Removal of mixed cationic dyes by a biosorbent based on magnetic tragacanth gum hydrogel

Mehdi Jaymand (✉ m_jaymand@yahoo.com)

Kermanshah University of Medical Sciences

Research Article

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Abstract

A magnetic tragacanth gum-*grafted* poly(acrylic acid) hydrogel (TG-*g*-PAA/Fe₃O₄) was applied for removal of malachite green (MG), basic yellow 28 (BY28), and rhodamine 6G (Rh6G) cationic dyes from industrial simulated wastewater *via* the well-known batch method. The most important parameters such as initial dyes concentrations, adsorbent dosage, pH, and contact time that affected adsorption performance were optimized in all single, binary, and ternary systems. The adsorption for all dyes in all systems were well-fitted with Langmuir model than those of the Freundlich model that revealed the linearity of the process. Maximum adsorption capacities (Q_m) for MG, BY28, and Rh6G in ternary system were obtained as 626.5, 568.2, and 459.7 mgg⁻¹, respectively. Kinetic studies exhibited that the removal of all dyes in all systems were best-fitted with the pseudo-second-order model, which proved that the rate-limiting step might be the chemical adsorption. The hydrogel was regenerated by desorption process after loading process and reused for several times. As results, the removal efficiency of adsorbent almost remains the same for the first four cycles, and then decreased gradually.

1. Introduction

Nowadays, water pollution caused by synthetic dyes has become a global concern. Synthetic dyes are used annually in the different industries such as plastics, textiles, leather, paper, and dyestuff because of their coloring properties. These are toxic, non-degradable, bio-accumulative, mutagenic, and carcinogenic that cause serious health issues for human, aquatic fauna and flora¹⁻⁴. Wastewater containing synthetic dyes impedes sunlight penetration and upset photosynthetic activity of aquatic life. Also, it leading to dermatitis, allergy, and skin irritation as well as carcinogenic agent. Consequently, treatment of wastewater containing these dyes is high importance. Various methods have been used for removal of dyes from wastewater, including membrane filtration⁵, adsorption⁶, ion exchange⁷, photocatalytic⁸, coagulation⁹, advanced oxidation process (AOP)¹⁰, electrochemical¹¹, and biological methods¹². Among them, the adsorption method has been widely applied for the dyes removal because of its simplicity, high efficiency, low cost, and reusability features⁶. Various types of adsorbents such as graphene oxide/manganese dioxide (GO/MnO₂)¹³, activated carbon¹⁴, multi-functionalized fibrous silica (MF-KCC-1)¹⁵, nitrilotriacetic acid β -cyclodextrin-chitosan (NTA- β -CD-CS)¹⁶, polyaniline@zinc oxide (PANI@ZnO)¹⁷, and metal-organic framework (MOF)¹⁸ have been reported for the removal of dyes from wastewater.

Hydrogels are another category of potent sorbent for the removal of synthetic dyes owing to their excellent physicochemical properties, including swelling in aqueous media up to several times, colorlessness, odorlessness, non-toxicity, excellent environmental stability, and low production cost in most cases^{19,20}. Amongst, natural polymers-based hydrogels have been received more and more attention due to their superior physicochemical as well as biological features that lead to numerous biological as well as industrial applications^{20,21}.

Tragacanth gum (TG), an acidic polysaccharide, is a biocompatible and biodegradable natural polymer. TG achieves in two different forms containing ribbon and flake. Also, they are available, high thermal and

environmental stability, cheap, non-toxic, and eco-friendly ^{22,23}. TG is frequently applied in various fields, including pharmaceuticals [21], food and cosmetics industries ²⁴, emulsifier ²⁵, fat replacer ²⁶, and cross-linking agent ²⁷. TG composed mainly from branched acidic hetero-polysaccharides of D-galacturonic acid. Sugars include D-galactose, L-fucose (6-deoxy-L-galactose), D-xylose and L-arabinose generated after hydrolysis. TG is composed of two fractions of water-soluble and insoluble, so that tragacanthin (30–40%) act as the soluble fraction to create a viscous colloidal hydrosol, while bassorin (60–70%) act as the insoluble fraction to form a stiff gel ²⁸. The hydroxyl and carboxylic acid groups in TG backbone provide the proper opportunity for reacting with cross-linking reagents and chemical modification ²⁹. In this context, grafting of synthetic polymers (*e.g.*, poly(acrylic acid); PAA) can improve some physicochemical properties of the resultant hydrogel for its final usage aim. Some research projects have been conducted for the removal of organic dyes using TG-based hydrogels. For example, Sadeghi et al. applied a nanocomposite containing TG and poly(methyl methacrylate) (PMMA) reinforced with bentonite for the removal of acid blue 113 (AB-113), methyl orange (MO), and congo red (CR) dyes ³⁰. In another study, Mallakpour et al. synthesized TG/CaCO₃@EDTA nanocomposite for the adsorption of methylene blue dye ³¹.

Incorporation of Fe₃O₄ nanoparticles (NPs) into the hydrogel-based sorbent have been attracted a great deal of interest due to simple separation of magnetic hydrogels from aqueous solution by using a magnetic field. Magnetic hydrogels-based adsorbents have been used for various pollutants removal, including dyes ³², heavy metals ³³, phosphate ³⁴, ammonia ³⁵, and pesticide ³⁶.

