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High adsorption performance of pH responsive graphene oxide/polyacrylamide hydrogels for the removal of Drimarene Brilliant Blue

Mubeen Kousar[a], Maheen Almas[a], Shagufta Kamal[b], Khalid Mahmood Zia[a], Saima Rehman[a,*]

[a]*Department of Chemistry, Government College University, Faisalabad, Pakistan, Tel. +92 3335908881; emails: saimarehman@gcuf.edu.pk (S. Rehman), mubeenkousar172@yahoo.com (M. Kousar), maheenalmas.153@gmail.com (M, Almas), drkmzia@gcuf.edu.pk (K.M. Zia)*
[b]*Department of Biochemistry, Government College University, Faisalabad, Pakistan, email: shaguftakamal81@gmail.com*

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ABSTRACT

Hydrogels as adsorbent have attracted great scientific attention; however there are few reports regarding the high performing hydrogels in terms of adsorption capacity. In this study, a series of graphene oxide/polyacrylamide (GO/PAM) composite hydrogels were synthesized by free radical polymerization for the removal of dyes from wastewater. In order to investigate water uptake capacity of hydrogels, swelling kinetics and the equilibrium swelling ratios were determined in water and at different pH. The results revealed maximum water uptake at pH 8 and obey Quasi–Fickian diffusion ($n < 0.5$). The effect of different factors, that is, pH and initial dye concentration on the adsorption of dye were studied. The adsorption kinetics and isotherms of synthesized composite hydrogels were also studied for Drimarene Brilliant Blue K-4BL. The best dye removal was obtained at pH 8 and 200 ppm initial dye concentration. Results indicated that data of pseudo-first-order kinetic model is best fitted while the Weber–Morris diffusion model revealed the adsorption mechanism as single step adsorption and intra particulate diffusion as rate determining step. Moreover, modified Freundlich isotherm explains the adsorption of dyes by synthesized hydrogels better than that of Langmuir isotherm model. Excellent adsorption capacity, that is, 1,000 mg g^{-1} for the removal of Drimarene Brilliant Blue K-4BL was observed for GO reinforced polyacrylamide (PAM) hydrogels which is 6 folds higher compared to simple PAM hydrogels. Adsorption–desorption studies exhibited the appreciable reusability potential of the composite material with ~ 40% removal efficiency up to five successive cycles.

Keywords: Hydrogels; Graphene oxide; Polyacrylamide; Nano-composite; Drimarene Brilliant Blue dye; Adsorption–desorption potential

1. Introduction

In recent years, with an abrupt increase in suburbanization, industrial and agronomic land use, there is in a massive increase in the release of a variety of contaminants, causing adverse outcomes to the aquatic ecosystem [1]. An excessive number of effluents including dyes and auxiliary chemicals have been released into the water streams and channels consequently polluting the water. Therefore, there is a need for safe discharge of this industrial wastewater to ensure the safety of the environment and ecosystem. Among all contemporary methods, adsorption is considered a superior method due to its low cost, less energy input and simple handling [2].

Hydrogels are hydrophilic polymeric materials which show various novel properties of absorbing and retaining

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* Corresponding author.

huge amounts of water and biological liquids without any dissolution that make hydrogel a strong candidate for the treatment of dyes and pollutants from the industrial wastewater. Owing to the unique 3D network and presence of functional groups in hydrogels have great tendency to capture metal ions and dyes from the effluents [3]. Polyacrylamide hydrogels are regarded as versatile adsorbents for the treatment of contaminated waste water due to its unique chemical structure [4]. However, these hydrogels cannot be employed at large scales owing to their inferior thermomechanical properties. So, physical and chemical modification is done to improve the thermo-mechanical character as well as the adsorption ability. Physical techniques include the reinforcement of polyacrylamide with other materials without chemical reaction while chemical modifications involve grafting, co-polymerization, and cross-linking [5]. Nanocomposite hydrogels are the most promising adsorbents due to the persistent synergistic effect between the nano-fillers and polymer matrix, contributing to the outstanding thermo-mechanical properties and the high hydrodynamic radius as compared to pure polymer hydrogels [6].

Carbon based nanomaterials, like carbon aerogels, carbon nanotubes, graphene, and their composites represent promising type of adsorbents for waste water treatment. Graphene makes more thermodynamically stable ensembles with dyes in an aqueous medium. Graphene oxide is an oxidative mode of graphene, having groups like hydroxyl, epoxy, carbonyl and carboxyl groups. These oxygen-containing groups make graphene oxide hydrophilic and improve compatibility with polymer matrix and serve as binding sites for efficient adsorption of dyes via π–π interactions, electrostatic interactions and hydrogen bonds. Besides the high mechanical properties, large specific surface area and good biocompatibility make graphene oxide (GO) an excellent competitor as reinforcement for the fabrication of different composites [7].

In this work, graphene oxide reinforced polyacrylamide hydrogels have been synthesized and applied for removal of dyes from wastewater through adsorption; moreover adsorption–desorption parameters have been investigated for a commercial Drimarene Brilliant Blue K-4BL Dye, hence to find a potential adsorbent material.

2. Material and methods

2.1. Chemicals

Chemicals and reagents used in this work include natural graphite powder, sulfuric acid, hydrogen peroxide, hydrochloric acid, potassium permanganate, acrylamide (AAm), sodium nitrate ($NaNO_3$), deionized water, methylene-bis(acrylamide) (MBA), ammonium persulfate (APS), acetic acid, sodium acetate, ammonium hydroxide, ammonium chloride, potassium di-hydrogen phosphate and Drimarene Brilliant Blue K-4BL. All the chemicals and reagents were of analytical grade and purchased from Sigma-Aldrich.

