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# Efficient removal of perchlorate by a quaternary ammonium-functionalized hydrogel: performance and mechanisms

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# Abstract

Perchlorate ($ClO_4^-$) is a persistent and hazardous water pollutant that disrupts thyroid function. Hydrogels, with their tunable functionality and high capacity, offer a promising alternative, but their application for perchlorate removal remains largely unexplored. A novel hydrogel was synthesized via free-radical copolymerization of methacryloxyethyl trimonium chloride (MTAC) and N, N'-methylenebis (acrylamide) (MBA). The material was characterized using SEM, EDS, FTIR, XRD, and XPS. The MTAC hydrogel exhibited a high adsorption capacity for $ClO_4^-$, with experimental data best fitted by the Langmuir isotherm, showing a maximum capacity of 425.22 mg/g at 298 K. The adsorption process is primarily driven by strong electrostatic interactions from quaternary amine groups, supplemented by ion exchange and hydrogen bonding. The adsorption energy reached -3.59 eV. The adsorption process was fast, spontaneous, and exothermic, remaining effective over a wide pH range (5–9) and in the presence of common competing anions. The hydrogel demonstrated excellent regenerability over five cycles. MTAC/Sodium alginate (SA) beads were used in fixed bed packing, which achieved a treatment capacity of 5346 bed volumes, reducing $ClO_4^-$ from 500 μg/L to below the drinking water standard (70 μg/L). Furthermore, the column facilitated easy regeneration and exhibited an enrichment factor as high as 122.9 fold. This work successfully developed a MTAC-based hydrogel for the removal of $ClO_4^-$. The hydrogel demonstrated high capacity and regenerability in real water samples and column experiments, making it an ideal candidate material for practical end-of-pipe water treatment applications.

***Keywords***: Perchlorate; Hydrogel; Adsorption; Quaternary ammonium; Water treatment

## 1. Introduction

Perchlorate ($ClO_4^-$), a persistent and highly water-soluble inorganic pollutant, has been widely detected in aquatic environments worldwide. This strongly oxidizing oxyanion is extensively used in munitions, aerospace, and fireworks industries, and serves as an additive in producing tanning agents, rubber, lubricants, and magnesium batteries [1]. Its discharge has led to frequent detection of perchlorate at high concentrations in surface water, groundwater, and even drinking water [2–4]. Critically, perchlorate ions compete with iodide for uptake by the thyroid gland due to their similar ionic radii and charge [5]. This competition disrupts the synthesis and secretion of thyroid hormones ($T_3$ and $T_4$), leading to thyroid dysfunction [6]. These effects are especially detrimental to vulnerable groups such as children, pregnant women, and newborns, potentially causing impaired skeletal and central nervous system development in infants [7], metabolic disorders, and growth retardation [8]. Consequently, both the WHO Guidelines for Drinking-Water Quality and China's National Standards for Drinking Water Quality (GB5749–2022) have set a maximum allowable concentration of 0.07 mg/L for $ClO_4^-$.

Various technologies have been developed to remediate perchlorate contamination, broadly categorized as physical, chemical, and biological treatments, as well as combined processes [9]. However, conventional methods face challenges: the high activation energy and stability of $ClO_4^-$ render chemical reduction slow, metal catalysts may cause secondary pollution [10]. Bioremediation, while suitable for large-scale remediation, typically proceeds at a slow rate [11]. Combined treatments remain exploratory and require further development for large-scale application [12,13].

Among these, physical methods like adsorption, membrane filtration, and ion exchange are most commonly used for trace $ClO_4^-$ removal, offering advantages of low cost, high efficiency, and operational simplicity [14–16]. Consequently, innovating and improving ion-exchange and adsorption materials is a major research focus. Nevertheless, traditional adsorbents like activated carbon and resins face challenges such as difficult regeneration, complex synthesis, and high cost [17–19]. Moreover, most novel materials including granular ferric hydroxide (GFH) [20], nano-hydroxyapatite [21], calcined hydrotalcite [22], nano zero-valent iron [23], montmorillonite [24], and metal–organic frameworks [25] remain largely experimental, with complex preparation procedure and unproven practical applicability.