As the above-discussion, we hypothesize that magnetic modified natural gums-based hydrogels as biosorbent can be opened up the frontiers for the removal of synthetic dyes from industrial effluents owing to their superior physicochemical as well as biological features. Consequently, a facile strategy was applied for efficient removal of rhodamine 6G (Rh6G), basic yellow 28 (BY28), and malachite green (MG) dyes from single, binary, and ternary systems using TG-*g*-PAA/Fe₃O₄ biosorbent (Schemes 1 and 2). The effects of different parameters such as pH, contact time, initial concentration, and sorbent dosage were studied and optimized.

2. Experimental

2.1. Materials

The magnetic hydrogel (TG-*g*-PAA/Fe₃O₄) was synthesized in our laboratory ³⁷. The MG, Rh6G, and BY28 cationic dyes were obtained from (Sigma-Aldrich, St. Louis, MO, USA). Sodium hydroxide (NaOH), hydrogen chloride (HCl), sodium carbonate (NaCO₃), and sodium chloride (NaCl) were provided from Sigma-Aldrich.

2.2. Swelling properties

The swelling properties of the TG-*g*-PAA/Fe₃O₄ hydrogel was assessed by the well-established gravimetric method. For this aim, the dried hydrogel was cut and weighed. The species were immersed in deionized water and weighed at the predetermined time intervals. The swollen species were taken out, the additional

water on the surface was removed using a filter paper, and weighed again. The swelling ratio (SR) was quantified by the following equation.

$$SR = \frac{W_t - W_i}{W_i} \times 100(1)$$

where, W_t is weight of swelled hydrogel at time t , and W_i is the initial weight of the hydrogel.

2.3. Zero point charge (pH_{zpc}) of TG-g-PAA/ Fe_3O_4 hydrogel

In adsorption process, removal efficiency is significantly depends on the zero point charge (pH_{zpc}) of adsorbent. For investigation the pH_{zpc} value of the adsorbent, NaCl solution (30 mL; 0.1 molL^{-1}) were added to Erlenmeyer flasks, and pH of solutions were adjusted between 1 to 9 using dilute solution of NaOH or HCl (0.1 molL^{-1}). The preliminary pH values were denoted as pH_i . Afterward, the sorbent (0.10 g) was added to each flask, and stirred till no variation in pH values was observed between two successive readings. The equilibrium pH (pH_e), which was used to calculate ΔpH ($pH_i - pH_e$). Graph of ΔpH against pH_i gave the pH_{zpc} value at which the ΔpH reads zero ^{38,39}.

2.3. Adsorption processes

2.3.1. Single dye system

The well-established batch approach was used for the removal of MG, BY28, and Rh6G cationic dyes. In a typical experiment, the TG-g-PAA/ Fe_3O_4 hydrogel was immersed in 100 mL solutions of MG, BY28, and Rh6G dyes with concentration of 100 to 700 mgL^{-1} . The pH of solutions were adjusted in the range of 3 to 9 through the addition of HCl or NaOH solutions (0.1 molL^{-1}). The removal processes were performed at contact times of 10–120 minutes. The sorbent dosage was optimized using 1, 2, 4, 6, 8, 10 gL^{-1} of hydrogel. The industrial condition was stimulated through the addition of sodium carbonate (0.003 molL^{-1}) and sodium chloride (0.01 molL^{-1}) to the dyes solutions. The removal efficiency (R) and equilibrium adsorption capacity (q_e) of the sorbent were calculated using a UV-vis spectrophotometer (at 618, 528 and 439 nm for MG, Rh6G, and BY28, respectively) by equations 2 and 3, respectively.

$$R(\%) = \frac{(C_o - C_e)}{C_o} \times 100(2)$$

$$q_e = \frac{(C_o - C_e)}{W} \times V(3)$$

where, C_o (mgL^{-1}) and C_e (mgL^{-1}) are the initial and final concentrations of each dye, respectively, V is the dye solution volume (mL), and W is the mass of sorbent (g) ^{40,41}.

2.3.2. Binary dyes system

In a binary removal system, 100 mL (400 mgL^{-1}) of dyes solutions taken for experiment at optimized condition. The removal efficiency for each dye was calculated by a UV-vis spectrophotometer using equations 2 and 3.

2.3.3. Ternary dyes system

In ternary system, 33.33 mL (400 mgL^{-1}) of each dye was taken for process under optimized condition. The concentrations of each dye was quantified by a UV-vis spectrophotometer using equations 2 and 3.

2.4. Regeneration and reusability

The dye(s) loaded TG-*g*-PAA/Fe₃O₄ sorbent was immersed in various solvents at various pH's (3 to 10) and stirred in ambient condition. Consequently, the hydrogel was isolated by an external magnet bar, and the dyes concentration were calculated by a UV-vis spectrophotometer according to Eq. 4.

$$\text{Desorption(\%)} = \frac{C_e}{C_o} \times 100(4)$$

where, C_o (mgL^{-1}) and C_e (mgL^{-1}) are the initial and final concentrations of dye(s), respectively. The regenerated TG-*g*-PAA/Fe₃O₄ hydrogel was taken for adsorption-desorption process under optimized condition for several times.

2.5. Characterization

The Ultraviolet-visible spectra were provided using a Specord 210 Plus spectrophotometer (Analytik-Jena AG, Germany).