2.2. Synthesis of graphene oxide

Graphene oxide nanoparticles were synthesized by using modified Hummers method. Briefly, graphite powder and $NaNO_3$ were mixed in H_2SO_4 in a volumetric flask kept at ice bath with continuous stirring for 4 h followed by the addition of potassium permanganate. The mixture was diluted with slow addition of water and stirring for 2 h at 35°C. The above mixture was kept in a reflux system at 98°C for 10–15 min. After 10 min, the change in temperature to 30°C showed a brown colored solution. After10 min, the temperature was changed to 25°C and maintained for 2 h. The solution was finally treated with H_2O_2 by which color changed to bright yellow. Stirring was continued for 1 h. The mixture was kept without stirring for 3–4 h until the particles were settled at the bottom. The particles were separated by centrifugation and washed repeatedly with deionized water until pH-neutral. After centrifugation the gel-like substance was dried at 60°C for more than 6 h to GO nanoparticles [8].

2.3. Synthesis of polyacrylamide films

Polyacrylamide hydrogels were synthesized by following the method reported by Alam et al. [9], with some modifications. The measured amounts of acrylamide were dissolved into distilled water. The quantities of methylene-bis(acrylamide) (MBA), APS (Table 1) were mixed with this solution and stirred for about half an hour. The solution was bubbled by N_2 gas at room temperature and poured into mold. It was placed in the oven for 5 h at 70°C. The formed gel was removed from mold and was rinsed with distilled water.

2.4. Synthesis of graphene oxide/polyacrylamide nanocomposites

Composite hydrogels were synthesized via free radical polymerization of acrylamide at 70°C for 5 h, by using weighed amounts of APS as an initiator, methylene-bis(acrylamide) (MBA) as cross-linker and graphene oxide as represented in Table 1. Before addition, graphene oxide nanoparticles were suspended in aqueous media and sonicated at room temperature for 20 min to ensure the homogenous dispersion of particles into the solution. The solution was stirred for about half an hour until viscous pre-polymer solution was obtained. The solution was bubbled by N_2 at room temperature and poured into polypropylene mold. After polymerization, the gel was rinsed with de-ionized water to remove the unreacted monomers [9].

2.5. Water uptake capacity

In order to explore water uptake capacities of the synthesized hydrogels, swelling ratios in different pH buffer solutions and in water were investigated. Sample hydrogels were immersed in distilled water and different buffer solutions with the pH range from 2 to 10 (2, 4, 6, 8, and 10). The weight of the samples was measured after every 30 min for the first 5 h and the final observations were recorded after 24 h, water uptake capacity or swelling ratios were calculated by using the following equation:

$$Q_1 = \frac{\left(W_{\text{wet}} - W_{\text{dry}}\right)}{W_{\text{dry}}} \tag{1}$$

Table 1
Composition of nano-composites (hydrogels) via free radical polymerization by varying the concentration of reinforcement

Sr#	GO content (%)	Concentration of GO-particles (g)	Concentration of PAM (g)	Concentration of MBSA (g)	Concentration of APS (g)	Volume of distilled water (mL)
1.	0	0	2	0.02	0.02	18
2.	0.1	0.002	2	0.02	0.02	18
3.	0.2	0.004	2	0.02	0.02	18
4.	0.3	0.006	2	0.02	0.02	18
5.	0.4	0.008	2	0.02	0.02	18
6.	0.5	0.01	2	0.02	0.02	18
7.	0.6	0.012	2	0.02	0.02	18

where Q_1 is the water uptake capacity at a given time; W_{wet} is the weight of swollen gel; W_{dry} is the weight of dry hydrogel.

2.6. Adsorption studies

Adsorption experiments were performed in 10 mL of dye solution at room temperature. About 0.05 g hydrogels were added to the solution of Drimarene Brilliant Blue K-4BL having concentration of 50 mg L^{-1}. After 24 h the residual dye concentration was estimated through spectrophotometer at specific absorption wavelength of about 592 nm. All the experimentations were performed in triplicate.

2.6.1. Effect of pH

The effects of pH for the adsorption capacity of dye of the composites were investigated as the method pronounced in the above section 2.6 by varying the pH of dye solution from 2 to 12.

2.6.2. Effect of dye concentration and isotherms models

Effects of dye concentration on the dye adsorption capacity of the composites were also investigated via same approach as mentioned before just by varying the concentration of dye. Adsorption isotherms were achieved by adding the hydrogel samples in dye solutions having different initial concentrations. In equilibrium adsorption isotherm experiment, 50 mg of hydrogel was added in 10 mL of dye solution having different concentration ranging from 50 to 250 mg L^{-1}. After 24 h, the residual amount of dye was estimated by UV spectrophotometer.

The adsorption ability of prepared hydrogels was determined by using the equation

$$q_e = \frac{\left(C_o - C_e\right)V}{m} \tag{2}$$

where q_e is the adsorbed amount in mg g^{-1} of hydrogel; C_o is the initial of the dyes as mg L^{-1}; C_e is the equilibrium concentration of the dyes as mg L^{-1}; V is the volume of the solution in L; m is the amount of the hydrogel used in g.

The adsorption models were studied by using reaction-based models like Langmuir and Freundlich models. The adsorption isotherms depicted how the contaminants interact with the prepared hydrogel/sorbent material.

2.6.3. Adsorption kinetics

Adsorption kinetics was investigated by taking the dye solution of 200 mg L^{-1} and after specific time intervals the concentration of the dye solution was checked by UV spectrophotometer at the wavelength of 592 nm. Adsorption kinetics parameters were calculated by using pseudo-first-order and pseudo-second-order kinetics models in addition to intraparticle diffusion model.

