

## Article

# Production of FeCl<sub>3</sub>-Treated Amine Functional Polymer Gel for Enhanced Removal of Methyl Orange and Congo Red Anionic Dyes

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## Abstract

Synthetic dyes such as Methyl Orange (MO) and Congo Red (CR) are recalcitrant, toxic, mutagenic and resistant to conventional biodegradation, and their industrial discharge continues to contaminate aqueous ecosystems worldwide. This study reports the synthesis and characterization of a poly(MMA-co-2-AEMA) copolymer gel (Fe-Copolymergel-NH<sub>2</sub>) treated with FeCl<sub>3</sub>. It evaluates its adsorption performance from aqueous solution against the anionic azo dyes MO and CR. Extensive characterization using N<sub>2</sub> adsorption–desorption at 77 K, FTIR-ATR, XPS, SEM, and TEM revealed that Fe modification significantly improved the material's textural properties, increasing its specific surface area from 8.11 m<sup>2</sup>/g to 12.55 m<sup>2</sup>/g and creating a highly irregular, interconnected, sponge-like morphology. Adsorption experiments showed that Fe-Copolymergel-NH<sub>2</sub> achieved competitive Langmuir maximum monolayer adsorption capacities of 3201.9 mg/g for CR and 1089.8 mg/g for MO. Kinetic modeling demonstrated that adsorption strictly followed the PSO model, primarily governed by chemisorption via electrostatic attractions and complexation within the internal structure at Fe<sup>3+</sup> coordination centers. Thermodynamic analysis revealed that the dye removal process was spontaneous and exothermic. Consequently, the successful integration of Fe<sup>3+</sup> coordination centers resolves the adsorption and structural limitations of pure polymer matrices, positioning Fe-Copolymergel-NH<sub>2</sub> as a highly promising and efficient adsorbent for the remediation of dye-contaminated industrial wastewater.

**Keywords:** FeCl<sub>3</sub> treatment; polymer gel; anionic dye; adsorption thermodynamics; adsorption kinetics



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## 1. Introduction

The pervasive contamination of aqueous environments by synthetic dyes poses a critical environmental concern, driving the urgent development of highly efficient, structurally robust adsorbent materials for effective wastewater remediation [1]. The widespread discharge of synthetic dyes from industrial activities, particularly in the textile, paper, and food manufacturing sectors, poses significant threats to aquatic ecosystems and human health [2]. These risks are compounded by the dyes' recalcitrant nature, chemical stability, inherent

toxicity, and resistance to conventional biodegradation processes [3,4]. Among these, MO and CR, both anionic azo dyes extensively used in textile industries, are particularly problematic owing to their widespread application and potential to induce severe toxic effects, including skin and eye damage, mutagenicity, carcinogenicity, kidney failure, genetic mutations, cancer, and disruptions to respiratory and reproductive systems in aquatic life and humans [5,6]. Consequently, the effective removal of these dyes from industrial wastewater streams is critical for environmental protection and public health [3,7]. This imperative has catalyzed extensive research into various advanced wastewater treatment technologies, including chemical precipitation, photocatalysis, membrane separation, electrochemical treatment, coagulation-flocculation, ion exchange, biological methods, membrane filtration, photochemical degradation, and anaerobic bioremediation [8–10]. Among these techniques, adsorption has emerged as a prominent method owing to its cost-effectiveness, operational simplicity, high efficiency in removing a broad spectrum of pollutants, absence of toxic byproducts, ease of application, straightforward and scalable synthesis of adsorbents, flexibility, and environmental benignity [11]. Polymer-based adsorbents, particularly hydrogels, have garnered considerable interest due to their tunable physicochemical properties, high surface area, exceptional adsorption capacities for various organic pollutants, including anionic dyes like MO and CR, high swelling ratios, and porous microstructures enabling mechanisms such as electrostatic attraction, hydrogen bonding, van der Waals forces, and  $\pi$ - $\pi$  interactions [12–14]. However, current hydrogel adsorbents often suffer from limitations, such as low adsorption capacities, poor mechanical stability, and difficulty in regeneration, which hinder their large-scale practical deployment for wastewater treatment [15]. Consequently, there is an urgent need to develop novel, mechanically robust, and highly efficient polymeric hydrogel systems—such as those utilizing metal-ligand coordination—to overcome these deficiencies and enable sustainable remediation [16,17]. Such modifications facilitate superior adsorption of recalcitrant organic pollutants, including anionic dyes, by introducing specific interactions that extend beyond conventional physisorption. Furthermore, incorporating positively charged moieties within these polymeric networks significantly enhances their affinity and removal efficiency for anionic dyes [18]. Within this landscape, cationic polyelectrolyte hydrogels bearing protonatable  $-\text{NH}_2$  and quaternary-ammonium groups together with related  $\text{Fe}^{3+}$ -coordinated networks have attracted particular interest as high-capacity platforms for anionic azo-dye removal because the electrostatic pairing with the  $-\text{SO}_3^-$  substituents of MO and CR drives  $q_0$  values that exceed those of activated carbons and biochars of comparable cost [6,14,15].