Hydrogels are functional polymeric materials featuring a three-dimensional crosslinked network [26]. Their excellent hydrophilicity, high water content, tunable porosity, and abundant functional groups make them attractive for adsorption, filtration, controlled release, and ion exchange [27]. By incorporating charged or polar groups, hydrogels can interact with target ions via electrostatic attraction or hydrogen bonding, enabling efficient pollutant removal [28]. Methacryloxyethyl trimonium chloride (MTAC), a polymerizable quaternary ammonium monomer, is widely used in synthesizing anion-exchange adsorbents and flocculants [29–31].

Compared with conventional quaternary ammonium adsorbents, the MTAC-based hydrogel adopts a structurally integrated strategy in which quaternary ammonium groups are uniformly incorporated into a three-dimensional network via aqueous free-radical polymerization. The covalent immobilization of MTAC enhances structural stability and reduces potential functional group leaching during repeated use. In addition, the hydrated network promotes rapid ion diffusion, mitigating mass-transfer limitations typical of conventional resins. These features collectively contribute to improved adsorption capacity and favorable kinetics for perchlorate removal.

In this study, an MTAC-based co-crosslinked hydrogel was synthesized via aqueous free-radical polymerization using $K_2S_2O_8$/TEMED as a redox initiator system and MBA as the crosslinker to construct a three-dimensional polymer network. The crosslinking degree was systematically optimized to balance structural stability and accessibility of adsorption sites.The adsorption performance of the resulting hydrogels was evaluated through batch experiments, examining the effects of temperature, pH, initial concentration, and coexisting ions. To further assess practical applicability, MTAC/sodium alginate (SA) composite microspheres were prepared for fixed-bed column experiments using real water matrices. Finally, the adsorption mechanism was analyzed based on kinetic, isotherm, thermodynamic investigations and DFT calculations.

## 2. Materials and Methods

### 2.1. Reagents

[2-(Methacryloyloxy)ethyl]trimethylammonium chloride solution (MTAC) (75% by weight in water, containing 600 ppm MEHQ anti-oxidant agent), N,N’-Methylenebis(acrylamide) (MBA), TEMED, and $K_2S_2O_8$ were purchased from Shanghai Maclin Biochemical Technology Co., Ltd. Sodium alginate (SA) was obtained from Aladdin Reagent Co., Ltd. Sodium perchlorate monohydrate ($NaClO_4 \cdot H_2O$) and other reagents were acquired from Sinopharm Chemical Reagent Co., Ltd. All chemical reagents were analytical grade and used as received. Solutions were prepared using ultrapure water produced from a purification system.

## 2.2. Preparation of hydrogels

**Preparation of MTAC hydrogels**. The MTAC hydrogel was synthesized via free-radical polymerization in 2 mL centrifuge tubes. Briefly, 0.04 g of MBA was dissolved in 1 mL of deionized water, followed by adding 400 μL of MTAC solution. The mixture was vortexed until fully dissolved. Then, 5 μL of TEMED (catalyst) and 50 μL of potassium persulfate (KPS, 40 g/L) solution were added to initiate polymerization at room temperature. The mixture was allowed to polymerize and gel for 24 h. The resulting gel was immersed in deionized water for 24 h to remove unreacted monomers, then freeze-dried for another 24 h to obtain the lyophilized MTAC hydrogel. For comparison, hydrogels with different MTAC-to-MBA mass ratios (1:10, 1:2, 1:1, 2:1, 4:1, and 8:1) were synthesized similarly.

**Preparation of MTAC/SA hydrogel**. MTAC hydrogel powder (0.1 g) was dispersed in 2 mL deionized water at 45 °C under stirring. Then, 0.06 g of sodium alginate (SA) was added and vortexed to form a homogeneous sol, which was sonicated for 10 min for complete dissolution and degassing. The sol was dropwise added into a 5.0 wt% $CaCl_2$ solution via syringe and needle, allowing crosslinking and solidification for 24 h. The resulting hydrogel beads were repeatedly washed with deionized water and freeze-dried. The synthesis route is shown in Figure 1.

## 2.3. Analytical methods and characterization

Details of material characterization methods are provided in Text S1 in

Supplementary materials.