2.7. Reusability of hydrogels

Dye adsorbed composite hydrogels were investigated for the dye desorption studies. The dye-loaded hydrogels were stir-treated with 30 mL of 4% HCl in 50/50 water/ethanol (v/v) solution for 3 h to desorb the dye. Subsequently, the hydrogels were washed with distilled water and then reused for adsorption processes again. The adsorption/desorption cycles were successively conducted five times with fresh dye solution [10].

3. Results and discussion

3.1. Water uptake capacity

This study signifies the water holding capacity of the respective hydrogel. The swelling process of hydrogels depends on various factors like the hydrophobicity and hydrophilicity of the matrix, ionization extent of hydrophilic groups etc. Fig. 1 reveals the swelling kinetics and equilibrium swelling ratios of synthesized graphene oxide/polyacrylamide (GO-PAM) hydrogels at room temperature. Increasing the GO content from 0.1% to 0.6% increases the q_e values approximately 2-fold. The swelling percentage of polyacrylamide (PAM), 0.1% GO-PAM, 0.2% GO-PAM, 0.3% GO-PAM, 0.4% GO-PAM, 0.5% GO-PAM and 0.6% GO-PAM in distilled water was 537%, 960%, 1,100%, 1,280%, 1,520% and 1,700% respectively as in Fig. 1. These higher water absorption capacities are due to the ionization extent of the hydrogels. It might be due to the fact that functional groups like –COOH, –OH, C=O, and C–O–C etc. have a chance of more homogenous dispersion in the pre-polymer matrix. This uniform dispersion leads to a strong effect on the microstructures of the polymer matrix

Table 2
Swelling kinetics parameters of composites at different pH value

Kinetic parameters	pH	2	4	6	8	10
	PAM	0.699	0.812	0.92	0.867	0.989
	0.1% GO-PAM	0.963	0.965	0.922	0.971	0.852
	0.2% GO-PAM	0.933	0.953	0.944	0.943	0.852
R^2	0.3% GO-PAM	0.946	0.91	0.983	0.969	0.963
	0.4% GO-PAM	0.917	0.87	0.973	0.924	0.939
	0.5% GO-PAM	0.965	0.891	0.977	0.953	0.977
	0.6% GO-PAM	0.975	0.892	0.922	0.975	0.952
	PAM	0.212	0.232	0.054	0.148	0.214
	0.1% GO-PAM	0.193	0.13	0.032	0.058	0.051
	0.2% GO-PAM	0.242	0.182	0.148	0.09	0.052
k	0.3% GO-PAM	0.178	0.097	0.037	0.083	0.081
	0.4% GO-PAM	0.298	0.134	0.042	0.219	0.104
	0.5% GO-PAM	0.203	0.098	0.014	0.169	0.037
	0.6% GO-PAM	0.216	0.081	0.05	0.108	0.029
	PAM	0.212	0.232	0.403	0.288	0.213
	0.1% GO-PAM	0.193	0.13	0.491	0.405	0.406
	0.2% GO-PAM	0.242	0.182	0.274	0.351	0.41
n	0.3% GO-PAM	0.178	0.097	0.461	0.359	0.339
	0.4% GO-PAM	0.298	0.134	0.437	0.193	0.326
	0.5% GO-PAM	0.203	0.098	0.609	0.24	0.46
	0.6% GO-PAM	0.216	0.081	0.435	0.296	0.507

Table 3
Different isotherm parameters for the adsorption of Drimarene Brilliant Blue K-4BL on PAM and GO-PAM composites

Composites	Langmuir			Freundlich		
	R^2	$q_{\max}$	K_L	R^2	K_{MF}	1/n
PAM	0.401	166.66	0.006	0.61	73.84	0.05
0.1% GO-PAM	0.765	333.33	0.035	0.839	281.18	2×10^{-3}
0.2% GO-PAM	0.905	500	0.035	0.92	395.44	9×10^{-3}
0.3% GO-PAM	0.908	1,000	0.016	0.927	348.62	0.075
0.4% GO-PAM	0.955	1,000	0.032	0.95	505.72	0.041
0.5% GO-PAM	0.985	1,000	0.090	0.986	665.141	0.024
0.6% GO-PAM	0.982	1,000	0.333	0.986	889.802	5×10^{-3}

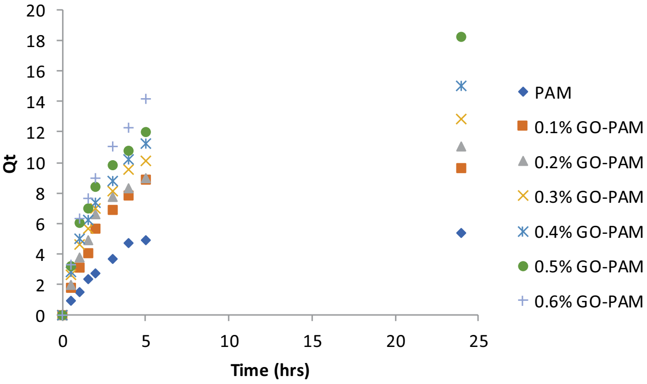

Fig. 1. Swelling behavior of hydrogels at room temperature.

network. The nanostructure of GO particles impart exceptional behavior; there is a chance of involvement of some synergetic intermolecular interactions between nano-particles and pre-polymer matrix network chains that induce the water holding capability of gel and ultimately the swelling ratio of the hydrogel has increased.

