Effective removal of crystal violet from aqueous solution by graphene oxide incorporated hydrogel beads as a novel bio-adsorbent: kinetic, isotherm and thermodynamic studies

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ABSTRACT
This study revealed the facile preparation of graphene oxide (GO) containing sodium alginate (SA) and hydroxyethyl cellulose (HEC) hydrogel beads that could be used as a low-cost and environmentally friendly bio-adsorbent for the removal of crystal violet (CV). The thermogravimetric analysis (TGA) and absorbency under load (AUL) test results demonstrated that the thermal stability and mechanical strength of SA-HEC hydrogel beads were enhanced by the existence of GO. The SA-HEC/GO bio-adsorbents displayed superior adsorption capability toward cationic CV dye molecules and the adsorption capacity increased from 123.16 mg g\(^{-1}\) to 312.72 mg g\(^{-1}\) at pH 5 by incorporation of 1 wt% GO. The CV adsorption is well-described by pseudo-second-order model and was mainly controlled by intra-particle diffusion. Also, the Langmuir and Temkin isotherm models confirmed the physical monolayer adsorption of CV. The calculated thermodynamic parameters such as Gibbs free energy (\(\Delta G^°\)), enthalpy (\(\Delta H^°\)) and entropy (\(\Delta S^°\)) indicated that the adsorption of CV onto SA-HEC/GO bio-adsorbents was spontaneous and it was favored at high temperatures. The bio-adsorbent retained its ability to adsorb CV with a removal efficiency of 79.4% for up to six cycles.

1. Introduction
Due to the direct or indirect pollution of water resources through global climate change, various industrial activities, and population growth, the necessity for clean water has been increasing worldwide.\(^{[1,2]}\) For this reason, effective management of water has become one of the priority issues of the 21st century to protect clean water resources and ensure their sustainability. One of the key approaches to this issue is the treatment and reuse of industrial wastewater containing significant concentrations of dyes, heavy metals, and other chemicals.\(^{[3]}\) Among these pollutants, synthetic dyes, which form toxic and carcinogenic products by oxidation, hydrolysis, or other chemical reactions, have negative effects on the ecological environment and human and animal health.\(^{[4,5]}\) Also, the presence of these dye molecules in the aquatic environment inhibits the photosynthetic activity by reducing the light transmittance.\(^{[6]}\) Therefore, these pollutants are required to be removed from industrial wastewater before discharging to the environment.
The most innovative approach in removing synthetic dye molecules in the recent years is using nanoparticle doped hydrogels based on natural polymers as bio-adsorbents. Three-dimensional hydrogels as promising bio-adsorbents have high porous structure, high swelling ability, biocompatibility, biodegradability, nontoxicity and high adsorption capacities. Poly saccharide-based hydrogels demonstrate good dye removal capabilities in aqueous solutions because of their free functional group diversity, such as hydroxyl, carboxyl, and amino groups, which can serve as the active sites and retain dye molecules by electrostatic interaction, hydrogen bonding and van der Waals attraction. Furthermore, polysaccharides such as alginate, chitosan, cellulose, and starch are low-cost, abundant, renewable, and environmentally friendly materials, and these properties make them widely used, effective, and sustainable adsorbents.

Sodium alginate (SA), as an anionic polysaccharide, has numerous free carboxyl groups, which facilitate the efficient adsorption of cationic dyes onto the polymer chains via electrostatic interaction. Also, these free carboxyl groups can be easily cross-linked by exchanging sodium ions with divalent and trivalent cations such as Ca$^{2+}$, Ba$^{2+}$ and Fe$^{3+}$ to produce a stable network polymer structure. Therefore, SA can be easily shaped into different forms such as beads, films or membranes. Hydroxethyl cellulose (HEC) is one of the nonionic, nontoxic and water-soluble cellulose derivatives. An important feature of HEC is its compatibility with a wide variety of other water-soluble polymers.

However, these biopolymers have some drawbacks such as water solubility, low chemical and thermal stability, and insufficient mechanical strength that limit their further application in water treatment. The efficient strategies to overcome these limitations can be the incorporation of the appropriate additives, further modification of biopolymers and making though hydrogels like double network structure. Among them, the incorporation of nanoparticles into the network structure is an effective strategy to improve the mechanical and thermal stability of the biopolymers.

Graphene oxide (GO) is a two-dimensional, biocompatible and nontoxic nanomaterial having high specific surface area, and various oxygen containing functional groups which make GO compatible with water soluble polymers. The reinforcement function of GO leads to obtain more stable, efficient, and effective polymer nanocomposites with great potential to be used in a variety of water-related applications. As well as improving the mechanical strength and thermal stability, the oxygenated functional groups of GO nanosheets such as epoxy, hydroxyl, carboxyl and carbonyl groups also enhance the adsorption ability of the hydrogels. Especially, the negative surface charge of GO nanosheets originating from these functionalities makes GO a favorable adsorbent for the removal of cationic dyes from aqueous solutions through strong electrostatic interactions.

On the other hand, the leaching tendency of physically trapped GO from the polymer matrix and its high dispersibility in water restricts the recovery and reusability of the resulting adsorbent. The most effective way to overcome this problem is to immobilize GO nanosheets by chemically bonding to the polymer matrix. To this end, epoxy groups of GO can be covalently bonded with the active amino group-containing polymers such as hyperbranched polyethylenimine (PEI) via the nucleophilic ring-opening reaction. Thus, the occurrence of such a chemi cal bonding in the presence of the primary polymer network forms a secondary network; this new construction is called a double network structure. As a result of this double network structure, nanocomposite hydrogel adsorbents exhibit further improved chemical stability, mechanical strength, reusability, and adsorption capacity. Thus, these polysaccharide based GO doped hydrogels become excellent candidates as bio-adsorbents in wastewater treatment applications.