3. Results And Discussion

3.1. Swelling behavior

The swelling properties of the TG-*g*-PAA/Fe₃O₄ hydrogel was investigated in numerous pH values (2, 7, and 9) as depicted in Fig. 1. During swelling, the volume of the sorbent increased significantly that can improve dyes uptake significantly. As seen, by increasing time in all pH values the swelling ratio was increased, and after 350 minutes the swelling ratio reached equilibrium. In addition, increasing the pH value lead to increasing the swelling ratio. The highest swelling ratio was obtained as 316% after 350 minutes at pH 9.

3.2. pH_{zpc} measurement

The pH_{zpc} value for the TG-*g*-PAA/Fe₃O₄ hydrogel was measured as 4.65 (regression coefficient (R^2) 0.983). Consequently, the surface of the TG-*g*-PAA/Fe₃O₄ adsorbent will be negatively charged above pH_{zpc} and positively charged below pH_{zpc}. Therefore, TG-*g*-PAA/Fe₃O₄ hydrogel can be easily adsorb cationic dyes at pH values higher than 4.65 due to efficient physical interactions between dyes and hydrogel matrix (Fig. 2).

3.3. Removal condition optimization

The most important parameters, including pH, initial dye concentration, adsorbent dosage, and contact time that influence removal process were optimized as follows.

3.3.1. Effect of pH

The effect of pH on removal efficiency of MG, Rh6G, and BY8 dyes were studied in single, binary, and ternary systems in the range of 3 to 9 as depicted in Fig. 3. As expected, at acidic pH values (especially below pH_{zpc} ; 4.65) the sorbent did not showed acceptable removal efficiency owing to its positively charged surface. In contrast, above pH_{zpc} removal efficiency was increased in all systems for all dyes due to excellent physical interactions (*e.g.*, ionic and hydrogen bonding) between dyes and hydrogel matrix.

In single system (Fig. 3a), the highest removal efficiencies for MG (95%), Rh6G (79%), and BY28 (86%) were obtained at pH 8, 7 and 7, respectively. In binary system composed of MG and BY28 dyes, the highest removal efficiencies were obtained as 91 and 76%, respectively, at pH 8 and 7, respectively (Fig. 3b). In MG and Rh6G binary system, the highest removal efficiencies were obtained as 89 and 76%, respectively, at pH 8 and 7, respectively. The optimal pH value for the removal of BY28 (88%) and Rh6G (82%) dyes in binary system was obtained as 7 for both dyes. In the case of this binary system, hydrogen bonding between the dyes as well as matrix and π - π stacking between dyes lead to higher removal efficiency than those of the other systems.

Finally, in ternary system the optimal pH value for the removal of MG (92), BY28 (78%) and Rh6G (74%) dyes were obtained 8, 7, and 7, respectively. As the results, pH 7 was selected as the optimal pH value for all dyes and systems. In addition, Table 1 summarize the results of pH optimization study.

Table 1
The results of pH optimization study.^a

System type	Optimal pH			Maximum removal (%)		
Single	MG	Rh6G	BY28	MG	Rh6G	BY28
	8	7	7	95	79	86
Binery	MG + RhB	MG + BY28	Rh6G + BY28	MG + Rh6G	MG + BY28	Rh6G + BY28
	8 and 7	8 and 7	7 and 7	89 and 76	91 and 76	82 and 88
Ternary	8 and 7 and 7			92 and 74 and 78		
^a Condition: 25°C; dye concentration 400 mgL ⁻¹ , adsorbent dosage 8 mgL ⁻¹ , contact time 90 minutes.						

3.3.2. Effect of adsorbent dosage

In adsorption process, adsorbent dosage optimization is an important stage owing to commercial and environmental aspects of wives. The effect of adsorbent dosage on removal efficiencies of MG, BY28, and Rh6G dyes was studied in single, binary, and ternary systems as illustrated in Fig. 4.

The removal efficiencies of all dyes were increased continuously with the increasing of adsorbent dosage up to 8 gL^{-1} in all single, binary, and ternary systems, and after which the removal efficiencies did not changed significantly. The maximum removal of MG, BY28 and Rh6G dyes in optimum sorbent dosage (8 gL^{-1}) were obtained as 91, 86, and 79%, respectively, in this system (Fig. 4a). As seen in Fig. 4b, in MG and BY28 binary system the maximum removal were obtained as 83 and 76%, respectively.

In MG and Rh6G binary system, the maximum removal were obtained as 85 and 76%, respectively (Fig. 4c). In BY28 and Rh6G binary system, the maximum removal were quantified as 88 and 82%, respectively (Fig. 4d). Finally, in MG, BY28, and Rh6G ternary system, the maximum removal were calculated to be 87, 78, and 74%, respectively (Fig. 4e). As the results, the optimum sorbent dosages for all single, binary, and ternary systems was selected as 8 gL^{-1} for all dyes.

3.3.3. Effect of initial dye concentration

In general, the wastewater containing dyes was concentrated before treatment. Therefore, the optimization of initial dyes concentrations is particular of interest in adsorption processes. As seen in all single, binary and ternary systems, the sorbent can be adsorb approximately 100% of dyes up to concentration of 300 mgL^{-1} under optimized condition. In contrast, at higher concentrations, the saturation of the adsorbent active sites led to lower quantities of dyes adsorption. As the high concentration of wastewater and acceptable removal efficiency of dyes up to concentration of 400 mgL^{-1} , this concentration was selected as the optimal value for all dyes in all systems.