It has been observed that when the GO particles content has been increased from 0.3% to 0.6% by weight, there has been an obvious increase in the swelling ratios which can be attributed to the active surface area as nanoparticle exhibit high surface area to volume. This behavior has dealt with the synergetic effect of GO particles and polymer network chains [11].

3.2. pH-sensitive behavior of super-adsorbent hydrogel nanocomposites

Experimental data indicated that all hydrogels showed low swelling values at low pH or we can say at high acidic environments, that is, pH = 2 as shown in Fig. 2. It might be due to the protonation of the COOH groups, present on the surface of hydrogel in abundant; and there occurred hydrogen bonding among various functional groups, on hydrogel surface, like –OH, –COOH, –C=O, NH_2 and C–O–C etc. This H-bonding resulted into the shrinkage of the hydrogels' networks that minimized the swelling ability of that hydrogel sample.

When the pH of media was increased (pH > 3), up-to pH 8, maximum number of carboxylic groups got ionized to carboxylic ions (COO^-) and a lot of hydrogen bonds got broken down resulting in the increase in electrostatic repulsive forces of the anionic groups of the hydrogels chain network

Table 4
Kinetics parameters of pseudo-first-order, pseudo-second-order and intraparticle diffusion models

Composites	Pseudo-first-order kinetic				Pseudo-second-order kinetic			Intraparticle diffusion		
	$q_{e,\exp}$	R^2	$q_{e,\mathrm{cal}}$	k_1	R^2	$q_{e,\mathrm{cal}}$	k_2	R^2	k_d	C
	(mg g^{-1})		(mg g^{-1})	min^{-1}		(mg g^{-1})	(mg g^{-1} min^{-1})		(mg g^{-1} min$^{1/2}$)	
0.1% GO-PAM	1.79	0.853	1.832	0.0115	0.637	1.43	0.0093	0.907	0.1467	–0.2982
0.2% GO-PAM	1.99	0.802	2.202	0.0092	0.446	4	0.0011	0.8694	0.1659	–0.437
0.3% GO-PAM	2.27	0.758	2.636	0.0092	0.398	4.81	0.0008	0.8606	0.1951	–0.5955
0.4% GO-PAM	2.19	0.806	2.570	0.0092	0.445	5.39	0.0006	0.8958	0.1933	–0.6244
0.6% GO-PAM	1.77	0.935	1.883	0.0092	0.644	3.66	0.0012	0.9367	0.1523	–0.4171

structure. Swelling capacity went uphill with the increase in the pH value. Experimental data as represented in table 2 have shown the maximum swelling of the hydrogels at pH 8. Higher osmotic pressure due to low ionic strength of the medium solution contributed to higher swelling ratio at pH 8.

Beyond this value, the swelling capabilities of hydrogel turned down due to the presence of higher osmotic pressure of the media solution. This behavior owed the screening effect casted by the counter ions, that is, NH_4^+ ions, that shielded the anions, that is, COO^- ions. Hence, the electrostatic repulsive forces became weaker and weaker, resulting in the continuous decline in the swelling ratios.

The homogeneous dispersion of lower GO content in the composite matrix has increased the swelling ability up to 0.3%; it has been observed that 0.6 wt.% GO content with same matrix concentration has indicated a good swelling capacity at various pH values as shown in Fig. 2. So, the uniform distribution of particles improves the swelling behavior of the gel and it is possible with low concentration of the reinforcement. This develops the intermolecular electrostatic interactions between the matrix and dispersed particles along hydrogen bonding and strong covalent bonding. When placed in solutions of various pH, the presence of hydrophilic groups, in abundance, has become the cause of swelling differences of gels [12].

The swelling kinetics of the composite hydrogels was also investigated by applying Fick's Law:

$$F = \frac{Q_t}{Q_e} = kt^n \quad (3)$$

where Q_t and Q_e are the swelling ratios at time instant 't' and at equilibrium respectively, k is the swelling constant, and n is the swelling exponent. Swelling exponent 'n' value explains the mechanism of water transport. Here, in Table 2, the n values are less than 0.5 that indicate Quasi–Fickian diffusion; penetration of water molecules or the diffusion process is favorable due to relaxation of polymer chain molecules.

The hydrogel with 0.6 wt.% GO content, has shown maximum swelling because here the micro-phase separation is more less, GO particles are not wrapped into the gel but are present on the surface, so here, GO particles itself has responded to the external media more as compared to the matrix network [13].

Effect of pH on the swelling behavior was also studied. The swelling ratio was low at lower pH but it started to increase gradually with the increase in pH value upto the pH 8 and then it tends to be in decreased values as shown in Fig. 3.

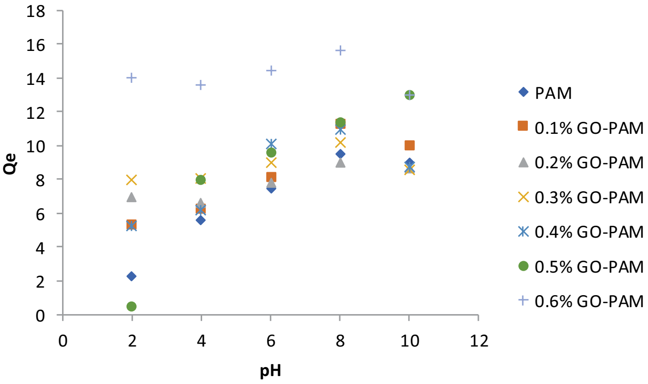

Fig. 2. Water uptake or swelling capacities of hydrogels at different pH values.

At the low pH values H^+ are higher in concentration and these ions tend to bind or make physical cross linking with the hydrophilic functional groups of the hydrogel and narrow down the polymer network. Due to this bonding the hydrogel showed restricted expansion in weight or size at pH 2.