The goal of this study is to investigate the adsorption performance of new designed graphene oxide incorporated sodium alginate and hydroxyethyl cellulose based double network hydrogel (SA-HEC/GO) bio-adsorbents on the removal of cationic crystal violet (CV) dye from aqueous solutions, and to evaluate the adsorption mechanism through kinetic, isotherms, and thermodynamic studies. For this reason, GO incorporated SA-HEC/GO double network hydrogels were successfully produced in the form of beads. In this network structure, the main function of biocompatible SA is to form the bead structure, while HEC increases the water absorption capacity of the network and improves the dispersibility of GO with the formation of interactions between its hydroxyl groups and oxygen containing functional groups of GO. This combination in structure not only imparts improved dispersibility to nanocomposites but also provides enhanced stability and mechanical properties. To the best of the authors’ knowledge, SA-HEC/GO nanocomposite beads have not been studied to remove CV from aqueous solutions. Although there are some studies on the usage of SA/GO hydrogel beads for the adsorption of cationic dyes from aqueous solutions, in this study the double network hydrogel bead adsorbent obtained by the support of SA/GO systems with HEC was designed as a new material for cationic CV adsorption. Crystal violet is one of the most widely used cationic dyes in various industries, which is very dangerous and can cause several health problems in the human body if inhaled or consumed. After obtaining the novel SA-HEC/GO double network hydrogel beads containing different amounts of GO, their structural, thermal and morphological properties were characterized using FTIR, TGA, and SEM. Swelling and water absorption under load tests were carried out. This work also explores the influences of important parameters such as GO content, adsorption time, pH, adsorbent amount, initial dye concentration and temperature, on the adsorption of CV. The adsorption performance of SA-HEC/GO nanocomposite beads was evaluated through kinetic, isotherms, and thermodynamic parameters of the adsorption process. In addition, the reusability of the composites was determined.
2. Experimental

2.1. Materials

Sodium alginate (SA, ≥2,000 cP of 2% (w/w) in water at 25 °C), hydroxyethyl cellulose (HEC, average MW 250000), polyethyleneimine (PEI, 50% (w/w) in water, average MW 750000), glutaraldehyde (25% (w/w) in water), crystal violet (CV), calcium chloride (CaCl₂), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were all purchased from Sigma–Aldrich and used without further purification. Natural graphite powders, potassium permanganate (KMnO₄), sodium nitrate (NaNO₃), sulfuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂) were the products of Merck and were used as received. Deionized water was used to prepare aqueous solutions.

2.2. Methods

2.2.1. Synthesis of graphene oxide nanosheets

The modified Hummer’s method was used to synthesize graphene oxide nanosheets as detailed explained in our previous study.[22] Briefly, GO nanosheets were prepared with two main steps, which include oxidation of natural graphite powder and exfoliation of the resulting graphite oxide. Firstly, H₂SO₄ and NaNO₃ were added to graphite powder (1 g) at 0-5 °C and stirred at 500 rpm for 30 min. Then, KMnO₄ was added slowly to this solution under stirring for 2 hours. An increase in viscosity and color change was observed after raising the temperature to 35 °C. The temperature rose to 95 °C with dropping a predetermined amount of water and the obtained solution was stirred at 700 rpm for 30 min. Finally, a color change from brown to golden yellow was observed with the addition of H₂O₂. The resulting graphite oxide was washed with 10 wt% HCl and distilled water. The exfoliation process of graphite oxide was achieved by ultrasonication for 2 hours in an ice bath. After freeze-drying, the GO nanosheets were obtained as a spongy powder.

2.2.2. Synthesis of SA-HEC/GO nanocomposite hydrogel beads

SA (1 g) and HEC (1 g) were separately dissolved in 50 mL distilled water by gentle heating and stirring on a hot plate with a stirrer. 0.5 wt% of GO stock solution was prepared by ultrasonication of GO (1 g) in deionized water for 2 hours. The polymer solutions and specified amount of GO aqueous dispersion were combined and stirred with a magnetic stirrer for 2 hours to obtain a homogeneous solution. Spherical beads were obtained with dropwise addition of resulting SA-HEC/GO solution into the 400 mL of 2 wt% CaCl₂ solution at a dropper speed of 400 rpm using a peristaltic pump under constant stirring conditions and further stirred for 4 hours on a magnetic stirrer. Then, the SA-HEC/GO beads were repeatedly washed with distilled water and were treated with 300 mL of distilled water containing PEI (0.4 g) under stirring at 400 rpm for 20 hours. At the end of this process, the beads were washed 2-3 times with distilled water. As a final process, the beads were placed in 300 mL of distilled water containing glutaraldehyde (2 mL) and stirred for 2 hours at 50 °C. The obtained beads were removed from this solution, repeatedly washed with distilled water and freeze-dried for 48 hours.

The nanocomposite hydrogel beads were prepared by adding different amounts of GO (0.1, 0.5 and 1.0 wt%) and designated, respectively, as SA-HEC/GO-1, SA-HEC/GO-2, and SA-HEC/GO-3. Also, as a control sample, GO-free hydrogel beads were prepared with the aforementioned process.

2.3. Characterization

The percentage yield of the hydrogel beads was determined according to the following equation:

\[ \text{% yield} = \frac{\text{Actual weight of hydrogel beads}}{\text{Total weight of polymers and other components}} \times 100 \]  

Fourier Transform Infrared (FT-IR) spectra analysis was conducted using a Perkin Elmer, Spectrum100 spectrophotometer having a diamond attenuated total reflectance (ATR) accessory at room temperature. The freeze-dried samples were scanned in the range of 4000 to 400 cm⁻¹ wavelength with an average of 16 scans and at a resolution of 4 cm⁻¹.

Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere with a heating range from 30 °C to 800 °C and 10 °C min⁻¹ of heating rate by a Seiko TG/DTA 6300 thermal analyzer. Scanning electron microscopy (SEM) analysis was carried out using an FEI inspect S50 scanning electron microscope at 20 kV.

The swelling characteristic of SA-HEC hydrogel beads with different GO content were investigated by immersing freeze-dried hydrogel beads into distilled water at room temperature. The weights of the beads were recorded at predetermined time intervals.

The swelling percentage (% S) was calculated based on the following equation:

\[ \text{% S} = \frac{w_s - w_0}{w_0} \times 100 \]  

where \( w_0 \) and \( w_s \) are the weight of dry and swollen hydrogel beads at time \( t \), respectively. Three samples were studied for each composition and the average of these was reported. In addition, the pH effect on the swelling performance of the hydrogel beads was studied at various pH values from 2.0 to 9.0.

To determine the swollen strength of the hydrogel beads, the water absorbance under load (AUL) tests were carried out that show how much moisture the hydrogel can absorb under a given pressure.[26] The test apparatus used in this study can be seen in Fig. 3a. Freeze-dried hydrogel beads were weighed and placed in the inner cylinder of the apparatus with a porous stone bottom (5,063 cm²) to cover the entire bottom area. The hydrogel beads were subjected to load (50 g cm⁻²) by placing a cylindrical solid apparatus on top of the beads. The whole set was deposited in an external
cylindrical container and distilled water was added dropwise to the outer petri dish at a temperature of 25 °C. Particular attention was paid to ensuring the water level in the external cylindrical container reached the height of the sample but not exceed the level of the porous stone plate to ensure complete saturation throughout the experiment. After the porous stone was completely saturated with water, the beads were left under load for 1 hour, and finally, the cylindrical load was taken off and the beads were weighed. This experiment was repeated three times for each sample and the results were averaged. AUL values of hydrogel beads were calculated according to Eq. (3).

\[
AUL \% = \frac{w_1 - w_0}{w_0} \times 100
\]

where \(w_0\) and \(w_1\) are the weight of the dried and swollen hydrogel beads, respectively.