In detail, the adsorbent can be remove 91, 86 and 79% of MG, BY28 and Rh6G dyes, respectively, at concentration of 400 mgL^{-1} in single system (Fig. 5a). In MG and BY28 binary system, the removal efficiencies at dyes concentration of 400 mgL^{-1} were quantified as 83 and 76%, respectively (Fig. 5b). In binary system composed of MG and Rh6G dyes, the sorbent can adsorbed 85 and 76% of dyes, respectively (Fig. 5c). The removal efficiency of BY28 and Rh6G dyes at optimal concentration were calculated to be 88 and 82%, respectively (Fig. 5d). Finally, at the ternary system, the removal efficiencies of MG, BY28 and Rh6G dyes at concentration of 400 mgL^{-1} were obtained as 87, 78, 74%, respectively (Fig. 5e).

3.3.4. Effect of contact time

The effect of contact time on removal efficiencies of MG, BY28 and Rh6G dyes in all single, binary, and ternary systems were investigated and the results obtained are summarized in Fig. 6. As seen, the highest removal efficiencies for all dyes in all systems (except MG in single system; 80 minutes) were obtained to be 90 minutes, and after which the removal efficiency of each dye is not changed significantly. Therefore, 90 minutes was selected as the optimum contact time for all dyes in all systems.

3.4. Time-dependent Removal process

Time-dependent removal of MG, BY28 and Rh6G dyes in single, binary, and ternary systems were performed on the above-mentioned optimal condition, and electronic spectra as well as photographs are illustrated in Figs. 7, 8, and 9.

3.5. Adsorption isotherms

Langmuir and Freundlich isotherm models were applied for adsorption isotherm study in all single, binary and ternary systems (equations 5 and 6, respectively).

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \quad (5)$$

$$q_e = K_F C_e^{1/n} \quad (6)$$

In these equations, q_e (mgg^{-1}) is the adsorbed dye concentration on the sorbent, C_e (mgL^{-1}) is the equilibrium concentration of dye in the bulk solution, Q_m (mgg^{-1}) is the monolayer adsorption capacity, K_L (Lmg^{-1}) is the Langmuir constant, K_F and n are the Freundlich constants.

Another important parameter in the Langmuir isotherm model is dimensionless constant (R_L ; otherwise known as equilibrium parameter) that investigated by following Eq. 4².

$$R_L = \frac{1}{1 + a_L C_0} \quad (7)$$

In Eq. 7, R_L is the shape of the Langmuir isotherm, a_L (Lmg^{-1}) is the Langmuir constant associated to the energy of adsorption, and C_0 (mgL^{-1}) is the initial concentration of dyes. The a_L obtained from the slope of the Langmuir isotherm. If $R_L > 1$, $R_L = 1$, $R_L = 0$, and $R_L < 1$ the adsorption process are considered as unfavorable, linear, irreversible, and favorable, respectively.

Langmuir and Freundlich isotherm plots for the removal of MG, BY28 and Rh6G dyes in single system are depicted in Fig. 10. The R^2 values for all dyes in Langmuir model are approach's to one, which revealed the Langmuir model is well-fitted in comparison with the Freundlich model to describe the adsorption process. In the case of binary (Fig. 11) and ternary (Fig. 12) systems were also obtained the similar results. These data confirm the linearity of the adsorption process.

Some Langmuir and Freundlich isotherm models parameters are summarized in Tables 2 and 3, respectively. According to R_L and $1/n$ values (< 1), the adsorption of all dyes onto/into the sorbent are favorable. In addition, the Q_m vales for MG, BY28 and Rh6G dyes in single, binary, and ternary systems were quantified and listed in Table 2.

Table 2
Langmuir isotherm model parameters at 25°C for single, binary, and ternary systems.

Dye(s)	$Q_{\max}$ (mgg ⁻¹)	K_L (Lmg ⁻¹)	R_L	R^2
MG	641.7	0.148	0.0053	0.9922
BY28	583.4	0.237	0.0059	0.9896
Rh6G	473.5	0.253	0.0067	0.9864
MG + BY28	634.3/572.1	0.172/0.246	0.0055/0.0063	0.9923/0.9841
MG + Rh6G	627.6/451.3	0.18/0.268	0.0055/0.0071	0.9908/0.9837
BY28 + Rh6G	591.8/479.3	0.224/0.241	0.0054/0.0062	0.9864/0.9872
MG + BY28 + Rh6G	626.5/568.2/459.7	0.179/0.251/0.276	0.0057/0.0065/0.0074	0.9945/0.9945/0.9883

Table 3
Freundlich isotherm model parameters at 25°C for single, binary, and ternary systems.