When recent studies on dye adsorption of polymer gels are examined, Toprak et al. synthesized an  $\text{NH}_2$ -functionalized copolymer gel from vinyl benzyl chloride and 2-aminoethyl methacrylate, followed by  $\text{FeCl}_3$ -catalyzed Friedel-Crafts hyper-crosslinking to yield HyPolygel- $\text{NH}_2$  with superior capacities of 5234 mg/g for CR and 1816 mg/g for MO via electrostatic interactions and hydrogen bonding [4]. Similarly, Zhang et al. fabricated maleic anhydride-acrylamide copolymer-based sodium alginate hydrogels (MAH@AA-P/SA/H) that demonstrated maximum adsorption capacities of 685 mg/g for CR and 653 mg/g for methylene blue, alongside high removal of metal ions such as  $\text{Cu}^{2+}$  (754 mg/g) and  $\text{Cr}^{6+}$  (738 mg/g) [19]. Further advancements include the development of trimethylammonium chloride- and methacrylamide-based hydrogels, which achieved impressive methyl orange adsorption capacities of 950 and 994 mg/g, respectively [14]. Furthermore, poly(acrylamide-co-methacryloxyethyltrimethylammonium chloride) hydrogels have demonstrated remarkable adsorption capacities of 840.85 mg/g for CR within 10 min, with the overall process being governed by chemisorption and exhibiting good reusability [3]. In a different approach, Li et al. developed quaternary ammonium hydrogels that achieved over 99% removal efficiency for Direct Red 23, with a maximum

adsorption capacity of 1540.19 mg/g, highlighting the potential for highly efficient anionic dye removal through targeted cationic polymer design [20]. These high adsorption capacities and efficiencies underscore the potential of cationic hydrogels as effective adsorbents for anionic dyes. Conversely, cyclodextrin-acrylamide-based adsorbents have demonstrated high efficiency in removing both cationic and anionic dyes, achieving rapid equilibrium times of 15–20 min and significant adsorption capacities for MO [21]. Despite these advancements, many hydrogels still face challenges related to mechanical robustness, reusability, and broad applicability across diverse wastewater matrices. For instance, while xanthan gum-based hydrogels show promise for dye removal, their efficacy is often limited by factors such as ionic strength and pH, necessitating careful optimization for practical applications [22]. These limitations highlight the ongoing need for novel hydrogel architectures that balance enhanced structural integrity and chemical stability with high adsorptive performance across a broader range of environmental conditions.

In this study, we synthesized a mesoporous amine hydrogel, Fe-Copolymergel-NH<sub>2</sub>, by treating a poly(MMA-co-2-AEMA) copolymer gel with FeCl<sub>3</sub>. The textural characterization, surface chemistry, and adsorption behavior of this hydrogel for MO and CR were investigated. The adsorption kinetics (PFO and PSO), equilibrium (Langmuir/Freundlich isotherm), and thermodynamics of copolymergel-NH<sub>2</sub> and Fe-copolymergel-NH<sub>2</sub> were systematically studied. It was determined that Fe-copolymergel-NH<sub>2</sub> is highly effective in CR adsorption.

## 2. Materials and Methods

### 2.1. Materials

2,2'-Azobisisobutyronitrile (AIBN) was purchased from Sigma-Aldrich (St. Louis, MO, USA), and CR > 75.0% was obtained from Acros Organics (Geel, Belgium). FeCl<sub>3</sub> was supplied by Isolab Chemical (Istanbul, Turkey). MO, 1,2-dichloroethane (DCE), N, N-dimethylformamide (DMF), methyl methacrylate (MMA), and 2-aminoethyl methacrylate (2-AEMA) were purchased from Merck (Darmstadt, Germany). All chemicals were of analytical grade and used as received without further purification.