### 2.3. Adsorption of CV

The adsorption performance of freeze-dried SA-HEC/GO nanocomposite hydrogel beads was studied in different conditions, such as GO content, initial pH, adsorbent dosage, contact time, the initial concentration of CV and temperature.

The stock solution of CV was prepared with the concentration of 1 g L\(^{-1}\) by dissolving the CV in deionized water and a series of aqueous CV dye solutions were prepared from this stock solution. pH of the medium was adjusted using 0.1 M HCl and 0.1 M NaOH solutions to have final values ranging from 1 to 8. Batch adsorption studies were performed by immersing the hydrogel beads (50-400 mg) into 50 mL CV solution (25-200 mg L\(^{-1}\)) and followed by placing them in a shaker at 150 rpm at different temperatures (298–323 K). At specific time intervals, 5 ml solution was taken and filtered with 0.22 μm filter membrane. The concentration of CV in the filtrate solution was measured using a Shimadzu, UV 1800, double beam UV-VIS Spectrophotometer at 590 nm. The removal efficiency (%) of CV dye and the adsorption capacity (\(q_e\)), the amount of CV adsorbed by per gram of hydrogel bead, were calculated by using Eqs. (4) and (5), respectively.

\[
% \text{RE} = \frac{(C_0 - C_e)}{C_0} \times 100
\]

\[
q_e = \frac{(C_0 - C_e) \cdot V}{w}
\]

where \(C_0\) and \(C_e\) are the initial and equilibrium concentrations of CV solutions (mg L\(^{-1}\)) at each time interval, \(w\) is the weight of the freeze-dried hydrogel beads (g) and \(V\) is the volume of the CV dye solution (L).

The adsorption kinetic experiments were performed at different time intervals with an initial CV concentration of 50 mg L\(^{-1}\) at pH 5. The pseudo-first-order\(^{[27]}\) (Eq. (6)), the pseudo-second-order\(^{[28]}\) (Eq. (7)) and the intra-particle diffusion\(^{[29]}\) (Eq. (8)) kinetic models were used to investigate the kinetics of the adsorption by using the following formulas:

\[
\ln(q_e - q_t) = lnq_e - k_1 t
\]

\[
t = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}
\]

\[
q_t = k_3 \sqrt{t} + C
\]

where \(q_e\) (mg g\(^{-1}\)) is the amount of CV adsorbed at equilibrium, \(q_t\) (mg g\(^{-1}\)) is the amount of CV adsorbed at time \(t\); \(k_1\) (min\(^{-1}\)), \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) and \(k_3\) (mg g\(^{-1}\) min\(^{-1}\)) are the rate constants of pseudo-first-order, pseudo-second-order and intra-particle diffusion model, respectively. In Eq. (5), \(C\) is the intercept which represents the thickness of the boundary layer. By plotting the linear curves of \(\ln(q_e - q_t)\) against time \(t\), \(t/qt\) against \(t\) and \(qt\) against \(t^{1/2}\), the values of \(q_e\), \(k_1\), \(k_2\) and \(k_3\) were calculated.

To examine the adsorption phenomenon, the adsorption isotherm studies were carried out with a dose of 200 mg beads for 210 min by changing the initial concentration of CV in the range of 25–200 mg L\(^{-1}\) at a pH of 5. Equilibrium adsorption data were fitted to Langmuir\(^{[30]}\), Freundlich\(^{[31]}\) and Temkin\(^{[32]}\) isotherm models.

The Langmuir equation (Eq. (9)) is expressed as follows:

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}
\]

where \(q_e\) (mg g\(^{-1}\)) is the equilibrium adsorption capacity, \(q_m\) (mg g\(^{-1}\)) is the maximum adsorption capacity when monolayer forms on the adsorbent, \(C_e\) (mg L\(^{-1}\)) is the equilibrium concentration of CV in solution and \(K_L\) (L mg\(^{-1}\)) is Langmuir constant related to the free energy of adsorption and the affinity of the binding sites. By plotting the \(C_e/q_e\) versus \(C_e\) curve, the values of \(q_m\) and \(K_L\) can be calculated. The characteristics of Langmuir isotherm can be further explained in terms of a dimensionless separation factor \(R_L\) (Eq. (10)), which is defined by

\[
R_L = \frac{1}{1 + \frac{K_L}{C_e}}
\]

The Freundlich equation (Eq. (11)) is commonly expressed as follows:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

where \(K_F\) (L mg\(^{-1}\)) and \(n\) are the Freundlich constants related to the adsorption capacity and the intensity of the adsorption process, respectively. These constants are determined from linear plots of \(\ln q_e\) versus \(\ln C_e\).

The Temkin equation (Eq. (12)) is given by the following equation:

\[
q_e = \beta \ln K_T + \beta \ln C_e
\]

\[
\beta = \frac{RT}{b}
\]

where \(K_T\) (L mg\(^{-1}\)) is the Temkin equilibrium binding constant related with the energy of adsorption, \(T\) (Kelvin) is the absolute temperature, \(R\) (8.314 J mol\(^{-1}\) K\(^{-1}\)) is the universal gas constant and \(b\) is the Temkin isotherm constant and \(\beta\) (J mol\(^{-1}\)) is the Temkin constant related to the heat of
adsorption. From the linear plot of \( q_e \) versus \( \ln C_e \), the Temkin constants of \( K_T \) and \( \beta \) can be achieved.

The thermodynamic parameters of the adsorption of CV onto SA-HEC and SA-HEC-GO composite bio-adsorbents such as the enthalpy change (\( \Delta H^0 \)), entropy change (\( \Delta S^0 \)) and standard Gibbs free energy change (\( \Delta G^0 \)) were calculated according to the following Eqs. (13) and (14):

\[
\Delta G^0 = -RT \ln K_e
\]

\[
\ln K_e = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]

where \( K_e \) is the thermodynamic equilibrium constant, \( T \) is the temperature (K) and \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) determined from the Langmuir adsorption model. The slope and intersection point of the linear plot of \( \ln K_e \) versus \( 1/T \) was used to calculate the \( \Delta H_0 \) and \( \Delta S_0 \) values.