Dye(s)	n	K_F (Lmg ⁻¹)	R^2
MG	4.11	178.4	0.9695
BY28	4.04	161.7	0.9574
Rh6G	3.79	152.9	0.9392
MG + BY28	4.05/4.01	172.3/154.6	0.9323/0.9309
MG + Rh6G	4.02/3.57	171.7/146.2	0.9346/0.9376
BY28 + Rh6G	4.08/3.82	166.2/159.1	0.9341/0.9294
MG + BY28 + Rh6G	4.01/3.94/3.48	164.1/151.3/142.72	0.9766/0.9674/0.9534

3.6. Adsorption kinetic

The sorption rates of MG, BY28 and Rh6G dyes onto/into the TG-*g*-PAA/Fe₃O₄ hydrogel were evaluated using pseudo-first-order and pseudo-second-order kinetic models (equations 8 and 9, respectively).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where, q_e (mgg^{-1}) is the loaded amount of dyes at the equilibrium, q_t (mgg^{-1}) is the loaded dyes amount at time t , k_1 and k_2 are the pseudo-first-order and pseudo-second-order equation rate constants, respectively. The kinetic study results such as correlation coefficient, k_1 and k_2 values are represented in Table 4. As seen, the adsorption of MG, BY28 and Rh6G dyes in all systems (single, binary, and ternary) are well-fitted with the pseudo-second-order model ($R^2 > 0.98$) than those of the pseudo-first-order model. As these data, the rate-limiting step might be the sorption of dyes onto/into the adsorbent, but not the mass transport.

Table 4

Adsorption kinetic parameters for the sorption of MG, BY28, and Rh6G dyes onto/into adsorbent in single, binary, and ternary systems.

Pseudo-first-order			Pseudo-second-order	
Dye(s)	$k_1 \times 10^{-2} (\text{min}^{-1})$	R^2	$k_2 \times 10^{-3} (\text{g} (\text{mg} \cdot \text{min})^{-1})$	R^2
MG	1.69	0.969	3.02	0.998
BY28	1.76	0.954	2.91	0.993
Rh6G	1.83	0.942	2.73	0.991
MG + BY28	1.71/1.81	0.961/0.952	2.98/2.83	0.997/0.991
MG + Rh6G	1.74/1.87	0.969/0.951	2.96/2.63	0.996/0.984
BY28 + Rh6G	1.72/1.79	0.951/0.947	2.97/2.79	0.994/0.993
MG + BY28 + Rh6G	1.62/1.72/1.86	0.967/0.949/0.941	2.97/2.77/2.52	0.993/0.989/0.984

3.7. Regeneration and reusability study

In industrial process, regeneration and re-usability of an adsorbent is an important stage from economic and industrial point of views. The desorption ability of the TG-*g*-PAA/Fe₃O₄ hydrogel was assessed in various solvents (Eq. 10), and the results obtained are presented in Table 5.

$$\text{Desorption}(\%) = \frac{\text{Amount of dye liberated by acid}}{\text{Amount of dye in the adsorbent}} \times 100(10)$$

As experiment results, the mixture of water/methanol (93/7 v/v) at pH 3 showed the highest desorption efficiency. According to chemical composition of adsorbent, at acidic condition (pH 3) the carboxylic acid groups of hydrogel (more especially PAA segments) are fully protonated that resulted to weaken physical interactions (e.g., ionic) and facile desorption of cationic dyes from adsorbent.

The regeneration of the adsorbent was achieved through desorption process as mentioned above, and then the adsorbent was taken for several adsorption–desorption cycles under optimized condition in ternary system. As illustrated in Fig. 13, the removal efficiency of MG, BY28, and Rh6G dyes using TG-*g*-PAA/Fe₃O₄ hydrogel almost remains the same for the first four cycles, and after which the removal efficiency decreased

gradually owing to saturation of adsorbent surface that lead to the decrease in the availability of attaching sites ⁴³.

Table 5
Desorption values of MG, BY28 and Rh6G dyes from TG-*g*-PAA/Fe₃O₄ hydrogel.^a

Eluent	Desorption efficiency (%) ^a		
	MG	BY28	Rh6G
Water (pH 7)	57	54	55
Methanol (pH 7)	49	47	46
Ethanol (pH 7)	47	45	44
Water (pH 3)	87	84	88
Water/Methanol (93:7 v/v) (pH 3)	96	95	97
Water/Ethanol (93:7 v/v) (pH 3)	95	93	96
^a Desorption condition: T = 25°C, time = 70 minutes, adsorbent amount = 0.50 g, and desorption eluent volume = 100 mL, ternary system.			

3.8. Adsorption mechanism

As the chemical composition of TG-*g*-PAA/Fe₃O₄ hydrogel, the electrostatic interactions (*e.g.*, hydrogen bonding and ionic) between the polymeric matrix as well as Fe₃O₄ NPs and dyes are the main physicochemical reason for the adsorption of MG, BY28, and Rh6G cationic dyes. In addition, π - π stacking as well as hydrogen bonding interactions may be occurred between dyes as their chemical structures (Scheme 3).

3.9. Removal efficiency comparison

The removal efficiencies of TG-*g*-PAA/Fe₃O₄ hydrogel in removal of MG, BY28, and Rh6G dyes was compared with some other sorbents (Table 6). As seen, the TG-*g*-PAA/Fe₃O₄ hydrogel has acceptable Q_m in comparison with others.

Table 6

Comparison of the $Q_{\max}$ (mgg^{-1}) of other adsorbents in removal of MG, BY28, and Rh6G dyes in ternary system.

