered as the rate limiting step[25]. In this study, the predicted plots did not show linearity and did not pass through origin, which manifested the involvement of intraparticle diffusion process but it was not the only rate-limiting step throughout the adsorption process[19].

As seen in Table 2, intercept C values increased with increasing dye concentrations, from 5.55 to 12.54 mg/L, 5.04 to 16.43 mg/L and 2.79 to 10.78 mg/L for PAM/graphite, Gu-g-PAM/graphite and GA-g-PAM/graphite at 303 K indicating the increase of boundary layer thickness[22]. Furthermore, based on $r^2$ values listed in Table 2, the dye adsorption fitted with pseudo second order kinetic model followed intra particle diffusion.

**Thermodynamics of adsorption**

To conclude whether the adsorption process is spontaneous or not, adsorption thermodynamics is necessary and the parameters were obtained as[28]

$$\ln k = \Delta S/R - \Delta H/RT \qquad \dots (15)$$

$$\Delta G = - RT \ln K \qquad \dots (16)$$

where, ΔG is change in Gibbs free energy (J $mol^{-1}$), R gas constant (J $K^{-1}$ $mol^{-1}$), T temperature (K), ΔH is change in enthalpy (J $mol^{-1}$), k equilibrium constant, ΔS change in entropy (J $K^{-1}$ $mol^{-1}$). Thermodynamic studies for the adsorption of RR-M5B on GA-g-PAM/graphite is shown in Figure 5 (supporting information) and also the thermodynamic parameters are listed in Table 3. It was observed that adsorption of RR-M5B increased with increase of temperature from 303 to 323 K.

The obtained ΔH values were positive (18.64, 15.0 and 36.87 kJ/mol) for PAM/graphite, Gu-g-PAM/graphite and GA-g-PAM/graphite respectively for 40 mg/L of RR-M5B adsorption. The positive ΔH endorses endothermic process and the positive values of ΔS indicate good affinity of dye toward PAM/graphite composites. The ΔG controls the rate of reaction. As the ΔG value decreases, the reaction rate increases. The ΔG values of the GA-g-PAM/graphite were determined to be -3.43, -4.18, -

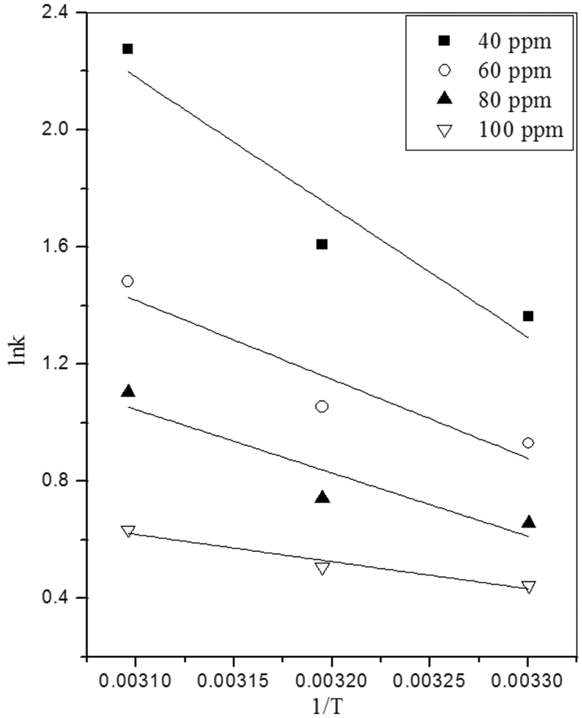

Fig. 5 — Thermodynamic studies for the adsorption of RR-M5B on GA-g-PAM/graphite.

Table 3 — Thermodynamic parameters for the adsorption dye RR-M5B onto polymer composite.