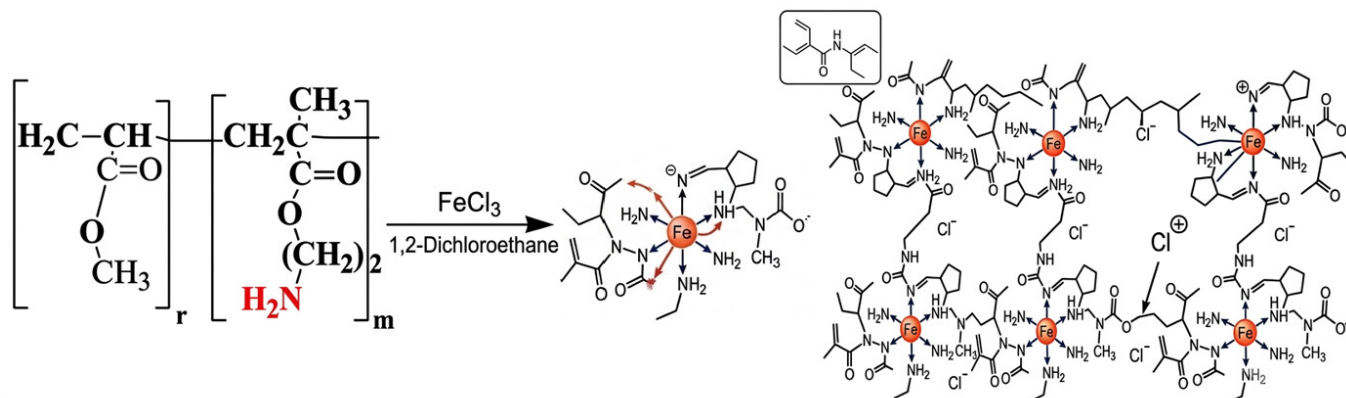
### 2.2. Preparation of Copolymergel-NH<sub>2</sub>

The NH<sub>2</sub>-functionalized copolymer gel was synthesized via free-radical polymerization [4,23]. In a typical experimental procedure, 5.21 g of DMF, 3.24 g of 2-AEMA, and 7.12 g of MMA were dissolved in a Pyrex tube, and the reaction mixture was prepared by adding 17 mg of AIBN. Prior to the reaction, the mixture was purged with Ar gas to remove dissolved oxygen and prevent potential inhibition of the radical species. Polymerization was then carried out in a temperature-controlled reaction vessel at 80 °C for 2 h. After the reaction was complete, the resulting gel-like product was purified and washed with pure H<sub>2</sub>O to remove unreacted monomers and residual initiator. The purified copolymer gel was then dried at 40 °C, yielding 6.82 g.

### 2.3. Preparation of Fe-Copolymergel-NH<sub>2</sub>

The Fe-modified polymer hydrogel, designated as Fe-Copolymergel-NH<sub>2</sub>, was synthesized via FeCl<sub>3</sub>-mediated coordination crosslinking following the literature procedure, and the proposed binding geometry is illustrated in Scheme 1 [4]. Initially, the previously synthesized Copolymergel-NH<sub>2</sub> was placed in a reaction vessel and subjected to swelling in DCE for 2 h. This process was conducted under an argon atmosphere with slow magnetic stirring to ensure the polymer network was sufficiently expanded. Subsequently, the mixture was cooled to approximately 0 °C in an ice bath. 1.52 g of anhydrous FeCl<sub>3</sub> was then added to the cooled PolygelNH<sub>2</sub> mixture, and the mixture was stirred for 10 min to achieve

a homogeneous dispersion. The reaction temperature was then gradually increased to 80 °C, and the mixture was stirred continuously for 24 h. Following the reaction, the resulting Fe-Copolymergel-NH<sub>2</sub> was purified by multiple washes with methanol and deionized water, then centrifuged. As a result of this step, Fe-Copolymergel-NH<sub>2</sub> with improved surface and pore properties was synthesized by removing FeCl<sub>3</sub> and unreacted substances.