Adsorbent	Dyes			Q_m (mgg^{-1})	References
	MG	BY28	Rh6G		
Akash Kinari coal	+	-	-	83.42	42
Copper sulfide nanoparticles	+	-	-	253.2	44
Expanded polystyrene foam	+	-	-	1197.3	45
Acid-treated Sawdust	+	-	-	25	46
Natural safiot clay	-	+	-	166	47
TG- <i>g</i> -PAA/Fe ₃ O ₄ hydrogel	+	+	+	626.5/568.2/459.7	This work

4. Conclusions

The performance of TG-*g*-PAA/Fe₃O₄ hydrogel in the removal of MG, BY28, and Rh6G dyes from simulated industrial single, binary and ternary systems were investigated, and the most important affected parameters such as pH (7), adsorbent amount (8 gL^{-1}), contact time (80 minutes), and dyes concentrations (400 mgL^{-1}) were optimized. The adsorption isotherm of MG, BY28, and Rh6G dyes by TG-*g*-PAA/Fe₃O₄ hydrogel were investigated by Langmuir and Freundlich models, and it was revealed that the adsorption of all dyes in all systems well-fitted with the Langmuir adsorption isotherm model, which proved the linearity of the adsorption process. The Q_m values for MG, BY28, and Rh6G dyes were quantified for single, binary and ternary systems. In ternary system, the Q_m values were obtained to be 626.5, 568.2, and 459.7 mgg^{-1} , respectively.

In addition, it was revealed that the adsorption process in all systems and for all dyes were best-fitted with the pseudo-second-order model that proved the rate-limiting step might be the adsorption step. The dye-loaded hydrogel was regenerated through desorption process by mixed water/methanol (93/7 v/v; pH 3), and then reused for several times. It was revealed that the removal performance almost remains the same for the first four cycles, and then decreased gradually.

As the results, it could be concluded that owing to high adsorption capacity of adsorbent, mild process condition (*e.g.*, pH 7 and 25°C), and low cost and eco-friendly nature of adsorbent the TG-*g*-PAA/Fe₃O₄ hydrogel can be applied for efficient removal of mixed cationic dyes from industrial effluents.

Declarations

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Competing interests

The authors declare no competing interests.

Availability of materials and data

All data generated or analyzed during this study are included in this article.

References

1. Crini, G. Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer. *Dyes and Pigments* **77**, 415–426 (2008).
2. Deniz, F. & Kepekci, R. A. Bioremoval of Malachite green from water sample by forestry waste mixture as potential biosorbent. *Microchemical Journal* **132**, 172–178 (2017).
3. Machado, F. M. *et al.* Adsorption of Reactive Red M-2BE dye from water solutions by multi-walled carbon nanotubes and activated carbon. *Journal of hazardous materials* **192**, 1122–1131 (2011).
4. Machado, F. M. *et al.* Adsorption of Reactive Blue 4 dye from water solutions by carbon nanotubes: experiment and theory. *Physical Chemistry Chemical Physics* **14**, 11139–11153 (2012).
5. Zeng, H. *et al.* A novel strategy for enhancing the performance of membranes for dyes separation: Embedding PAA@ UiO-66-NH₂ between graphene oxide sheets. *Chemical Engineering Journal* **403**, 126281 (2021).
6. Wang, H. *et al.* Effective adsorption of dyes on an activated carbon prepared from carboxymethyl cellulose: Experiments, characterization and advanced modelling. *Chemical Engineering Journal* **417**, 128116 (2021).
7. Xu, L. *et al.* Electrostatic Self-Assembly Synthesis of Three-Dimensional Mesoporous Lepidocrocite-Type Layered Sodium Titanate as a Superior Adsorbent for Selective Removal of Cationic Dyes via an Ion-Exchange Mechanism. *Langmuir* (2021).
8. Kiwaan, H., Atwee, T., Azab, E. & El-Bindary, A. Photocatalytic degradation of organic dyes in the presence of nanostructured titanium dioxide. *Journal of Molecular Structure* **1200**, 127115 (2020).
9. Demissie, H. *et al.* Modification of high content nanocluster-based coagulation for rapid removal of dye from water and the mechanism. *Separation and Purification Technology* **259**, 117845 (2021).
10. Alderete, B. L. *et al.* Evaluation of toxicity and mutagenicity of a synthetic effluent containing azo dye after advanced oxidation process treatment. *Chemosphere* **263**, 128291 (2021).
11. Lu, J., Ayele, B. A., Liu, X. & Chen, Q. Electrochemical removal of RRX-3B in residual dyeing liquid with typical engineered carbonaceous cathodes. *Journal of Environmental Management* **280**, 111669 (2021).