| Adsorbent | Concen-tration of dye (mg/L) | K | | | ΔG (KJ/mol) | | | ΔH (KJ/mol) | ΔS (J $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| | | 30 ·C | 40 ·C | 50 ·C | 30 ·C | 40 ·C | 50 ·C | | |
| PAM/ graphite | 40 | 1.17 | 1.35 | 1.85 | -0.39 | -0.79 | -1.65 | 18.64 | 62.58 |
| | 60 | 0.98 | 1.09 | 1.20 | -0.04 | -0.21 | -0.49 | 8.00 | 26.28 |
| | 80 | 0.84 | 0.90 | 0.97 | -0.07 | -0.26 | -0.51 | 6.00 | 18.37 |
| | 100 | 0.72 | 0.76 | 0.76 | -0.71 | -0.73 | -0.84 | 2.47 | 5.49 |
| Gu-g-PAM/ graphite | 40 | 2.18 | 2.61 | 3.16 | -1.97 | -2.49 | -3.09 | 15.00 | 55.97 |
| | 60 | 1.80 | 2.01 | 2.25 | -1.49 | -1.82 | -2.18 | 9.00 | 34.63 |
| | 80 | 1.41 | 1.41 | 1.52 | -0.87 | -0.90 | -1.13 | 3.07 | 12.90 |
| | 100 | 1.22 | 1.30 | 1.38 | -0.51 | -0.68 | -0.86 | 4.87 | 17.76 |
| GA-g-PAM/ graphite | 40 | 3.91 | 4.99 | 9.72 | -3.43 | -4.18 | -6.11 | 36.87 | 132.44 |
| | 60 | 2.53 | 2.87 | 4.41 | -2.34 | -2.74 | -3.98 | 22.41 | 81.25 |
| | 80 | 1.93 | 2.10 | 3.01 | -1.66 | -1.93 | -2.96 | 17.98 | 64.44 |
| | 100 | 1.56 | 1.66 | 1.89 | -1.12 | -1.32 | -1.70 | 7.70 | 29.01 |

6.11 (kJ/mol) for 40 mg/L of dye at temperatures of 303, 313 and 323 K respectively. Small and negative values of ΔG suggested that the adsorption was spontaneous[29]. The values of ΔG obtained in this study are within ranges of a physisorption[30], which fitted well with the results of Dubinin-Radushkevich isotherm and Pseudo second order kinetics.

### Adsorption mechanism

The various adsorption parameters results states that adsorbent GA-g-PAM/graphite shows higher percentage of RRM5B removal. This could be due to coulombic interaction between $–SO_3^-$ group of dye and amine group of adsorbent, hydrogen bonding and Vander Walls forces between dye and GA-g-PAM/graphite. The possible interaction between dye and GA-g-PAM/graphite is proposed in Figure 6.

FT-IR spectra of GA-g-PAM/graphite before adsorption (curve a) and dye loaded GA-g-PAM/graphite (curve b) are shown in Figure 7 (supporting information) also confirms adsorption of dye over adsorbent surface. In spectrum (a), bands at 3445, 3294, 1621, 1584, 1249, 1179 and 1097 $cm^{-1}$ are attributed to aromatic -C-H, -OH, amide –I, amide –II, $-CH_2OH$, C-N-C and C-O-C groups of GA-g-PAM/graphite respectively. A-g-PAM/graphite after adsorbing RRM5B shows characteristics bands of both dye and GA-g-PAM/graphite. The spectrum (b) shows bands at 3371, 1535, 1412, 1319, 855 and 750 $cm^{-1}$ due to secondary -N-H, -N=N-, -C-N, -S=O, -C-N of triazine, -C-Cl groups respectively[31]. The characteristic peaks corresponding to GA-g-PAM/graphite in spectrum 2(b) exhibit certain shifts in their wave numbers, possibly caused by the interaction of dye and GA-g-PAM.

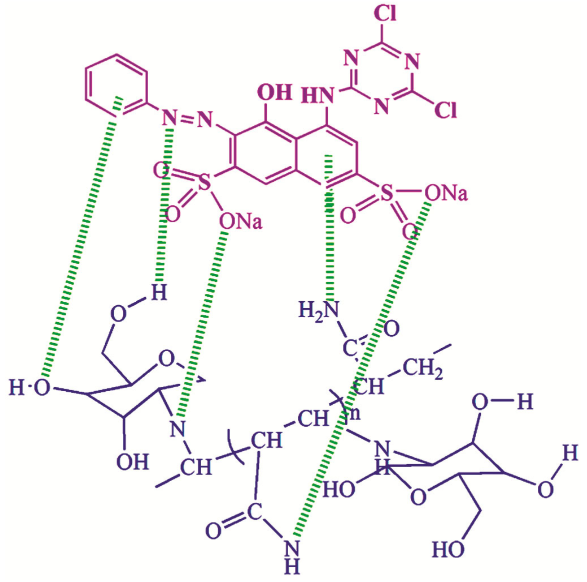

Fig. 6 — Adsorption mechanism between RRM5B and GA-g-PAM/ graphite

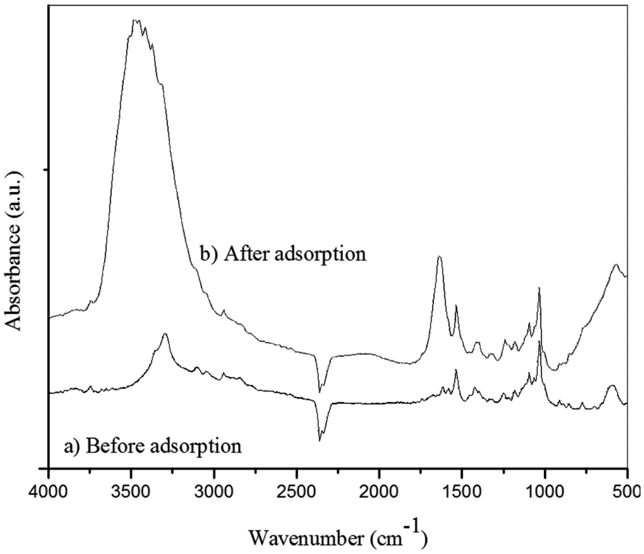

Fig. 7 — FT-IR Spectrum (a) GA-g-PAM/graphite and (b) dye loaded GA-g-PAM/graphite.