To reusability study of SA-HEC/GO bio-adsorbent beads was performed by using 0.1 M HCl as the desorbing agent. In the experiment, CV adsorbed 200 mg hydrogel beads were collected and treated with 100 mL 0.1 M HCl to achieve complete desorption. Then, the hydrogel beads were washed with distilled water, freeze-dried, and placed in an aqueous CV solution for further adsorption testing. Using the same bio-adsorbent beads, 6 repeats of the adsorption-desorption cycle was applied.

3. Results and discussion

To develop new generation bio-adsorbents with enhanced chemical and thermal stability and high adsorption capacity for cationic dye removal, nanocomposite hydrogel beads with a high surface area were synthesized by incorporating GO nanosheets, a versatile nanoparticle, into the biopolymers of sodium alginate and HEC. For these syntheses, GO having various oxygen-containing functional groups with a C/O ratio of 2.3 was produced by the modified Hummers method. The resulting GO nanosheets had a few-layer structure with a thickness of 1.16 nm, an interlayer distance of 0.88 nm, and a lateral size of 159.2 nm. In order to further increase the mechanical strength of the nanocomposite hydrogel beads, a double network structure was formed in which the SA chains were cross-linked with glutaraldehyde while GO was chemically bonded with multi amino-functional PEI via its oxygen-containing functional groups. By the treatment of nanocomposite hydrogel beads with PEI, the GO nanosheets gets locked in the structure by chemically bonding to the polymer matrix and the leaching tendency of GO from the matrix is hindered. In this way, with the formation of this double network structure, the efficiency, chemical stability, mechanical strength and so reusability of nanocomposite hydrogel beads bioadsorbents are increased.

The percentage yields of hydrogel beads were found to be 96.68%, 97.85%, 95.47% and 97.50%, for SA-HEC, SA-HEC/GO-1, SA-HEC/GO-2 and SA-HEC/GO-3, respectively. The chemical structure of the resulting nanocomposite hydrogel beads with the double network structure and the interfacial interactions between functional groups on polymer matrix and GO nanosheets were identified with ATR-IR analysis, as seen in Fig. 1a. For GO, the major bands that appeared at around 3200, 1722, 1416 and 1046 cm\(^{-1}\) are respectively assigned to the stretching vibrations of O-H, C=O, C-O-C and C-O indicating the functional groups (hydroxyl, carboxyl, carbonyl and epoxy) on the GO nanosheets. Also, stretching vibrations of aromatic C=C bonds can be seen at 1613 cm\(^{-1}\).\(^{[22]}\) Fig. 1.a shows the FTIR spectrum of the neat SA-HEC hydrogel, the common absorption bands of SA and HEC at 3380, 2936, 2863, 1300 and 1034 cm\(^{-1}\) are respectively attributed to the O-H stretching, C-H symmetric stretching, C-H symmetric stretching, C-O stretching and C-O-C stretching vibrations, respectively.\(^{[33]}\) The two sharp peaks at 1604 and 1405 cm\(^{-1}\) correspond to the asymmetric and symmetric stretching vibrations of carboxylate ions of SA.\(^{[33]}\) The characteristic peaks of PEI, which is relatively less by weight in the polymer matrix, could not be detected due to the overlapping with the bands of SA and HEC main polymers. After the incorporation of GO into the polymer network, it was seen that the main characteristic bands of the FTIR spectra of the obtained nanocomposite beads were approximately similar to those of the neat hydrogel structure due to the relatively low content of GO in the polymer network.\(^{[33]}\) However, the absorption peak centered at 3380 cm\(^{-1}\) shifted and broadened to lower wavenumbers with the presence of GO nanosheets in the polymer matrix. It was also observed that the similar shift occurred for two

![Figure 1. ATR-IR spectra (a) and TGA curves (b) of GO and SA-HEC/GO nanocomposite hydrogel beads.](Image 324x410 to 552x739)
peaks centered at 1604 and 1034 cm$^{-1}$, while no significant change in the other peaks. These shifts in absorption bands of the oxygen-containing groups indicate the existence of intermolecular hydrogen bonding interactions between the functional groups of GO nanosheets and polymer chains by acting of GO as a physical crosslinking agent.[24,33,34]

The thermal stability of the synthesized bio-adsorbent beads was investigated by thermogravimetric analysis (TGA). Fig. 1b shows the TGA curves of GO, neat SA-HEC hydrogel beads and their nanocomposites. As shown in Fig. 1b, the TGA curves of the SA-HEC hydrogel and its GO incorporated forms exhibited a similar weight loss pattern that occurred in 3 distinct stages. For the neat hydrogel, the first stage appeared between room temperature and 150°C is attributed to the loss of adsorbed water molecules and retained moisture. The second weight loss that was occurred from 180 to 300°C was mainly due to degradation of the network structure and cleavage of certain functional groups. At the third stage, from 300°C to 600°C, a major weight loss was observed indicating the depolymerization of the polymer chains and the cleavage of the C-C bonds.[3,35] The TGA curve of GO is also seen in Fig. 1b. The two main stages around 100°C and at 150-300°C correspond to the loss of adsorbed water and the decomposition of oxygen-containing functional groups of GO sheets, respectively.[22] In addition, as seen from Fig. 1b, the thermal stability of the hydrogel beads was enhanced by increasing GO content in the polymer network structure. Comparing with the neat hydrogel, the second and third maximum degradation temperatures and residual weights were increased by the GO content, and also a relative decrease in weight loss rate was observed for the nanocomposites. These results indicated that the thermal stability of the hydrogel beads was increased, which was probably due to the increase in crosslink density with double network formation resulting from the formation of strong interactions between the GO nanosheets and the polymer matrix.[35]

The surface morphology of the freeze-dried neat SA-HEC and SA-HEC/GO-3 hydrogel beads were analyzed by SEM. As seen in Fig. 2, the beads were approximately 2.5 mm in average size with a spherical shape. The embedded image in Fig. 2a shows that the neat beads had a rough surface with deep wrinkles and even cracks. On the other hand, as shown in the embedded image of Fig. 2b, the GO incorporated beads exhibited an almost smooth and compact surface without any visible porosity, indicating the successful exfoliation of GO into the SA-HEC matrix. Moreover, SEM images with higher magnifications revealed that the inner structure of the hydrogels was porous and has plenty of cavities and folds, which increases the available adsorption sites by improving the specific surface area.[36]