**Scheme 1.** Experimental mechanism diagram of Fe- and Copolymergel-NH<sub>2</sub>.

#### 2.4. Characterization

The specific surface area ( $S_{\text{BET}}$ ) and pore size distributions (PSD) of Copolymergel-NH<sub>2</sub> and Fe-Copolymergel-NH<sub>2</sub> were determined through N<sub>2</sub> adsorption/desorption isotherms using a surface area and pore size analyzer, Quantachrome-Autosorb 1C (Quantachrome, Boynton Beach, FL, USA). The surface morphology and internal structural characteristics were examined via scanning electron microscopy (SEM, FEI QUANTA FEG 450, Graz, Austria) and transmission electron microscopy (TEM, Hitachi HT-7700, Tokyo, Japan), respectively. To evaluate the surface functional groups, Fourier transform infrared spectroscopy (FTIR-ATR, PerkinElmer, Santa Clara, CA, USA) was used. Additionally, changes in the crystalline structure were analyzed using X-ray diffraction (XRD; PANalytical Empyrean, Worcestershire, UK) over a  $2\theta$  range of 10–90°. The surface chemical components and electronic states were further characterized by X-ray photoelectron spectroscopy (XPS; Thermo Scientific K-Alpha, East Grinstead, UK) using an Al K $\alpha$  monochromatic X-ray source.

#### 2.5. Adsorption Experiments

Batch adsorption experiments were conducted to evaluate the performance of copolymer gel-NH<sub>2</sub> and Fe-copolymer gel-NH<sub>2</sub> adsorbents for the removal of anionic dyes from aqueous solutions. The procedure involved a 50 mL solution volume maintained at a constant agitation speed of 400 rpm, with dye concentrations quantified by UV-Vis spectrophotometry over the 200–800 nm spectral range. Adsorption isotherm and kinetic equilibrium studies were carried out for MO and CR anionic dyes at 100 mg/L in 50 mL using varying dosages of the polymer gel adsorbents (1, 2, 3, 4, and 5 mg). Furthermore, the influence of temperature and thermodynamic parameters was evaluated over the range of 20 °C to 40 °C. The equilibrium adsorption capacities ( $q_e$ ) of the dyes were calculated according to the following equation [24]:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

## 2.6. Adsorption Kinetics

To elucidate the rate-controlling mechanisms and investigate the temporal behaviour of the adsorption process for Copolymergel-NH<sub>2</sub> and Fe-Copolymergel-NH<sub>2</sub>, the experimental data were fitted to pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models. The PFO kinetic model implies that the adsorption process is governed by physical interactions, including H<sub>2</sub> bonding,  $\pi$ - $\pi$  stacking, and van der Waals forces, established between the functional groups of the adsorbent matrix and the aromatic structure of the dye molecule. The following equation expresses the linear form of the PFO model [24,25]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where  $q_e$  and  $q_t$  (mg/g) represent the adsorption capacities at equilibrium and at time  $t$  (min), respectively, and  $k_1$  (min<sup>-1</sup>) denotes the PFO rate constant.

The PSO kinetic model, which posits that the rate-limiting step involves chemisorption through electron sharing or exchange between the adsorbent and the dye molecules, is expressed as [26]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

in this expression,  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the PSO rate constant.

## 2.7. Adsorption Isotherms Models

To investigate the equilibrium relationship between the target anionic dyes and the synthesized adsorbents, the experimental data were analyzed using the Langmuir and the Freundlich isotherm models. These models are essential for characterizing the interaction between the dye molecules and the Fe-Copolymergel-NH<sub>2</sub> surface. The Langmuir model, which assumes that adsorption occurs on a homogeneous surface through monolayer coverage with no interaction between adsorbed molecules, is expressed in its linear form as follows [4]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_0} + \frac{C_e}{q_0} \quad (4)$$

In this equation,  $C_e$  (mg/L) is the equilibrium concentration of the dye,  $q_e$  (mg/g) is the amount of dye adsorbed at equilibrium,  $q_0$  (mg/g) represents the maximum monolayer adsorption capacity, and  $K_L$  (L/mg) is the Langmuir constant related to the energy of adsorption [27].