### Desorption and reusability studies

To unload the dye molecules from the dye adsorbed composite 0.1M NaOH were used. Desorption of dye increases as *p*H increases from 2 to 11. About 92-93% of the polymer composites would be leached after suspending the composites in 0.1 M NaOH. To investigate the reusability of the adsorbents, the adsorption-desorption cycle was repeated eight times. The percentage of desorption observed at *p*H 11 was 68.35% for GA-g-PAM/graphite, 59.13 % for Gu-g-PAM/graphite and 46.71% for PAM/graphite in the first cycle. Figure 8 represents the adsorption-desorption of dye onto GA-g-PAM/graphite. The adsorption capacity of GA-g-PAM/graphite still maintained above 64% after third adsorption-desorption cycle, but about 62% of the adsorption capacity was left at eight cycles. This might be due to the loss of adsorbents during the multiple washing steps after each cycle[32]. This result indicates that GA-g-PAM/graphite could be used as an efficient adsorbent for the removal of dye. The regeneration efficiency of the adsorbents were calculated as[33]

$$\text{Regeneration efficiency (\%)} = (q_e \text{ in the second run } / q_e \text{ in the first run}) \times 100 \qquad \ldots(17)$$

Where, $q_e$ is the equilibrium adsorption capacity.

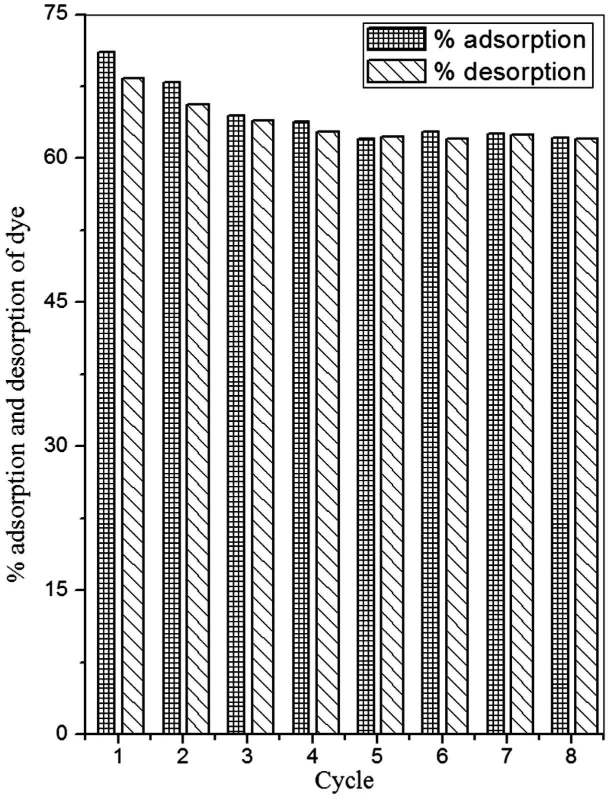

Fig. 8 — Adsorption-desorption of dye onto GA-g-PAM/graphite

## Conclusion

Modified PAM/graphite composites were prepared by grafting with glucose and glucosamine and used as adsorbents for the removal of RR-M5B dye. The structural characterization of the composites was done using FT-IR, $^{1}$H and $^{13}$C NMR analysis. FT-IR and desorption studies confirmed the involvement of amino and hydroxyl groups in dye adsorption. GA-g-PAM/graphite had shown good adsorption efficiency compared to PAM/graphite and Gu-g-PAM/graphite due to its functional groups. The kinetics of adsorption followed Pseudo-second order model and also indicates that intraparticle diffusion also plays a significant role in adsorption mechanism. The equilibrium data were fitted well with Langmuir isotherm. Thermodynamic study reveals adsorption of RR-M5B was found to be endothermic and spontaneous for all the composites. The adsorption is found to be pH dependant and maximum adsorption is observed at pH < 4. The desorption studies indicate the reusability of the composites. The results indicated that GA-g-PAM/graphite could be used as an effective adsorbent for removal of RR-M5B dye from aqueous solution.

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