### 2.4. Batch adsorption experiments

A $ClO_4^-$ stock solution (500 mg/L) was prepared and diluted to desired concentrations. We investigated the effects of adsorbent type (with varying MTAC:MBA ratios), dosage (5, 10, 15 mg), and initial $ClO_4^-$ concentration (5, 10, 20 mg/L). Adsorption kinetics were studied at these three concentrations. Isotherm experiments were conducted at 298, 308, and 318 K with an adsorbent dosage of 0.1 g/L. The effect of pH was examined from pH 3.0 to 9.0 (initial $ClO_4^-$ concentration: 5 mg/L), adjusted using 0.1 mol/L HCl or NaOH. The influence of coexisting anions ($NO_3^-$, $Cl^-$, $SO_4^{2-}$, $CO_3^{2-}$) was assessed by adding their salt solutions to 5 mg/L $ClO_4^-$ solutions. For regeneration, a mixed solution of 1 mol/L NaCl was used to desorb $ClO_4^-$ from the hydrogel. Performance in real water samples (tap water, Hou Lake water, Xiangjiang River water) spiked with 0.1 mg/L $ClO_4^-$ was also evaluated.

In a typical adsorption experiment, a 100 mL beaker containing the solution was placed in a thermostatic water bath and stirred at 298 K for 30 min. At predetermined intervals, 0.5 mL of suspension was sampled, diluted to 3 mL with deionized water, and filtered through a 0.22 μm syringe filter (ANPEL) for ion chromatographic determination. Details of the ion chromatography assay method are provided in Supplementary materials Text S2. Unless specified, all experiments used a 50 mL solution volume at initial pH (~6.3), without adjustment. All experiments were performed in triplicate.

The adsorption capacity ($q_e$), the removal efficiency (%), and the distribution coefficient ($K_d$) were calculated using equations of $q_e = \frac{(C_0 - C_e)V}{m}$ , $\frac{(C_0 - C_e)}{C_0} \times 100\%$ , and

$K_d=\frac{(C_0\text{-}C_e)}{C_e}\times\frac{V}{m}$, respectively; where V is the volume of the $ClO_4^-$ solution (mL), m is the mass of the adsorbent (g), and $C_0$ and $C_e$ are the initial and equilibrium solution concentrations of $ClO_4^-$ (mg/L), respectively. Details of mass transfer model, Langmuir and Freundlich isotherm models, and thermodynamics calculations are provided in Texts S3–S5.

### 2.5. Fixed-bed column adsorption experiment

Fixed-bed column experiments were conducted at room temperature using a column packed with MTAC/SA hydrogel beads. A 500 μg/L $ClO_4^-$ solution was pumped through the column at 4.0 mL/min using a peristaltic pump, and effluent was collected in 3 mL aliquots. For desorption, an eluent containing 10 wt% NaCl and 0.02 M $CaCl_2$ was pumped at the same flow rate. The fixed-bed $ClO_4^-$ adsorption capacity (mg/g) was calculated using the following equation:

$$q_\mathrm{f}=\frac{\left((C_\mathrm{f}\cdot\mathrm{BV}_\mathrm{max})\text{-}A\right)\cdot V}{m\cdot10^6} \tag{1}$$

where $C_\mathrm{f}$ is the influent $ClO_4^-$ concentration (μg/L), $\mathrm{BV}_\mathrm{max}$ is the maximum treated bed volume, $V$ is the column volume (mL), $m$ is the adsorbent mass (g), and $A$ is the area under the breakthrough curve (mg/L), calculated as:

$$A=\int_0^{\mathrm{BV}_\mathrm{max}} C\,\mathrm{dBV} \tag{2}$$

where $C$ is the effluent $ClO_4^-$ concentration (μg/L). To determine $A$ accurately, the breakthrough curve was fitted nonlinearly using the Boltzmann model:

$$C=A_2+(A_1\text{-}A_2)\cdot\frac{1}{1+\mathrm{e}^{(\mathrm{BV}\text{-}x_0)/\mathrm{dBV}}} \tag{3}$$

where $A_1$, $A_2$, $x_0$, and dBV are constants, for specific values are provided in Table S1.