12. Mishra, S., Cheng, L. & Maiti, A. The utilization of agro-biomass/byproducts for effective bio-removal of dyes from dyeing wastewater: a comprehensive review. *Journal of Environmental Chemical Engineering* **9**, 104901 (2021).
13. Verma, M. *et al.* Fabrication of GO–MnO₂ nanocomposite using hydrothermal process for cationic and anionic dyes adsorption: Kinetics, isotherm, and reusability. *Journal of Environmental Chemical Engineering* **9**, 106045 (2021).
14. Abdulhameed, A. S. *et al.* Statistical modeling and mechanistic pathway for methylene blue dye removal by high surface area and mesoporous grass-based activated carbon using K₂CO₃ activator. *Journal of Environmental Chemical Engineering* **9**, 105530 (2021).
15. Pishnamazi, M. *et al.* Adsorption of dyes on multifunctionalized nano-silica KCC-1. *Journal of Molecular Liquids* **338**, 116573 (2021).
16. Usman, M. *et al.* Simultaneous adsorption of heavy metals and organic dyes by β -Cyclodextrin-Chitosan based cross-linked adsorbent. *Carbohydrate Polymers* **255**, 117486 (2021).
17. Toumi, I., Djelad, H., Chouli, F. & Benyoucef, A. Synthesis of PANI@ ZnO hybrid material and evaluations in adsorption of congo red and methylene blue dyes: structural characterization and adsorption performance. *Journal of Inorganic and Organometallic Polymers and Materials*, 1–10 (2021).
18. Wang, G.-Q. *et al.* A hydrolytically stable cage-based metal–organic framework containing two types of building blocks for the adsorption of iodine and dyes. *Inorganic Chemistry Frontiers* **8**, 1083–1092 (2021).
19. Jaymand, M. Sulfur functionality-modified starches: Review of synthesis strategies, properties, and applications. *International Journal of Biological Macromolecules* **197**, 111–120, doi:<https://doi.org/10.1016/j.ijbiomac.2021.12.090> (2022).
20. Safarzadeh Kozani, P. *et al.* Polysaccharide-based hydrogels: properties, advantages, challenges, and optimization methods for applications in regenerative medicine. *International Journal of Polymeric Materials and Polymeric Biomaterials*, 1–15 (2021).
21. Soleimani, K., Derakhshankhah, H., Jaymand, M. & Samadian, H. Stimuli-responsive natural gums-based drug delivery systems for cancer treatment. *Carbohydrate polymers* **254**, 117422 (2021).
22. Verbeken, D., Dierckx, S. & Dewettinck, K. Exudate gums: occurrence, production, and applications. *Applied microbiology and biotechnology* **63**, 10–21 (2003).
23. Hong, K. H., Oh, K. W. & Kang, T. J. Preparation of conducting nylon-6 electrospun fiber webs by the in situ polymerization of polyaniline. *Journal of Applied Polymer Science* **96**, 983–991 (2005).
24. Hosseini, M. S., Hemmati, K. & Ghaemy, M. Synthesis of nanohydrogels based on tragacanth gum biopolymer and investigation of swelling and drug delivery. *International journal of biological macromolecules* **82**, 806–815 (2016).
25. Nejatian, M., Abbasi, S. & Azarikia, F. Gum Tragacanth: Structure, characteristics and applications in foods. *International Journal of Biological Macromolecules* **160**, 846–860 (2020).
26. Ghaderi-Ghahfarokhi, M., Yousefvand, A., Ahmadi Gavlighi, H., Zarei, M. & Farhangnia, P. Developing novel synbiotic low-fat yogurt with fucoxylogalacturonan from tragacanth gum: Investigation of

- quality parameters and *Lactobacillus casei* survival. *Food Science & Nutrition* **8**, 4491–4504 (2020).
27. Hemmati, K., Masoumi, A. & Ghaemy, M. Tragacanth gum-based nanogel as a superparamagnetic molecularly imprinted polymer for quercetin recognition and controlled release. *Carbohydrate polymers* **136**, 630–640 (2016).
 28. Zare, E. N., Makvandi, P. & Tay, F. R. Recent progress in the industrial and biomedical applications of tragacanth gum: A review. *Carbohydrate polymers* **212**, 450–467 (2019).
 29. Sayadnia, S., Arkan, E., Jahanban-Esfahlan, R., Sayadnia, S. & Jaymand, M. Thermal-responsive magnetic hydrogels based on Tragacanth gum for delivery of anticancer drugs. *Journal of Polymer Research* **28**, 1–13 (2021).
 30. Sadeghi, S., Moghaddam, A. Z. & Massinaei, M. Novel tunable composites based on bentonite and modified tragacanth gum for removal of acid dyes from aqueous solutions. *RSC advances* **5**, 55731–55745 (2015).
 31. Mallakpour, S. & Tabesh, F. Tragacanth gum based hydrogel nanocomposites for the adsorption of methylene blue: Comparison of linear and non-linear forms of different adsorption isotherm and kinetics models. *International journal of biological macromolecules* **133**, 754–766 (2019).
 32. Chen, X., Huang, Z., Luo, S.-Y., Zong, M.-H. & Lou, W.-Y. Multi-functional magnetic hydrogels based on *Millettia speciosa* Champ residue cellulose and Chitosan: Highly efficient and reusable adsorbent for Congo red and Cu²⁺ removal. *Chemical Engineering Journal* **423**, 130198 (2021).
 33. Wu, S., Guo, J., Wang, Y., Huang, C. & Hu, Y. Facile preparation of magnetic sodium alginate/carboxymethyl cellulose composite hydrogel for removal of heavy metal ions from aqueous solution. *Journal of Materials Science* **56**, 13096–13107 (2021).
 34. Zhou, Y. *et al.* Phosphate removal by a La (OH)₃ loaded magnetic MAPTAC-based cationic hydrogel: Enhanced surface charge density and Donnan membrane effect. *Journal of Environmental Sciences* **113**, 26–39 (2022).
 35. Fazilati, A., Mokhtarian, N., Latifi, A. M. & Fazilati, M. Synthesis of Acrylic Acid Polymer Hydrogel Nano Fe₃O₄ to Remove Ammonia from Sugarcane Field Waste. *Advances in Materials Science and Engineering* **2020** (2020).
 36. Tiwari, A. & Bind, A. Adsorption of pesticide (captan) onto super paramagnetic poly (styrene-co-acrylic acid) hydrogel from aqueous solution using batch and column studies. *Analytical Chemistry Letters* **4**, 267–278 (2014).
 37. Sayadnia, S., Arkan, E., Jahanban-Esfahlan, R., Sayadnia, S. & Jaymand, M. Tragacanth gum-based pH-responsive magnetic hydrogels for “smart” chemo/hyperthermia therapy of solid tumors. *Polymers for Advanced Technologies* **32**, 262–271 (2021).
 38. Shenvi, S. S., Isloor, A. M., Ismail, A. F., Shilton, S. J. & Al Ahmed, A. Humic acid based biopolymeric membrane for effective removal of methylene blue and rhodamine B. *Industrial & Engineering Chemistry Research* **54**, 4965–4975 (2015).
 39. Preethi, S., Sivasamy, A., Sivanesan, S., Ramamurthi, V. & Swaminathan, G. Removal of safranin basic dye from aqueous solutions by adsorption onto corncob activated carbon. *Industrial & engineering chemistry research* **45**, 7627–7632 (2006).