The Freundlich isotherm model is employed to describe multilayer adsorption on heterogeneous surfaces with sites of varying affinities. The linear mathematical representation of the Freundlich model is given by [28]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

where  $K_F$  (mg/g) is the Freundlich constant representing the adsorption capacity and  $1/n$  is the heterogeneity factor. These parameters, derived from the intercept and slope of the linear regression, provide a comprehensive understanding of the maximum adsorption potential and the interaction favorability between the adsorbent's surface and anions [24,29].

## 2.8. Adsorption Thermodynamics

To characterize the energetic changes associated with the adsorption process, the thermodynamic parameters, specifically the Gibbs free energy change ( $\Delta G^0$ ), enthalpy change ( $\Delta H^0$ ), and entropy change ( $\Delta S^0$ ), were determined using the van't Hoff equation [30]. The distribution coefficient ( $K_d$ ) employed in the thermodynamic analysis was calculated as:

$$K_d = \frac{q_e}{C_e} \quad (6)$$

where  $q_e$  is the equilibrium adsorption capacity, and  $C_e$  is the equilibrium dye concentration. The values of  $\Delta H^0$  and  $\Delta S^0$  were obtained from the slope and intercept of the van't Hoff plot of  $\ln K_d$  versus  $1/T$ , according to:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (7)$$

Negative values of  $\Delta G^0$  indicate the spontaneous nature of the adsorption process. At the same time, the signs of  $\Delta H^0$  and  $\Delta S^0$  provide insight into the endothermic or exothermic nature and the degree of disorder at the solid–liquid interface [31]. The standard Gibbs free energy change was computed using the relation:

$$\Delta G^0 = -RT \ln K_d \quad (8)$$

where a decrease in these values with increasing temperature indicates a greater favorability of the adsorption process under thermal influence. The calculated  $\Delta H^0$  and  $\Delta S^0$  values, obtained from the slope and intercept of the van't Hoff plot, indicate whether the mechanism is dominated by physisorption or chemisorption [32]. Spontaneity was further evaluated through the fundamental Gibbs–Helmholtz relation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

### 2.9. Water Swelling Percentage

The swelling behavior of the synthesized copolymer gel was evaluated by immersing a known mass of the dried sample in deionized water until equilibrium swelling was attained. The swollen hydrogel was then removed, carefully blotted with filter paper to eliminate excess surface moisture, and weighed to determine the equilibrium water content. The swelling percentage ( $S_w$  %) was subsequently calculated using the formula:

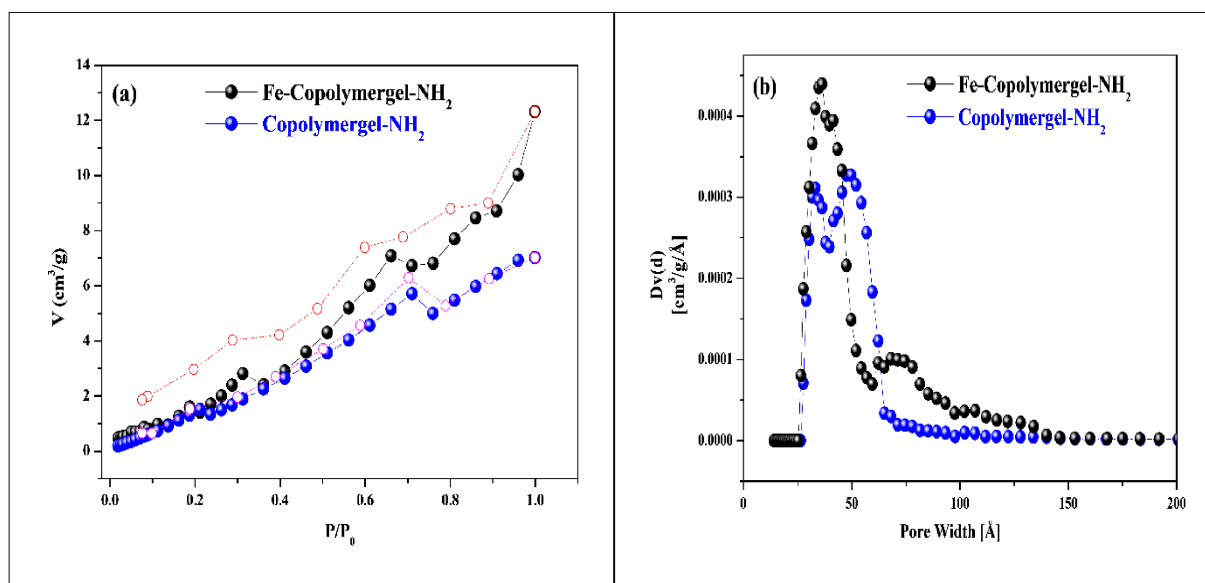
$$S_w(\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (10)$$

where  $W_s$  and  $W_d$  represent the weight of the swollen hydrogel at equilibrium and the weight of the dried polymer sample, respectively.