3.1. Swelling studies

The swelling behavior of the hydrogel beads in distilled water was determined, and their equilibrium swelling capacities are given in Fig. S1 (supplementary material). As shown in Fig. S1a (supplementary material), a similar swelling trend was observed for all samples, exhibiting a two-step swelling increase consisting of a rapid increase during the initial 30 min and the subsequent slower increase. The hydrogel beads reached the equilibrium swelling capacities in approximately 180 min. When GO is incorporated into
the polymer network, a chemical bonding is formed between GO nanosheets and PEI, leading to the formation of a secondary network structure, increasing the cross-linked density.\cite{22} This double network, which has a denser structure, restricts the diffusion of water, reducing the swelling capacity of the hydrogel beads. Increasing the GO content will increase the secondary network density, as there will be more oxygen-containing functional groups to bind with PEI amino groups. In this way, the increase in crosslinking density restricts the motion of polymer chains and weakens the affinity between the hydrogel matrix and water, resulting in a decrease in swelling capacity. Moreover, the oxygen-bearing functional groups on the surface of the GO nanosheets are thought to strongly interact with the functional groups of SA and HEC, possibly hindering the swelling process of the hydrogel beads.\cite{37}

![Image](https://via.placeholder.com/150)

To investigate the effect of the pH values of the medium, the swelling studies were carried out in the pH range of 2 to 8 and the obtained swelling values were given in Fig. S1b (supplementary material). For SA-HEC hydrogel beads, amine groups of PEI and carboxylic groups of SA are predominantly responsible for the swelling process.\cite{21,22} At low pH values of 2 and 3, the amine groups and carboxylate ions are protonated, and –NH₃⁺, –COO⁻, –NH₂ and –COOH species are found together on the surface of polymer chains. The formation of ionic interactions and strong hydrogen bonds between these species leads to the shrinkage of the network structure and thus causes a lower swelling ratio.\cite{38} As the pH rises, ionization of carboxylic acid groups takes place and the formation of electrostatic repulsion between these negatively charged carboxylate ions expands the polymer chains and increases the penetration of water molecules into the polymer matrix, resulting in maximum swelling of the hydrogel beads at pH 5. Beyond this pH value, the observed slight decrease in swelling capacity can be attributed to the inhibition of repulsive forces by shielding the charge of carboxylate anions due to the shielding effect of Na⁺ ions.\cite{21} Additionally, SA-HEC/GO-3 nanocomposite hydrogel beads displayed a similar swelling tendency as neat hydrogel beads against pH changes of the medium.

As evaluating the swelling results, it was concluded that achieving high swelling capacity in a short time of 180 min around pH 5 with these hydrogel beads might indicate the potential to be used in the selective removal of cationic dyes from wastewater.

To evaluate the mechanical strength of the hydrogel beads during the swelling process, absorbency under load (AUL) tests were carried out. AUL values give information about how much water can be absorbed by hydrogel beads under a given pressure. These values are related to the crosslinking density of the hydrogel structure, which directly affects the mechanical strength.\cite{26,39} Fig. 3b compares changes in swelling and AUL values of hydrogel beads as a function of GO content. The neat hydrogel showed a decrease of 49.67% in water absorption under load compared with the free swelling value. On the other hand, this decrease was reduced by the addition of GO into the hydrogel structure. The calculated values of water absorption loss under load were 36.39%, 32.65% and 16.23% for SA-HEC/GO-1, SA-HEC/GO-2 and SA-HEC/GO-3, respectively. This loss in swelling under load, that is, the rise in AUL values, can be ascribed to the formation of double network structure by chemical bonding between GO and PEI, and strong interactions between GO and polymer chains. This behavior of GO results in an increment in crosslinking density and hence mechanical strength; which is further enhanced by the GO content of the hydrogel beads.

Consequently, the increase in mechanical strength, and also the absence of GO loss from the hydrogel bead structure and any structural deformation such as fragmentation or fracture during the swelling studies indicate that mechanically and chemically stable SA-HEC/GO hydrogel beads are obtained that can be used in aqueous medium applications.

### 3.2. CV Adsorption studies

The influence of GO content on the adsorption capacity of SA-HEC hydrogel beads for CV was investigated. As shown in Fig. 4a, the maximum adsorption value of neat SA-HEC adsorbent was 123 mg g⁻¹ and this value increased up to 312 mg g⁻¹ with the incorporation of 1 wt% GO into the network structure. GO nanosheets carry many negatively charged functionalities such as hydroxyl and carboxyl groups which can interact with cationic CV dye molecules by electrostatic or hydrogen bonding interactions. Also, the formation of strong π-π interactions between the delocalized aromatic π electrons of GO and the free electrons in the aromatic rings of CV affects the adsorption process positively.\cite{40} These many active adsorption sites of GO provide to have easily interacted with dye molecules, and thus the increment of GO content increases the adsorption performance by enhancing the affinity toward CV dye molecules.

The adsorption capacity of SA-HEC/GO nanocomposite hydrogel beads was improved by 91%, 129% and 153% with 0.1, 0.5 and 1.0 wt% GO loading compared with neat hydrogel beads.

The removal efficiency of dye molecules is strongly related to the molecular structure of the adsorbent, and the ionization degree of adsorbent and dye molecules, which can be directly influenced by the initial pH of the medium.\cite{41} Hence, the adsorption of cationic CV dye molecules onto SA-HEC/GO hydrogel bead adsorbents was studied as a function of pH in the range of 1 to 8, as shown in Fig. 4b. CV is known to be a synthetic cationic dye with three nitrogen atoms on it. At a very low pH value (~1), all three nitrogen atoms of the CV carry a positive charge and the solution color is yellow. As the pH increase, a green color is obtained corresponding to a form of CV dye with only one nitrogen atom on it. The pKa values related to the loss of these two protons are approximately 1.15 and 1.8. At neutral pH, both extra protons are lost and only one nitrogen atom is positively charged which is responsible for the adsorption of CV.\cite{25}

In adsorption studies performed at low pH values, all three nitrogen atoms of CV are positively charged, and competition between these cationic ions and hydronium cations...
in aqueous solution for free active sites of the hydrogel beads hinders the adsorption of the CV, resulting in lower adsorption capacity values.\[11\] Also, at low pH values, protonation of the amine groups of PEI occurs, so that the surface of the adsorbent becomes positively charged, and this inhibits the adsorption of CV molecules by generating strong electrostatic repulsion between positively charged adsorbent and adsorbate molecules. As the pH of the medium increases, the surface charge of the hydrogel beads becomes negative due to the deprotonation of PEI amine groups and ionization of the carboxylic acid groups originating from SA and GO, and CV loses its extra protons and carries only one positively charged nitrogen atom. Thus, the formation of electrostatic interactions between deprotonated groups on hydrogel beads and the nitrogen ion of CV rapidly increases the adsorption and it reaches a plateau toward pH 5. Moreover, the formation of strong hydrogen-bond interactions among functional groups and the decrease in the number of competing hydronium cations in aqueous solution as the pH increases also contribute to the adsorption of cationic CV dye molecules. When the pH is above 5.0 to neutral 7.0, there are no more ionizable sites on the hydrogel beads, and therefore the weakening of the interactions between adsorbate and adsorbent causes a relative decrease in adsorption capacity. The observed reduction in CV adsorption with increasing pH to 8 can be also attributed to the dye precipitation, which occurs at higher pH values. Based on these results, all subsequent adsorption measurements were performed at pH 5.