40. Vafaei, M. A., Shakeri, A., Salehi, H., Razavi, S. R. & Salari, N. The effect of nanosheets on polymer hydrogels performance in Rhodamine B dye removal by forward osmosis process. *Journal of Water Process Engineering* **44**, doi:10.1016/j.jwpe.2021.102351 (2021).
41. Wang, W. *et al.* High-performance two-dimensional montmorillonite supported-poly (acrylamide-co-acrylic acid) hydrogel for dye removal. *Environmental Pollution* **257**, 113574 (2020).
42. Khan, T. A., Singh, V. V. & Kumar, D. Removal of some basic dyes from artificial textile wastewater by adsorption on Akash Kinari coal. (2004).
43. Wadhera, P., Jindal, R. & Dogra, R. Synthesis of semi interpenetrating network hydrogel [(GrA-Psy)-cl-Poly (AA)] and its application for efficient removal of malachite green from aqueous solution. *Polymer Engineering & Science* **59**, 1416–1427 (2019).
44. Bagheri, A. R. *et al.* Modeling and optimization of simultaneous removal of ternary dyes onto copper sulfide nanoparticles loaded on activated carbon using second-derivative spectrophotometry. *Journal of the Taiwan Institute of Chemical Engineers* **65**, 212–224 (2016).
45. Li, W. *et al.* Studies on the adsorption of dyes, Methylene blue, Safranin T, and Malachite green onto Polystyrene foam. *Separation and Purification Technology* **276**, 119435 (2021).
46. Adebisi, A.-R., Ayanpeju, G. K., Wewers, A. F. & Oladipo, M. A. Removal of Malachite Green from Single and Multi-Dye Aqueous Solutions by Acid-Treated Sawdust. *Oriental Journal of Chemistry* **35**, 1384 (2019).
47. El Kassimi, A., Boutouil, A., El Himri, M., Laamari, M. R. & El Haddad, M. Selective and competitive removal of three basic dyes from single, binary and ternary systems in aqueous solutions: A combined experimental and theoretical study. *Journal of Saudi Chemical Society* **24**, 527–544 (2020).

Scheme

Schemes 1-3 are available in the Supplementary Files section.

Figures

Figure 1

Swelling behavior of TG-*g*-PAA/Fe₃O₄ hydrogel at pH 2, 7 and 9.

Figure 2

The pH_{zpc} value for the TG-*g*-PAA/ Fe_3O_4 hydrogel.

Figure 3

The effect of pH on the removal efficiencies of MG, BY28, and Rh6G dyes in single (a), binary (b, c, and d), and ternary (e) systems (condition: 25 °C; dye concentration 400 mgL⁻¹, adsorbent dosage 8 mgL⁻¹, and contact time 80 min).

Figure 4

The effect of sorbent dosage on the removal efficiencies of MG, BY28, and Rh6G dyes in single (a), binary (b, c, and d), and ternary (e) systems (condition: 25 °C; pH 7; dye concentration 400 mgL⁻¹; and contact time 90 minutes).

Figure 5

The effect of dye concentration on the removal efficiencies of MG, BY28 and Rh6G dyes in single (a), binary (b, c, and d), and ternary (e) systems (condition: 25 °C; pH 7, contact time 90 minutes, and adsorbent dosage 8 mgL⁻¹).

Figure 6

The effect of contact time on the removal efficiencies of MG, BY28 and Rh6G dyes in single (a), binary (b, c, and d), and ternary (e) systems (condition: 25 °C; dye concentration 400 mgL⁻¹; pH 7, and adsorbent dosage 8 mgL⁻¹).

Figure 7

Time-dependent removal of MG (a), BY28 (b), and Rh6G (c) in single system.

Figure 8

Time-dependent removal of MG+BY28 (a), MG+Rh6G (b), and BY28+Rh6G (c) in binary system.

Figure 9

Time-dependent removal of MG, BY28, and Rh6G dyes in ternary system.

Figure 10

Plots of Langmuir (a) and Freundlich (b) isotherm models for the sorption of MG, BY28 and Rh6G dyes in single system.

Figure 11

Plots of Langmuir (left column) and Freundlich (right column) isotherm models for the sorption of MG, BY28 and Rh6G dyes in binary systems.

Figure 12

Plots of Langmuir (a) and Freundlich (b) isotherm models for the sorption of MG, BY28 and Rh6G dyes in ternary system.

Figure 13

Removal efficiencies of MG, BY28, and Rh6G dyes in ternary system under several consecutive cycles at optimized condition.

Supplementary Files

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- [GraphicalAbstract.docx](#)
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