## 3. Results and Discussion

### 3.1. Surface Area and Pore Volume Characterization of Fe-Copolymergel-NH<sub>2</sub>

The textural properties of Copolymergel-NH<sub>2</sub> and Fe-Copolymergel-NH<sub>2</sub> were evaluated through N<sub>2</sub> adsorption–desorption isotherms and Non-Local Density Functional Theory (NLDFT) pore size distributions, as illustrated in Figure 1. Figure 1a displays the N<sub>2</sub> adsorption–desorption isotherms for both materials. According to the IUPAC classification, both samples exhibit Type IV isotherms with a distinct H3-type hysteresis loop occurring at relative pressures ( $P/P_0$ ) between 0.4 and 1.0 [33,34]. This behaviour is characteristic of mesoporous materials with slit-shaped pores. Notably, the adsorption volume of Fe-Copolymergel-NH<sub>2</sub> is significantly higher than that of the pristine Copolymergel-NH<sub>2</sub> across the entire pressure range. The increased N<sub>2</sub> uptake at high relative pressures ( $P/P_0 > 0.8$ ) suggests that the FeCl<sub>3</sub> treatment and subsequent crosslinking process enhanced the total pore volume and specific surface area, likely due to structural rearrangement or the formation of new coordination sites within the polymer matrix [4].



**Figure 1.** (a) N<sub>2</sub> adsorption/desorption isotherms and (b) NLDFT pore size distribution of Fe- and Copolymergel-NH<sub>2</sub>.

The pore-size distribution curves, calculated using the NLDFT method, are shown in Figure 1b. Both materials exhibit a predominant pore diameter of 20–60 Å, confirming the mesoporous nature of the copolymer gels. For Fe-Copolymergel-NH<sub>2</sub>, the peak intensity is markedly higher compared to Copolymergel-NH<sub>2</sub>, indicating a higher density of mesopores within this size regime. This increase in porosity and available surface area is expected to facilitate the diffusion and sequestering of bulky anionic dye molecules, such as MO and CR, thereby enhancing the overall adsorption capacity [35].

The textural properties of Copolymergel-NH<sub>2</sub> and Fe-Copolymergel-NH<sub>2</sub> were calculated through N<sub>2</sub> adsorption–desorption isotherms and NLDFT pore size distributions at 77 K, as shown in Table 1. The FeCl<sub>3</sub> treatment of the NH<sub>2</sub>-copolymergel resulted in a significant enhancement of the specific surface area and pore structure. The BET surface area increased from 8.11 m<sup>2</sup>/g for Copolymergel-NH<sub>2</sub> to 12.55 m<sup>2</sup>/g for Fe-Copolymergel-NH<sub>2</sub>, representing an increase of approximately 55%. This improvement suggests that incorporating Fe<sup>3+</sup> ions and their subsequent coordination with amine groups within the polymer matrix likely prevented the collapse of the polymer network or induced structural rearrangements that exposed more active surface sites.