The influence of the initial dosage of SA-HEC/GO-3 hydrogel beads on the adsorption performance was examined in the range of 50–400 mg adsorbent dose with the concentration of 50 mg L\(^{-1}\) CV at initial pH of 5 and temperature of 25 °C, by evaluating the adsorption capacity (\(q_e\)) and removal efficiency of CV dye molecules. From Fig. 4c, it can be seen that the CV removal increased up to a certain limit with increasing the adsorbent dosage from 50 to 200 mg, and a maximal was reached for an adsorbent dosage of 200 mg with 98.5% removal efficiency; then it remained almost constant. On the other hand, it was observed that the \(q_e\) values, which increased slightly with the increase of the adsorbent dose at the beginning, reached maximum CV adsorption of 312.66 mg g\(^{-1}\) for an adsorbent dosage of 200 mg in equilibrium and then decreased by increasing the adsorbent dose up to 400 mg. This is an expected result because of the availability of a greater number of free adsorption sites and a larger surface area, which results in the favored adsorption of CV with increasing the adsorbent dosage and thus an increase in removal efficiency. However, increasing the amount of adsorbent above 200 mg provides a
large number of free adsorption sites for a constant initial dye concentration leading to a reduction in the number of dye molecules adsorbed per unit weight of adsorbent, and therefore the values of adsorption capacity were reduced. As a result of these studies, for achieving high removal efficiency and relatively high $q_e$ values, the adsorbent dosage was optimized as 200 mg for further studies.

### 3.3. Adsorption kinetics

Contact time between the adsorbate and adsorbent is another important parameter that affects the efficiency of the adsorption process, and so is the operating cost and time in practical applications. The adsorption performance of SA-HEC/GO nanocomposite hydrogel beads toward CV was analyzed as a function of contact time at an initial CV concentration of 50 mg L$^{-1}$, the adsorbent dosage of 200 mg, initial pH of 5 and temperature of 25$^\circ$C, as seen in Fig. 4d. For all samples, the adsorption capacity of CV increased with increasing contact time and after a while, the adsorption capacity slightly changed and a plateau was reached. This behavior can be explained by the phenomenon, in which the adsorption process is fast due to the existence of numerous free adsorption sites on the adsorbent surface in the initial stage, but it slows down since the adsorption sites are fully utilized as time progresses and, equilibrium is reached.[10]

In Fig. 4d, it is clearly seen that the time for the adsorption process to reach equilibrium becomes longer with the presence of GO and increasing its ratio. The adsorption equilibrium of CV onto SA-HEC and SA-HEC/GO-3 nanocomposite hydrogel beads was established after 150 and 210 min and the corresponding maximum adsorption amount reached 123 mg g$^{-1}$ and 312 mg g$^{-1}$, respectively. This result revealed that the more compact structure obtained with the addition of GO causes the solute diffusion to slow down, which delays the dye adsorption to reach equilibrium, as explained in the swelling part.

The determination of adsorption kinetics of SA-HEC/GO nanocomposite hydrogel beads to remove CV from aqueous solution is crucial to understand the mechanisms controlling adsorption and examine the adsorption performance of the adsorbents in the practical application of wastewater treatment.[8] To describe and better understand the kinetics of CV dye adsorption on the beads, the experimental data fitted to the Pseudo-first order model[28], the Pseudo-second order model[28] and the intra-particle diffusion model.[29] The values of rate parameters obtained from the linear fitting of these kinetic models are summarized in Table 1. The correlation coefficient ($r^2$) values of the kinetic models were used to compare the best fit of the kinetic model to the experimental data for CV adsorption onto hydrogel beads. As shown in Fig. 5 and Table 1, the obtained $r^2$ values of the pseudo-second-order model ($r^2 \geq 0.936$) were much higher than the pseudo-first-order kinetic model ($r^2 \geq 0.766$) for CV adsorption onto both adsorbents, which implies that the adsorption process proceeds mainly by surface chemisorption. Also, the calculated $q_e$ values of the pseudo-second-order model were closer to the experimental $q_e$ ones for all adsorbents, indicating a better fit of the experimental data to this model.

Adsorption is a multi-step process that contains the transportation of adsorbate molecules from the aqueous phase to the surface of the adsorbent followed by the diffusion of adsorbate molecules into the interior of the adsorbent pores.[42] The pseudo-first-order and pseudo-second-order kinetic models describe only the interactions between the active sites of the adsorbent surface and the adsorbate and ignore the effects of diffusion. Therefore, the intra-particle diffusion model, which controls the overall rate with the interactions between adsorbate and active sites of the adsorbent, was used to further elucidate the kinetic data and the adsorption process. From Table 1, it is clear that the intra-particle diffusion model also presented high correlation coefficient values ($r^2 \geq 0.919$) for all adsorbents. The deviation of the linear portion of the plot of $q_t$ versus $t^{1/2}$ from the origin can be explained by the existence of different mechanisms affecting the adsorption process. This result, together with the obtained high $r^2$ values, reveals that the adsorption of CV on hydrogel bead adsorbent is a multi-step process involving adsorption on the external surface by the Pseudo-second order model and diffusion of dye molecules into the interior by the intra-particle diffusion model.