Increased values of pH defeat this behavior of the hydrogels as the concentration of the H^+ ions begin to decrease and contrary to this the concentration of OH^- ions increases.

Repulsive forces between the solvent phase of higher pH value, that is, 8 and the hydrogels network are responsible for the maximum swelling ratios [14].

3.3. Adsorption studies

Adsorption parameters for Drimarene Brilliant Blue K-4BL were investigated by varying pH, GO content of hydrogels, and the concentration of the dye solution. Adsorption kinetics and isotherms have also been studied.

3.3.1. Effect of pH

The pH of the dye solution significantly affects the dye removal capacity of the composite. The % dye removal values change by varying the pH values of the solution as shown in Fig. 4.

The effect of pH on GO-PAM hydrogels was studied at different pH ranges. The pH dependent behavior

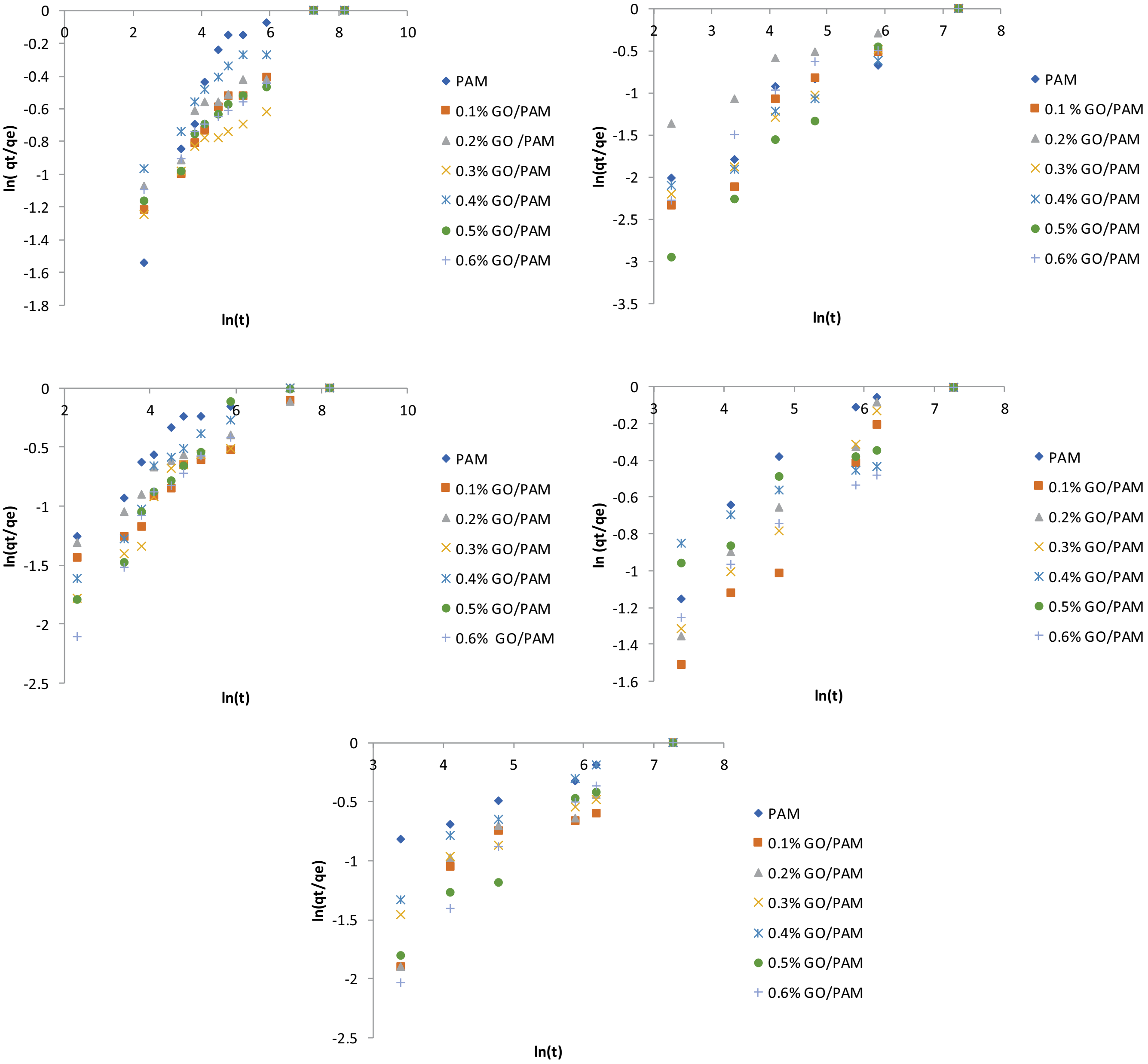

Fig. 3. Swelling kinetics of hydrogels at pH 2, 4, 6, 8 and 10.

of dye adsorption on GO-PAM hydrogels was observed. It might be due to the ionization of dye molecules and surface charge variation of hydrogels with change in pH of the solution. The adsorption of Drimarene Brilliant Blue K-4BL onto GO-PAM increased by increasing the pH of the solution till optimum adsorption of dye at pH 8 has been attained. Further increase in pH resulted in a slight decrease in adsorption capacity. This behavior is due to the presence of –OH and –COOH groups of GO at the surface of hydrogels, having negative charge being responsible for giving the chance to Drimarene Brilliant Blue K-4BL H_2CN^+ being attracted. The NH_2^+ group of dye and OH^- and $COOH^-$ group present at the surface of hydrogel are considered to be responsible for the development of electrostatic interaction. Moreover, the oxygen-containing groups of graphene oxide might serve as binding sites for efficient adsorption of dyes via π–π interactions, electrostatic interactions and hydrogen bonds. Sharma et al. also reported that –OH, COOH and NH_2 groups are involved in the dye adsorption process [8].