### 2.6. DFT Calculations

The interaction between MTAC and $ClO_4^-$ was investigated using density functional theory (DFT) in Materials Studio software. Adsorption energy and charge transfer were computed to evaluate interaction strength. The Dmol$^3$ module with the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was employed for geometry optimization and electrostatic potential mapping. Adsorption energies ($E_{\mathrm{ads}}$) were calculated as:

$$E_{ads}=E_{total}-E_{substrate}-E_{adsorbate} \tag{4}$$

## 3. Results and discussion

### 3.1. Characterizations

SEM images and elemental mapping of the MTAC hydrogel are shown in Figure 2a. The pristine MTAC hydrogel displayed a smooth, folded lamellar morphology without distinct particles (Figure 2a), indicating a continuous MBA-crosslinked polymer network. The SEM–EDS mapping results of the MTAC hydrogel reveal uniform distribution of C, O, N, and Cl elements throughout the sample, consistent with the chemical composition of the MTAC monomer. This confirms the successful preparation of the MTAC hydrogel via radical polymerization. The Cl signal originates from the quaternary ammonium chloride structure of MTAC. Its uniform distribution indicates that quaternary ammonium groups are evenly distributed throughout the gel network, which is crucial for subsequent adsorption of $ClO_4^-$.

Contact angle test (Figure S1) showed the MTAC hydrogel was hydrophilic, with contact angle of 26.26° at 1 s. The $N_2$ adsorption-desorption characterization (Figures 2b, c) indicated that the as-synthesized MTAC hydrogel had a low specific surface area (0.61

$m^2/g$), with average pore size of 9.76 nm. The detailed data on the specific surface area and pore size of the MTAC hydrogel are presented in Table S2.

### 3.2. Key parameters affecting $ClO_4^-$ adsorption

Initially, the impact of the MTAC:MBA mass ratio on the adsorption capacity of hydrogel was investigated. As shown in Figure 3a, hydrogels with a MTAC:MBA ratio of 1:1 or higher demonstrated superior adsorption performance, achieving $ClO_4^-$ removal efficiencies exceeding 90%. The removal efficiency correlated positively with MTAC content, indicating that a higher density of quaternary ammonium groups provides more active sites, thereby improving adsorption capacity[31]. Notably, the hydrogel with an 8:1 mass ratio attained a removal efficiency of 96.57% within 30 min. Considering the optimal balance between mechanical strength and preparation yield, the 8:1 MTAC: MBA hydrogel was selected for all subsequent experiments and designated as the MTAC hydrogel.

The relationship between adsorbent dosage and $ClO_4^-$ removal efficiency is shown in Figure 3b. Removal efficiency increased with higher dosages of the MTAC hydrogel, plateauing at 0.2 g/L, beyond which further increases yielded only marginal gains. Consequently, 0.2 g/L was chosen as the optimal dosage. In contrast, the adsorption capacity decreased as the dosage increased, from 46.7 mg/g at 0.1 g/L to 16.3 mg/g at 0.3 g/L. This decline is attributed to the limited availability of pollutants, which leads to unsaturated active sites at higher adsorbent loadings. As the proportion of unsaturated sites rises, the adsorption capacity per unit mass of adsorbent correspondingly decreases [31,32].

Figure 3c illustrates the effect of initial $ClO_4^-$ concentration on adsorption performance. As the concentration increased from 5 to 20 mg/L, the removal efficiency slightly declined from 96% to 92%, whereas the adsorption capacity rose markedly from 24.1 to 92.5 mg/g. This trend can be explained by the abundance of available binding sites on the adsorbent. Higher initial concentrations strengthen the adsorption driving force [33], leading to more pronounced uptake. Although high removal efficiencies are observed at low $ClO_4^-$ concentrations, the relatively low adsorption capacity suggests the presence of excess active sites [32], underscoring the strong potential of the as-synthesized MTAC hydrogel for treating higher-concentration effluents.

The influence of initial solution pH (3.0–9.0) on $ClO_4^-$ removal is shown in Figure 3d. Solution pH affects the protonation states of functional groups [34], thereby modifying the adsorbent surface charge [31] and significantly influencing the adsorption process. At pH 3.0, only partial $ClO_4^-$ removal occurred (64.2%); however, efficiency improved markedly at pH higher than 5.0. This behavior may be due to the high $H^+$ concentration under strongly acidic conditions, which hinders the diffusion of $ClO_4^-$ ions to active sites [35,36]. Additionally, protonation of amide groups ($–CONH_2$) to $–CONH_3^+$ could weaken hydrogen bonding and introduce electrostatic repulsion with quaternary ammonium groups [31]. The adsorption capacity reached a minimum at pH 3 (16 mg/g) and stabilized around 23 mg/g at pH 5, indicating effective interaction between $ClO_4^-$ and quaternary ammonium sites on MTAC hydrogels at pH $\geq$ 5.0. In summary, the MTAC hydrogel exhibits excellent adsorption stability across a broad pH range, owing to the persistent positive charge of its quaternary ammonium groups, which favors its practical applicability in $ClO_4^-$ adsorption [31,32,37].