### 3.4. Adsorption isotherms

The initial concentration of the adsorbate solution is a critical parameter since the adsorbent has the capacity to adsorb only a certain amount of adsorbate molecules through the available binding sites on its surface.[5] The influence of initial CV concentration on the equilibrium adsorption capacity of SA-HEC and SA-HEC/GO nanocomposite beads is analyzed as a function of contact time at an initial CV concentration of 14 mg L$^{-1}$, as explained in the swelling part.

| Model               | Parameter | SA-HEC | SA-HEC/GO-1 | SA-HEC/GO-2 | SA-HEC/GO-3 |
|---------------------|-----------|--------|-------------|-------------|-------------|
| Pseudo-first-order  | $q_e$ (mg g$^{-1}$) | 299.891 | 837.699     | 556.151     | 297.528     |
|                     | $k_1$ (h$^{-1}$)    | -0.039 | -0.036      | -0.022      | -0.014      |
|                     | $r^2$              | 0.905  | 0.766       | 0.800       | 0.994       |
| Pseudo-second-order | $q_e$ (mg g$^{-1}$) | 162.839 | 241.941     | 308.596     | 335.940     |
|                     | $k_2$ (g mg$^{-1}$ h$^{-1}$) | 0.009  | 0.007       | 0.008       | 0.017       |
|                     | $r^2$              | 0.936  | 0.978       | 0.992       | 0.998       |
| Intra-particle diffusion | $k_i$ (g mg$^{-1}$ h$^{-1}$) | 10.177 | 18.793      | 19.826      | 17.314      |
|                     | $C$ (mg g$^{-1}$)   | -2.729 | -23.776     | -16.819     | 52.984      |
|                     | $r^2$              | 0.919  | 0.979       | 0.994       | 0.978       |
was studied by varying the CV concentration from 25 to 200 mg L\(^{-1}\) and the relevant data was given in Fig. 6a. As can be seen, at lower dye concentrations, especially below 50 mg L\(^{-1}\), the amount of adsorbed CV is highly dependent on the initial dye concentration until saturation of available adsorption sites, and then it remains almost constant. For example, as the initial concentration of CV increased from 25 mg L\(^{-1}\) to 50 mg L\(^{-1}\), the adsorption capacity of 123.05 mg g\(^{-1}\) was obtained for neat SA-HEC hydrogel beads, and a slight increase in adsorption capacity was observed by rising up the initial dye concentration to 200 mg. Increasing the initial dye concentration provides an important driving force for adsorption by overcoming the mass transfer resistance of dye molecules between the adsorbent surface and aqueous phases\(^{[15]}\). Thus, the adsorption capacity enhances due to the increased mass transfer driving force and decreased resistance to the CV uptake up to equilibrium dye concentration.

Adsorption isotherm studies are of great importance for determining the interactions between adsorbent and adsorbate molecules, and the distribution of adsorbate molecules between the aqueous medium and the adsorbent surface when the adsorption equilibrium is reached. In this study, Langmuir, Freundlich, and Temkin isotherm models were used to investigate the CV adsorption phenomenon. Figures S2–S4 (supplementary material) indicate the linear fitting of CV dye adsorption data to different isotherm models. In addition, the regression coefficients and adsorption isotherm parameters, calculated from the slope and the intercept of linear plots were summarized in Table S2 (supplementary material). The linear regression coefficient, \(r^2\) values, is used to determine the most suitable isotherm model. As shown in Table S2 (supplementary material), both the Langmuir (\(r^2 > 0.983\)) and Temkin (\(r^2 > 0.980\)) models give a better fit to the experimental data than the Freundlich model (\(r^2 > 0.900\)) for all temperatures studied.

The Langmuir isotherm identifies the homogeneous monolayer adsorption of CV on the hydrogel beads surface, suggesting that CV adsorption mainly occurs on the carbonyl groups of SA that have equal adsorbate affinity, and the whole adsorbate surface is covered uniformly by CV dye molecules\(^{[12]}\). In addition, by incorporating GO into the SA-HEC hydrogel matrix, although new adsorption sites are introduced into the structure, they are believed to be energetically identical, having the same affinity toward CV dye molecules. This confirms that SA-HEC/GO nanocomposite hydrogel beads show a similar adsorption tendency as
smooth hydrogel beads. In the Langmuir isotherm model, the nature of the adsorption can be evaluated with dimensionless $R_L$ constant, which is defined as irreversible ($R_L=0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). The $R_L$ values calculated from Eq. (9) were between 0.033 and 0.161, which indicates favorable CV adsorption on all bio-adsorbents (Table S1, supplementary material). Based on data in Table S2 (supplementary material), there was an increase in the maximum monolayer adsorption capacity ($q_{\text{max}}$) of all bio-adsorbents with the progressive increase in temperature. This means that the adsorption process is endothermic, and the intermolecular forces between adsorbate and adsorbent become much stronger than those between adsorbate and solvent as the temperature increases. Also, as shown in Table S2 (supplementary material), the $K_L$ values increased with increasing GO content, suggesting that the affinity of SA-HEC/GO nanocomposite hydrogel beads toward CV dye enhanced with GO content. As a result, the CV dye molecules are more easily adsorbed on the surface of synthesized nanocomposite bio-adsorbents than neat beads.

The Temkin isotherm model, considering the interactions between adsorbent and adsorbate, was also applied to experimental data to determine whether the adsorption is a chemical or physical process. For all bio-adsorbents, the $\beta$ values related to the heat of sorption varied between 43.363 and 117.597 J mol$^{-1}$ at different temperatures studied (Table S2, supplementary material). These values, which are much smaller than the energy required for chemical adsorption, 4.184 kJ mol$^{-1}$, indicated that the adsorption process takes place physically. In addition, the high $r^2$ values obtained from the Temkin model show the homogeneous distribution of binding energies to all adsorption sites, which further confirms the monolayer adsorption of the Langmuir model.

Furthermore, the Freundlich model could also be used to explain the adsorption process due to the obtained $r^2$ values that were over 0.90. This result indicates that multilayer adsorption can also occur in the removal of CV dye molecules by nanocomposite hydrogel beads. As given in Table S2, the $n$ values calculated from the linear fitting of adsorption data were between 2.753 and 4.909, confirming the favorable adsorption of CV dye onto SA-HEC/GO bio-adsorbent beads.

### 3.5. Adsorption thermodynamics

The thermodynamic parameters are related to the energy changes of the dye removal process and give information about the nature of the adsorption process and how it occurs. Table 2 includes the thermodynamic parameters calculated from the adsorption studies of CV onto SA-HEC and SA-HEC/GO bio-adsorbent beads.

The obtained positive enthalpy change ($\Delta H^*$) values from the linear plots of $\ln K_e$ versus $1/T$ reveal that CV adsorption onto all bio-adsorbent beads is endothermic (Fig. 7). This can also be confirmed by the $q_{\text{max}}$ values obtained from the Langmuir adsorption isotherm model. The observed increase in $q_{\text{max}}$ values depending on the temperature indicates that the adsorption is endothermic. It is known that the adsorption of dye molecules on the adsorbent surface can occur physically or chemically depending on the magnitude of enthalpy value. The enthalpy values lower than 40 kJ mol$^{-1}$ correspond to physical adsorption and values greater than 40 kJ mol$^{-1}$ correspond to chemical adsorption. In this study, the obtained low $\Delta H^*$ values suggested that the removal of CV dye was mainly by physical adsorption through electrostatic interactions, hydrogen bonding and weak Van der Waals forces between dye molecules and the adsorbent surface. In addition, considering the entropy change ($\Delta S^*$) values (Table 2), it can be concluded that the interactions between the CV dye molecule and the bio-adsorbent surface are arbitrary during the adsorption process, and there is an increase in irregularity. It has been also reported that the Gibbs energy change ($\Delta G^*$) values less than 20 kJ mol$^{-1}$ are assigned to physical adsorption and values greater than 80 kJ mol$^{-1}$ are assigned to chemical adsorption. The calculated negative $\Delta G^*$ values that were less than 10 kJ mol$^{-1}$ indicate spontaneous physical adsorption of CV on all bio-adsorbent beads. The decrease in $\Delta G^*$ values as a function of temperature reveals the more suitable and spontaneous CV adsorption onto SA-HEC and SA-HEC/GO composite beads with the increase in temperature.