3.3.2. Effect of concentration and isotherm model

Results showed that at low concentration dye ions are adsorbed by specific sites, while at high concentration dye specific sites are saturated and the other sites are filled.

The adsorption studies described that the saturation of the surface was altered with dye solution concentration. At low dye solution concentration, binding sites adhere more dye whereas at high dye solution concentration, dye adsorb

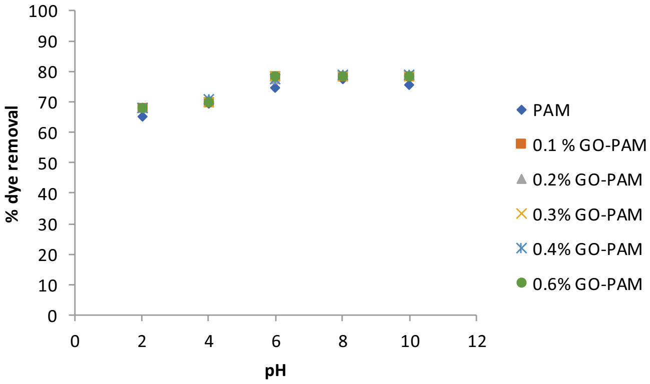

Fig. 4. Effect of pH on the percentage of dye removal.

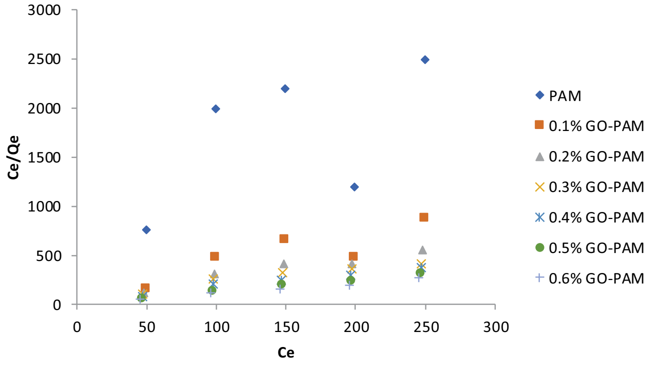

Fig. 5. Langmuir adsorption isotherm of Drimarene Brilliant Blue K-4BL on PAM and GO-PAM.

at lower rate. The binding sites in the increasing dye solution concentration resulted in saturation of binding sites at higher dye solution concentration [15].

In hydrogel adsorption character is attributed to nanoparticles. If the nanoparticles get wrapped into the matrix, the adsorption will go downhill. In the prepared nanocomposites, particles were mostly on the surface providing more binding sites to the dye ions. This made higher graphene oxide content composites to absorb more.

Both models were applied to determine the Drimarene Brilliant Blue K-4BL adsorption isotherm restrictions on the prepared hydrogels. Langmuir isotherm presumes that adsorption happens as mono-layer coverage of adsorbate on adsorbent homogeneous surfaces with a finite number of active binding sites. While Freundlich isotherm assumes that adsorption follows a multilayer coverage of adsorbate on heterogeneous surfaces. Based on the experimental data, Langmuir and Freundlich isotherm models were calculated [15].

The theory of Langmuir model has been supported upon the assumptions

- Uni-molecularity of adsorbed layers or homogeneous active sites
- $C_e/q_e = 1/Q_0b + C_e/Q_0$ (4)

where C_e is equilibrium concentration in mg L^{-1}, q_e is adsorbed concentration at equilibrium in mg g^{-1}, Q_0 is Langmuir constant of absorption capacity in mg g^{-1}, b is Langmuir constant w.r.t. energy of adsorption in L mg^{-1}.

Modified Freundlich isotherm model has been supported upon the assumptions

- Heterogeneous surfaces character
- Reliable by the exponential distribution of the active sites of surface
- $\ln q_e/C_e = \ln K_{\mathrm{MF}} + (1/n_{\mathrm{MF}} - 1)\ln C_e$ (5)

where q_e is the amount of solute that gets adsorbed, C_e is the equilibrium concentration of dye in solution, K_{MF} is the distribution coefficient.

The Table 3 listed above have correlation coefficient and other isotherm parameters for Langmuir isotherm model as well as for Modified Freundlich isotherm model. The correlation coefficient (R^2) values for the Modified Freundlich isotherms were larger than those of the Langmuir isotherms, depicting that Modified Freundlich isotherms have better corresponding than Langmuir isotherms via Figs. 5 and 6. High K_{MF} values indicated the high and favorable adsorption for the cationic dyes.

As the GO content increases the adsorption capacity increases due to availability of more active binding sites.

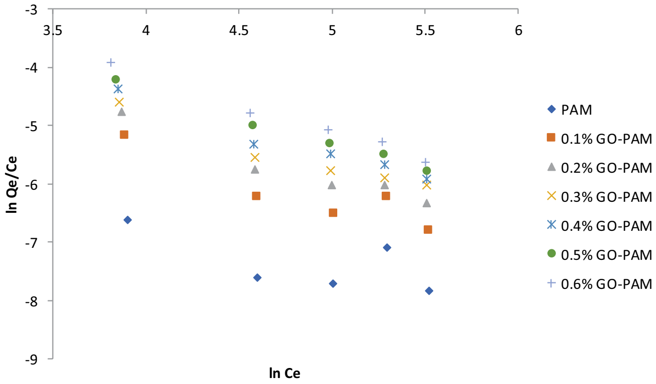

Fig. 6. Modified Freundlich adsorption isotherm of Drimarene Brilliant Blue K-4BL on PAM and GO-PAM.