Natural water contaminated with $ClO_4^-$ often contains competing anions such as $Cl^-$, $CO_3^{2-}$, and $SO_4^{2-}$. These ions can occupy active sites and weaken electrostatic attraction between the adsorbent and target contaminant [32]. To simulate realistic conditions, the effect of competing anions $ClO_4^-$ adsorption by the MTAC hydrogel was systematically evaluated using solutions with fixed concentrations (5 and 25 mg/L) of individual anions. Results for a blank sample (no competing anions) are included in Figure 3e for comparison. Among the anions tested, $CO_3^{2-}$ exerted the strongest inhibitory, followed by $SO_4^{2-}$, whereas $Cl^-$ and $NO_3^-$ showed comparable and weaker interference. This trend is attributed to the larger molecular volumes and higher charge densities of $CO_3^{2-}$ and $SO_4^{2-}$ relative to $ClO_4^-$ (Table S3), which hinder perchlorate adsorption [38]. In contrast, $Cl^-$ and $NO_3^-$, being monovalent with similar hydration radii and charge densities, only minimally affect perchlorate uptake, even at varying concentrations [37]. The impact of coexisting cations was further investigated (Figure S2), indicating that cations do not directly compete with adsorption sites but may slightly influence performance through ionic strength effects.

To assess the practical applicability of the MTAC hydrogel, its $ClO_4^-$ removal performance was further examined in different real water matrices: tap water, Houhu Lake water (from Yuelu District, Changsha, Hunan Province, China), and Xiangjiang River water. Given that typical $ClO_4^-$ concentrations in contaminated Chinese surface and groundwater range between 0.002 and 0.054 mg/L [39], all water samples were spiked with 0.1 mg/L $ClO_4^-$ prior to testing. As shown in Figure 3f, the MTAC hydrogel achieved over 90% $ClO_4^-$ removal at a dosage of 0.1 g/L and over 98% at 0.5 g/L. These results strongly support its potential for effective $ClO_4^-$ removal across diverse real-water environments.

### 3.3. Adsorption kinetics, isotherms and thermodynamics

As shown in Figure 4a, MTAC hydrogel quickly reached sorption equilibrium for different concentrations of $ClO_4^-$ within 10 min, with removal efficiencies of 92.6–96.3%. To quantitatively compare the adsorption rate, the mass transfer model has been further employed to fit the kinetic data. The mass transfer model can well describe the mass transfer phenomena and is beneficial to the engineering design (Texts S3). The mass transfer coefficients ($k_f$) in the system was calculated to be $1.9 \times 10^{-4}$ m•s$^{-1}$, the relatively high $k_f$ value ($1.9 \times 10^{-4}$ m·s$^{-1}$) suggests low external film mass-transfer resistance, which facilitates the transport of $ClO_4^-$ from the bulk solution to the hydrogel surface. Various adsorbents for $ClO_4^-$ removal are compared in Table S4. Among the reported systems, the MTAC hydrogel exhibits a relatively high external mass transfer coefficient ($k_f$), suggesting lower film diffusion resistance and more efficient transport of $ClO_4^-$ from the bulk solution to the adsorbent surface.

Although the relatively high mass transfer coefficient indicates low external film resistance and contributes to the rapid initial uptake, it does not solely govern the overall adsorption rate. The intraparticle diffusion plots exhibited multilinear characteristics and non-zero intercepts, confirming that adsorption proceeds through multiple stages rather than being controlled by a single diffusion step. Moreover, the pseudo-second-order model provided the best kinetic fit, suggesting that surface reaction and ion exchange dominate the rate-controlling mechanism (Figure S3). Overall, ClO4⁻ adsorption onto the MTAC hydrogel is governed by synergistic film diffusion, intraparticle diffusion, and surface electrostatic interaction processes.