![Figure 7](image)

**Figure 7.** The plots of $\ln K_e$ versus $1/T$ for the adsorption of CV onto SA-HEC/GO bio-adsorbent beads ($C_0$: 50 mg L$^{-1}$, m: 200 mg, V: 50 mL, pH: 5).

| Thermodynamic parameters | $\Delta H^*$ (kJ mol$^{-1}$) | $\Delta S^*$ (J mol$^{-1}$K$^{-1}$) | $\Delta G^*$ (kJ mol$^{-1}$) |
|--------------------------|-----------------------------|----------------------------------|-----------------------------|
| SA-HEC                   | 3.622                       | -18.516                          | -9.139                      |
| SA-HEC/GO-1             | 14.033                      | 19.407                           | -8.236                      |
| SA-HEC/GO-2             | 6.293                       | -5.464                           | -7.914                      |
| SA-HEC/GO-3             | 5.191                       | -24.613                          | -8.528                      |
3.6. Reusability studies

The reusability of SA-HEC/GO-3 nanocomposite hydrogel beads was performed by 6 cycles of consecutive adsorption-desorption studies. 0.1 M HCl was used in desorption studies to facilitate the diffusion of CV from the active sites of the bio-adsorbent. According to Fig. 8, the adsorption efficiency decreased from 98.5% to 79.4%, confirming that the adsorbent can be used with a high adsorption capacity of up to 6 cycles while protecting its structural stability. This reusability study result is an important matter proving that SA-HEC/GO bio-adsorbent beads show high performance, stability, and sustainability in long-term adsorption applications in aqueous media.

3.7. Comparison with other adsorbents

The performance of SA-HEC/GO bio-adsorbents on the adsorptive removal of CV from aqueous solution was determined by comparing the maximum adsorption capacity value with the other reported adsorbents[2,18,19,46–49] as displayed in Table 3. As shown, the maximum adsorption capacity of the proposed adsorbent is significantly higher compared to the other adsorbent materials presented in Table 3 due to the porous structure and the presence of abundant functional groups, which have a high affinity toward CV dye molecules. Hence, it can be concluded that SA-HEC/GO hydrogel beads can be promising bio-adsorbents with low cost and efficiency in removing cationic dyes from aqueous solutions.

Figure 8. The performance of SA-HEC/GO bio-adsorbent beads through multiple regeneration cycles (C0: 50 mg L−1, m: 200 mg, V: 50 mL, T: 298 K, pH: 5).

Table 3. Comparison of SA-HEC/GO bio-adsorbent beads with different adsorbents for the removal of CV.

| Adsorbents | qe (mg g−1) | Adsorption model | Kinetic model | Reference |
|------------|-------------|-----------------|--------------|-----------|
| Magnetic alginate composite beads | 37.5 | Langmuir | Pseudo-second-order | [46] |
| AM-GO-SA nanocomposite hydrogel | 100.3 | Redlich-Peterson | Pseudo-second-order | [2] |
| Alginate-calcium composite beads | 29.0 | Langmuir-Freundlich | Intra-particle diffusion | [47] |
| Alginate-whey composite beads | 220.0 | Langmuir-Freundlich | Pseudo-second-order | [47] |
| Biosilica/alginate nanobiocomposite | 21.3 | Langmuir | Pseudo-second-order | [49] |
| Grafted sodium alginate/ZnO/ graphene oxide composite | 13.9 | Freundlich | Pseudo-second-order | [49] |
| Alginate/bentonite beads | 498.2 | Langmuir | Pseudo-second-order | [49] |
| CarAlg/MMT nanocomposite hydrogels | 88.8 | Langmuir | Pseudo-second-order | This study |
| SA-HEC/GO nanocomposite hydrogel beads | 312.7 | Langmuir | Pseudo-second-order | This study |

4. Conclusion

In this study, novel environmentally friendly and sustainable bio-adsorbent beads are well designed for the efficient removal of CV. GO having plenty of oxygen-containing functional groups provided the formation of a double network structure when incorporated into the SA and HEC natural polymers, and bio-adsorbent beads with high mechanical strength, chemical, and thermal stability were obtained. These bio-adsorbents showed high swelling capacity in a short time of 180 min around pH 5. The values of water absorption loss under load were 49.67%, 36.39%, 32.65%, and 16.23% for SA-HEC, SA-HEC/GO-1, SA-HEC/GO-2 and SA-HEC/GO-3, respectively, this reduction implies that these nanocomposite bio-adsorbents exhibit high mechanical strength for use in aqueous media applications. The adsorption efficiency of the SA-HEC/GO hydrogel beads was significantly affected by GO content, initial pH, adsorbent dosage, contact time, temperature, and initial CV concentration. The GO incorporated bio-adsorbents displayed superior adsorption performance compared to neat hydrogels. Adsorption studies showed that the removal efficiency reached 98.5% with the adsorption capacity of 312.66 mg g−1 at pH 5 for the composite containing 1 wt% GO. The kinetic studies revealed that the pseudo-second-order model, together with the intra-particle diffusion model, can be used to explain the adsorption of CV. The monolayer adsorption of CV was confirmed by the Langmuir model, and also the Temkin model confirmed the homogeneous distribution of binding energies to all adsorption sites and physical adsorption took place. The results of thermodynamic studies showed that the adsorption of CV onto all bio-adsorbents was spontaneous and endothermic in nature. Bio-adsorbent beads showed high reusability and after six cycles of adsorption-desorption studies, the removal efficiency of 79.4% was obtained while protecting the structural stability. Consequently, low-cost GO doped SA-HEC hydrogel beads from sustainable sources with high adsorption capacity and enhanced mechanical strength and effective reusability were achieved with the potential to be used as a bio-adsorbent showing high capability in the removal of cationic dyes from aqueous medium.

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Conflict of interest

The authors report there are no competing interests to declare.

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