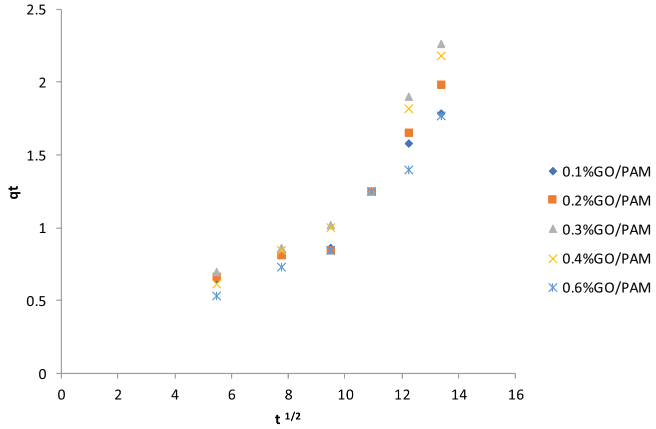

Fig. 7. Intraparticle diffusion of Drimarene Brilliant Blue K-4BL on GO-PAM.

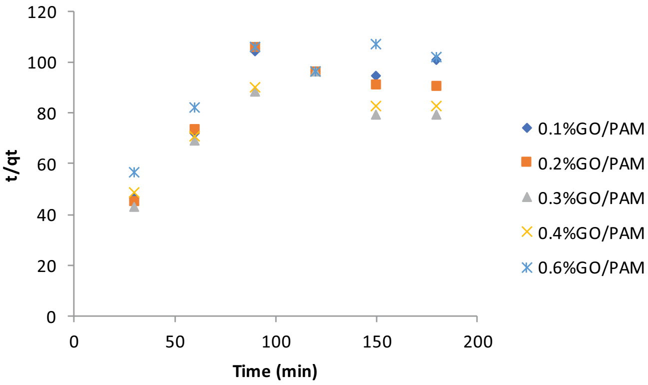

Fig. 8. Pseudo-second-order kinetic of Drimarene Brilliant Blue K-4BL on GO-PAM at pH 8.

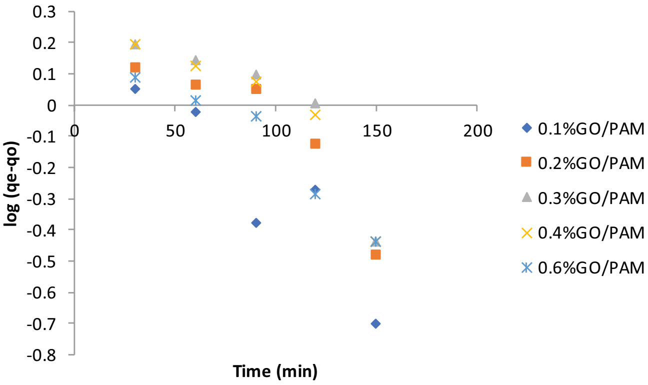

Fig. 9. Pseudo-first-order kinetic of Drimarene Brilliant Blue K-4BL on GO-PAM at pH 8.

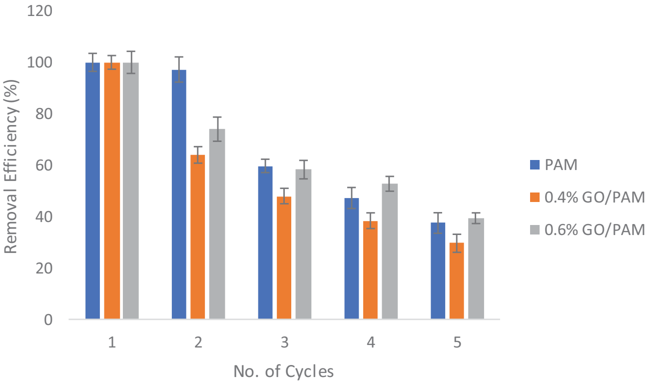

Fig. 10. Reusability of PAM and GO-NPs incorporated PAM hydrogels (dye concentration = 200 ppm, contact time = 90 min at 37°C).

This may be because, in GO nanoparticles, the major driving force for adsorption is electrostatic attraction of the oppositely charged species along with π–π interactions which are relatively stronger than the π–π interactions, van der Waals interaction and hydrogen bonding alone. The π–π interactions are responsible for the adsorption onto carbon nanotubes [16].

Increasing GO content upto 0.3% GO-PAM hydrogel, the adsorption capacity increases and then there no considerable increase in the adsorption has been observed; by this it can be concluded that after this concentration (>0.3%) aggregation of GO-NPs occurred due to intra-molecular forces. This might affect the rate of reaction initially and slight difference in their R^2 values but $q_{\max}$ ~ same. But significantly a considerable advancement has been observed in the adsorption capacity; as PAM has shown $q_{\max} = 166.66$ mg g^{-1} while composite has shown $q_{\max} = 1,000$ mg g^{-1}.

3.3.3. Adsorption kinetics

To investigate the diffusion method of dye onto the composite, Weber–Morris diffusion model has been applied.

$$q_t = k_d t^{1/2} + C \tag{6}$$

where q_t is the adsorption values at the time instant ‘t’, k_d is the diffusion rate constant in mg/g min$^{1/2}$, and C is a constant associated with boundary layer effect. According to the results obtained q_t vs. $t^{1/2}$ plots have been passed through the origin; so intraparticle diffusion is a sole rete determining or limiting step [17].