Adsorption isotherm experiments were conducted to evaluate the performance of MTAC hydrogels (Texts S4). Figure 4b and c shows the adsorption behavior of $ClO_4^-$ at temperatures of 298, 308, and 318 K. The equilibrium adsorption capacity ($Q_e$) increased gradually with rising equilibrium concentration ($C_e$) and eventually reached a plateau. The Langmuir model provided a better fit to the experimental data, indicating monolayer adsorption of $ClO_4^-$ onto the hydrogel surface [40]. The theoretical maximum adsorption capacities ($Q_m$) at 298, 308, and 318 K were calculated as 425.22, 395.22, and 364.15 mg/g, respectively. The adsorption process was more favorable at lower temperatures. As summarized in Table S5, the MTAC hydrogels exhibited a notably higher adsorption capacity compared to other reported adsorbents.

Thermodynamic parameters were calculated to further understand the adsorption behavior (Text S5). The standard Gibbs free energy ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes were determined using the Van’t Hoff equation. As list in Table S6, the ΔG° values at 298, 308, and 318 K were −23.42, −23.97, and −23.83 kJ/mol, respectively. The negative ΔG° and ΔH° values indicate that the adsorption of $ClO_4^-$ onto MTAC hydrogels is spontaneous and exothermic [41], being more favorable at lower temperatures. The magnitude of ΔH° may provide insights into the adsorption mechanism, the moderate enthalpy change (ΔH° = −17.16 kJ/mol) falls within the typical range of physisorption rather than chemisorption [42]. Moreover, the positive entropy change ($\Delta S°$ = 21.35 J/mol·K) suggests an ion-exchange process, likely due to the release of counterions ($Cl^-$) from the quaternary ammonium groups into the solution. Considering the fixed cationic sites in the MTAC hydrogel and the non-coordinating nature of $ClO_4^-$, the adsorption mechanism is therefore more reasonably attributed to electrostatic interactions.[43].

### 3.5. DFT calculations and adsorption mechanism

To gain deeper insight into adsorption process at the molecular level, density functional theory (DFT) calculations were carried out to calculate the adsorption energy and electron distribution. To simulate the interaction between $ClO_4^-$ and MTAC, and the electrostatic potential (ESP) distribution of MTAC, $ClO_4^-$, and the complex of MTAC and $ClO_4^-$ was further analyzed (Figure 5a). The red area in the ESP of MTAC was located in quaternary ammonium groups, indicating that its high potential due to their positive charge. $ClO_4^-$ carried a negative charge and surrounded by blue negative potential. The geometrically optimized adsorption complex of MTAC and $ClO_4^-$ suggested that O in $ClO_4^-$ and H of quaternary ammonium groups in MTAC were the main interaction sites. The calculated adsorption energy for the MTAC-$ClO_4^-$ complex was –82.87 kcal/mol (approximately –3.59 eV), indicating a thermodynamically favorable interaction between the adsorbent and $ClO_4^-$. The exothermic and spontaneous nature of the adsorption process was further confirmed by thermodynamic parameters ($\Delta H < 0$ and $\Delta G < 0$).

Charge population analysis revealed an electron transfer of 0.32 e from $ClO_4^-$ to the MTAC monomer, indicating significant charge redistribution and strong electrostatic interaction between perchlorate and the quaternary ammonium groups. This result confirms that adsorption is dominated by localized ionic binding rather than surface-area-dependent physical adsorption, explaining the high adsorption capacity despite the low BET surface area. Therefore, the DFT-calculated adsorption energy and charge transfer collectively demonstrate that the abundant cationic sites within the hydrated network are responsible for the efficient perchlorate capture.

As shown in Figure 5b, after $ClO_4^-$ adsorption, MTAC hydrogel numerous granular deposits appeared on the surface, particularly at edges and folds, increasing overall roughness. EDS mapping revealed pronounced Cl enrichment in these granular areas, whereas N and C distributions matched the hydrogel matrix. This suggests that $ClO_4^-$ accumulated as ion pairs or adsorption layers at active sites, visible as particles. The mapping confirms that adsorption primarily occurred at or near the surface, consistent with surface adsorption or ion exchange.