**Table 1.** Pore and surface structural parameters of Fe- and Copolymergel-NH<sub>2</sub>.

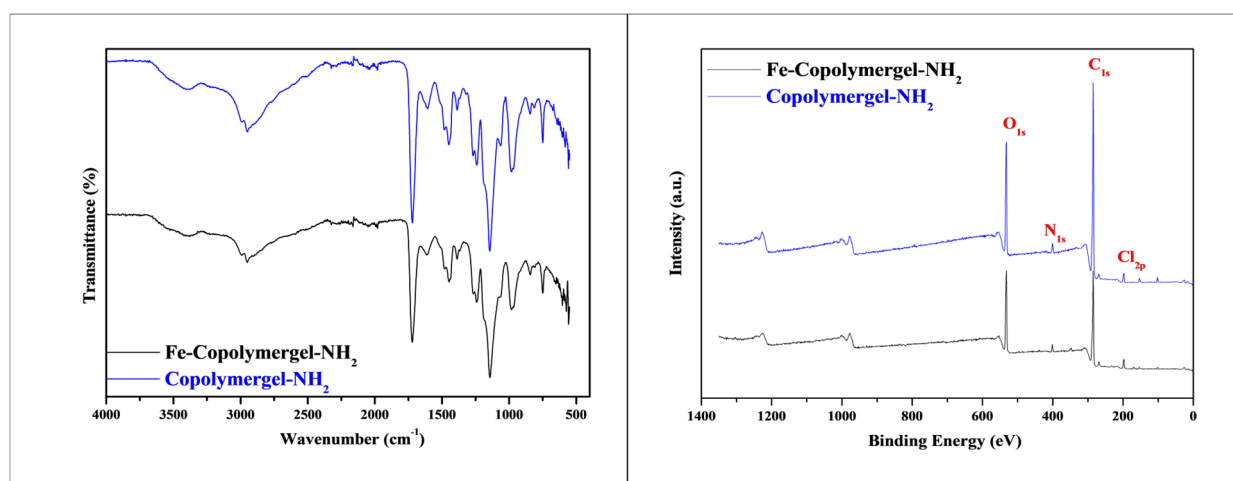
| Adsorbent                       | BET<br>(m <sup>2</sup> /g) | V <sub>DRmicro</sub> (cm <sup>3</sup> /g)<br>(<20 Å) | V <sub>meso</sub> (cm <sup>3</sup> /g)<br>(20 Å < V <sub>μp</sub> ) | V <sub>t</sub> (cm <sup>3</sup> /g)<br>(P/P <sub>0</sub> = 0.995) |
|---------------------------------|----------------------------|------------------------------------------------------|---------------------------------------------------------------------|-------------------------------------------------------------------|
| Copolymergel-NH <sub>2</sub>    | 8.11                       | 0.0013                                               | 0.0109                                                              | 0.0096                                                            |
| Fe-Copolymergel-NH <sub>2</sub> | 12.55                      | 0.0010                                               | 0.0125                                                              | 0.0135                                                            |

Analysis of the pore volume data reveals a clear shift toward higher porosity following the iron treatment. The total pore volume ( $V_t$ ) increased from 0.0096 to 0.0135 cm<sup>3</sup>/g, primarily driven by the expansion of the mesoporous volume ( $V_{meso}$ ), which rose from 0.0109 to 0.0125 cm<sup>3</sup>/g. Conversely, the microporous volume ( $V_{DRmicro}$ ) showed a slight decrease from 0.0013 to 0.0010 cm<sup>3</sup>/g, suggesting that some micropores may have been merged into larger mesopores or partially obstructed by the iron coordination complexes. The high mesoporous-to-micropore volume ratio minimizes mass-transfer resistance for

these large dye molecules, allowing efficient diffusion into the internal active sites of the Fe-Copolymergel-NH<sub>2</sub> adsorbent.

### 3.2. FTIR and XPS Analysis

As shown in Figure 2, the chemical structures and functional groups of pure Copolymer Gel-NH<sub>2</sub> and modified Fe-Copolymer Gel-NH<sub>2</sub> were investigated using FTIR-ATR spectroscopy and XPS. The spectrum of the copolymergel-NH<sub>2</sub> exhibits the characteristic peaks of the poly(MMA-co-2-AEMA) structure. A broad absorption band at approximately 3400–3500 cm<sup>−1</sup> is assigned to the N–H stretching vibrations of the primary amine groups [4]. The peaks observed at 2950 cm<sup>−1</sup> and 2870 cm<sup>−1</sup> correspond to the C–H asymmetric and symmetric stretching of the CH<sub>2</sub> and CH<sub>3</sub> groups in the polymer chain. The sharp, intense peak at 1723 cm<sup>−1</sup> is a defining feature of ester groups, corresponding to the C=O stretching vibration. Additionally, it shows a strong band at 1145 cm<sup>−1</sup> attributed to the C–O–C stretching vibration of the ester bond [36,37]. Following the treatment with FeCl<sub>3</sub>, the spectrum of Fe-Copolymergel-NH<sub>2</sub> retains the primary features, indicating structural stability. However, changes occur in the amine and carbonyl regions. The shift and broadening of the N–H/O–H band around 3400 cm<sup>−1</sup> suggest the participation of amine lone pairs in coordination with Fe<sup>3+</sup> ions [38]. Both samples exhibit prominent peaks at C 1s (~285 eV) and O 1s (~532 eV), originating from the PMMA and 2-AEMA monomer units, respectively. The presence of a distinct N 1s peak (~400 eV) in both spectra confirms the successful copolymerization of the amino-functionalized monomer into the gel matrix.