The experimental adsorption data were studied by pseudo-first-order and pseudo-second-order kinetic models of adsorption process. Lagergren first-order rate expression is as follows:

$$\log\left(q_e - q_t\right) = \log q_e \left(\frac{k_1 t}{2.303}\right) \tag{7}$$

where q_e and q_t are the amount of dye adsorbed at equilibrium and at time t and k_1 is the rate constant of first-order adsorption. The second-order kinetic model is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where k_2 is the rate constant of second-order adsorption.

By varying the pH values of the dye solution, the adsorption capacities of the synthesized hydrogels have been determined which show the maximum adsorption at pH 8. Preferably, adsorption kinetics has been studied at this pH value as shown in Figs. 8 and 9.

The kinetic model is more likely to predict the behavior over adsorption, which may involve forces through sharing of electrons between adsorbent and adsorbate. The Table 4 has shown correlation coefficients for the first-order kinetic model as well as second kinetic model. The correlation coefficient for second-order kinetic is low as compared to first-order kinetic model. In case of hydrogel effect on adsorption rate, it may be due to the increasing carboxyl group increases the initial adsorption rate. By increasing the negative charge group in hydrogels, there are interactions between the dye molecules and hydrogels.

Comparison of adsorption capacities of different adsorbents with this current work is given in Table 5, that has

Table 5
Comparison of maximum adsorption of dyes onto different adsorbent based on polyacrylamide and GO-NPs based composites

Adsorbent	Dye	Adsorption capacity (mg g^{-1})	References
Sodium alginate/acrylamide hydrogel	Methylene blue	78.10	[11]
Poly(N,N-dimethylacrylamide-co-2-hydroxyethyl methacrylate) hydrogel	Methylene blue	80.27	[11]
GO	Methylene blue	710	[18]
N-isopropylacrylamide/itaconic acid/pumice composite hydrogels	Methylene blue	22.18	[11]
Pineapple peel carboxymethyl cellulose-g-poly(acrylic acid-co-acrylamide)/graphene oxide hydrogels	Methylene blue	133.32	[11]
Pineapple peel carboxymethyl cellulose-g-poly(acrylic acid-co-acrylamide)/graphene oxide hydrogels	Neutral red	120.37	[11]
PVA/PCMC/GO/bentonite	Methylene blue	172.41	[10]
Graphene oxide (GO)/polyacrylamide (PAM) composite hydrogels	Methylene blue	292.84	[19]
Graphene oxide (GO)/polyacrylamide (PAM) composite hydrogels	Rhodamine 6G	288	[19]
β-CD/MGO/PAA hydrogel	Methylene blue	2,802.67	[20]
Nano-silica KCC-1 Methylimidazolium/tetrasulfide/amine	Acid orange II (AO)	676.7	[21]
GO-PAM hydrogel	Drimarene Brilliant Blue K-4BL	1,000	This work

proved the excellent adsorption potential of GO-PAM composite.

3.4. Reusability of the synthesized hydrogels

Generally, a good adsorbent requires good reusability to respond the demand of low cost. Five adsorption and desorption cycles were performed by immersing pure PAM, 0.4% GO-PAM and 0.6% GO-PAM composites in dye and 4% HCl water/ethanol solution respectively. After five cycles of the adsorption–desorption process, the synthesized hydrogels still retained appreciable adsorption capacities (~40%), indicating their good reusability for dye adsorption (Fig. 10). The loss of adsorption capacity can be attributed to the cohesive interaction of dye molecules with the active binding sites of composites, thus decreasing the adsorption capacity of composites. Owing to the excellent adsorption capacity (1,000 mg g^{-1}), even after 60% loss of adsorption efficiency, the hydrogels still have sufficient ability to remove dye from solution. The results revealed that the synthesized hydrogels can be applied as stable, low cost and effective adsorbent for dye removal [10].

4. Conclusion

Graphene oxide reinforced polyacrylamide composite hydrogels were successfully synthesized and applied for the removal of Drimarene Brilliant Blue K-4BL dye. Graphene oxide reinforced polyacrylamide hydrogels give a chance to develop thermo-mechanically stable (data not included) and highly efficient hydrogels in terms of adsorption that was ten times more as compared to the pure polyacrylamide. At pH 8, maximum water uptake capacity of composites owing to the improved microstructures has been observed. The pH dependent uptake of dye by the hydrogel, due to electrostatic and π–π interactions was observed, with maximum absorption capacity at pH 8. The expansion of polymer network chains of the hydrogel structure and ion complexes have established between hydrogel chains and the dye molecules by electrostatic forces; this causes the maximum removal rate. These significant characters of excellent water retention ability and the exposure of maximum adsorptive sites (due to prescence of abundant hydroxyl and hydrophilic groups of nano-composite) at same pH make the composite a super adsorbent. Equilibrium and kinetic studies suggested that modified Freundlich and pseudo-first-order models were best fitted with the experimental data. Regeneration and reusability studies of the hydrogels revealed almost 40% adsorption capacity after five cycles. Considering the extraordinary adsorption and recycling potential of synthesized composite hydrogels, these can be cost effective and promising candidate to remove dyes from effluents. We hope all these narrative traits and conditions that we have applied at laboratory scale will be able to pave real time ways in the industrial area successfully.

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Conflicts of interest/competing interests

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

Availability of data and material

Authors' contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by [Mubeen Kousar], [Maheen Almas], [Saima Rehman], [Shagufta Kamal] and [Khalid Mahmood Zia]. The first draft of the manuscript was written by [Mubeen Kousar] and [Saima Rehman] and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Ethics approval

The study has been conducted keeping in view the ethical considerations. No human or animal trials were included.

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