XRD patterns (Figure 5c) showed broad, diffuse peaks for both pristine and adsorbed MTAC hydrogel, indicating an amorphous structure [44]. After adsorption, diffraction intensity increased in the $2\theta$ range of 10–30°, with new local peaks emerging. This suggests $ClO_4^-$ incorporation induced partial structural ordering, likely due to electrostatic interactions and ion-pair formation between $ClO_4^-$ and quaternary ammonium groups. FTIR analysis (Figure 5d) identified key functional groups: the peaks at 3438, 1735, 1654, and 3000 $cm^{-1}$ are related to O–H/N–H stretching of the hydrogen-bonding network [44,45], ester C=O stretching of MTAC [46], C=O stretching of MBA [47], and C–H stretching in MTAC [48], respectively. The absorption peak at 960 $cm^{-1}$ corresponds to the $–N^+(CH_3)_3$ stretching [31,46]. After $ClO_4^-$ adsorption, the O–H peak intensifies, indicating the enhanced hydrogen bonding, likely with $ClO_4^-$. The new peak appearing at 1160 $cm^{-1}$ can be attributed to the C–N stretching of $N^+(CH_3)_3$ and/or Cl–O asymmetric stretching. The peak at 620 $cm^{-1}$ is related to the asymmetric bending of O–Cl–O in $ClO_4^-$ [46,48,49]. Other peaks (C=O, C–N) also intensifies, possibly due to changes in the hydrogen-bonding network and perchlorate-induced swelling affecting intermolecular interactions. Combined with FTIR analysis and thermodynamic calculations, it indicates that strong attractive interactions exist between MTAC and $ClO_4^-$, primarily involving electrostatic forces and hydrogen bonding interactions [50].

XPS analysis was employed to further elucidate the adsorption mechanism by comparing MTAC hydrogels before and after $ClO_4^-$ adsorption, as shown in Figure 6. Detailed peak area percentages are shown in Table S7. The N 1s and Cl 2p spectra were analyzed to monitor valence-state changes resulted from $ClO_4^-$ uptake. As shown in Figures 6a–c, a noticeable increase in oxygen content was observed after adsorption, along with the appearance of a characteristic perchlorate peak at 207.7 eV in the Cl 2p spectrum [40], confirming successful adsorption of $ClO_4^-$ onto the MTAC hydrogel. A slight shift in the Cl 2p peak position was also noted, consistent with the emergence of the $ClO_4^-$ signal. Moreover, after adsorption at different $ClO_4^-$ concentrations, the $Cl^-$ concentration in the solution showed a progressive increase (Figure S4). The presence of the $ClO_4^-$ peak together with the rising $Cl^-$ levels confirms that ion exchange between $Cl^-$ and $ClO_4^-$ is one of the primary adsorption mechanisms. As shown in Figure 6d–e, the N 1s spectrum was deconvoluted into two components, corresponding to the amide amino group ($–NH(CH_3)_2$) at around 399 eV [40] and the quaternary ammonium group (–

$N(CH_3)_3$) near 402 eV [51]. After adsorption, both N 1s peaks exhibited a positive shift, indicating successful adsorption of $ClO_4^-$ onto the quaternary ammonium groups. Given that these groups are the only positively charged moieties on the hydrogel surface, they serve as preferential adsorption sites for anionic species.

In summary, combining thermodynamic calculations with DFT, SEM, XRD, FTIR, and XPS analyses leads to the conclusion that the removal of $ClO_4^-$ is achieved through multiple synergistic mechanisms, including van der Waals forces, electrostatic attraction, hydrogen bonding, and ion exchange as shown in Figure 7.

### 3.6. Recyclability and applications

Cyclic adsorption–desorption tests were conducted to evaluate the regeneration performance and structural stability of the MTAC hydrogel. After each adsorption step, the hydrogel powder was recovered by vacuum filtration. Due to fine particle loss during filtration and handling, an average material loss of approximately 28.8% was observed over five cycles. In the regeneration process, 1 M NaCl solution was employed as the eluent. The high concentration of $Cl^-$ ions effectively displaced adsorbed $ClO_4^-$ via competitive ion exchange, regenerating the quaternary ammonium active sites [52]. Based on adsorption–desorption mass balance calculations, nearly complete desorption of $ClO_4^-$ was achieved in each cycle, with an average desorption amount of 22.98 mg $g^{-1}$ over five cycles. SEM analysis revealed granular deposits on the hydrogel surface after $ClO_4^-$ adsorption (Figure 5b), which largely disappeared following regeneration (Figure S5), confirming effective removal of surface-bound perchlorate.To further evaluate material stability, TOC analysis of the desorption solution after the final cycle showed a low value of 4.386 mg/L, indicating negligible organic leaching from the hydrogel matrix. As shown in Figure 8b, the $ClO_4^-$ removal efficiency remained above 85% throughout five cycles, demonstrating that the quaternary ammonium functional groups retained their activity during repeated use despite partial mechanical loss during recovery.

SEM images and elemental mapping of the MTAC/SA Gel Beads are shown in Figures 8a. The MTAC/SA Gel Beads exhibited a dense but porous 3D network with a wrinkled surface and irregular pores, indicating mechanical stability with sufficient porosity for mass transport. EDS showed a strong O signal from carboxyl and sugar chains of SA, and N signals confirming MTAC incorporation. The $Ca^{2+}$ crosslinking with alginate enhanced morphological stability and porosity, improving adsorption kinetics and reusability while facilitating powder recovery.

To overcome the challenge of recovering powdered adsorbents, the MTAC hydrogel was further engineered into MTAC/SA hydrogel beads, enhancing its potential for practical application. The performance of these beads as point-of-use (POU) materials was evaluated in a fixed-bed column system (Figure 8c; column parameters listed in Table S8). As shown in Figure 8d, with an initial $ClO_4^-$ concentration of 500 μg/L, the beads effectively treated 5346 bed volume (BV), equivalent to approximately 167.9 L of solution, reducing the effluent concentration below the drinking water standard limit of 70 μg/L. The saturated column adsorption capacity ($q_f$) was estimated at 39.1 mg/g (see Figure S6 for calculations), corresponding to a total treatment volume of 14,844 BV (≈ 466.1 L). The high treatment capacity is particularly promising for small-scale continuous systems, positioning the MTAC/SA hydrogel beads as a compelling POU material. It is worth noting that $q_f$ is influenced by various operational parameters such as empty bed contact time (EBCT), surface velocity, and initial concentration; thus, rational optimization of these factors could further improve $q_f$ [53]. Subsequent regeneration of the fixed-bed column (Figure 8e) revealed a significant desorption peak within the initial 0–4 BV, indicating high desorption efficiency. Greater than 90 % of the adsorbed $ClO_4^-$ was successfully recovered using approximately 15 BV of eluent, achieving an average enrichment factor of 122.9.

## 4. Conclusions

In this work, a novel hydrogel adsorbent based on the quaternary ammonium monomer MTAC was successfully synthesized and demonstrated to be highly effective for the removal of $ClO_4^-$ from aqueous solutions. The comprehensive investigation leads to the following key conclusions: (i) The MTAC hydrogel exhibited a remarkably high Langmuir adsorption capacity of 425.22 mg/g at 298 K. The adsorption process was rapid, spontaneous, and exothermic; (ii) The adsorbent maintained high efficiency across a broad pH range (5–9), significant tolerance to common competing anions like $Cl^-$ and $NO_3^-$, and retained over 85% of its initial removal efficiency after five adsorption-desorption cycles, underscoring its potential for real-world applications; (iii) The engineered MTAC/SA hydrogel beads demonstrated outstanding performance in a fixed-bed column, treating a substantial volume of water (5346 BV) before breakthrough and achieving an enrichment factor of 122.9 during convenient regeneration, highlighting their suitability for continuous, point-of-use treatment systems; (iv) A combination of experimental characterization (XPS, FTIR) and DFT confirmed that the removal of $ClO_4^-$

proceeds through multiple synergistic mechanisms, including van der Waals forces, electrostatic attraction, hydrogen bonding, and ion exchange. In summary, this study not only presents a novel and high-performance hydrogel adsorbent for perchlorate remediation but also provides a deep mechanistic understanding of the adsorption process. The material's high capacity, stability, regenerability, and proven efficacy in complex water matrices make it a highly promising and practical solution for addressing perchlorate contamination in water.

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