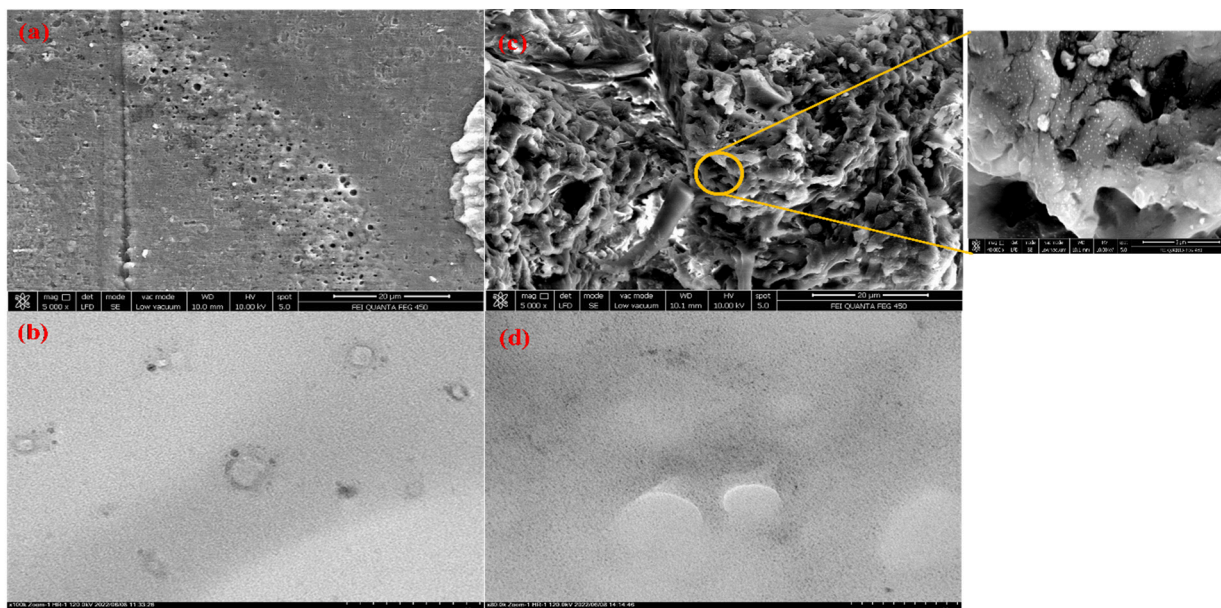


**Figure 2.** The FTIR spectra of Fe- and Copolymergel-NH<sub>2</sub>.

### 3.3. SEM and TEM Analysis

The surface morphology and internal structural properties of the synthesized materials were investigated using SEM and TEM to explore the effect of iron modification on the polymer framework. Figure 3 illustrates the significant morphological transition between the pristine Copolymergel-NH<sub>2</sub> and the modified Fe-Copolymergel-NH<sub>2</sub>. As shown in the SEM micrograph in Figure 3a, the surface of the pristine Copolymergel-NH<sub>2</sub> is relatively smooth and continuous, exhibiting only minor surface irregularities and a few visible micropores. This relatively uniform surface suggests a stable but less accessible polymer matrix. In stark contrast, the SEM image of Fe-Copolymergel-NH<sub>2</sub> (Figure 3c) reveals a dramatic shift toward a highly irregular, rough, and complex morphology. The surface appears highly fragmented, with a sponge-like structure characterized by deep voids and a high density of interconnected pores. Furthermore, in the magnified view of a section of Figure 3c, a regular distribution of iron compounds is identified. This open, rough surface

is highly advantageous for wastewater treatment applications, as it provides a larger active area and minimizes mass-transfer resistance for large anionic dye molecules.



**Figure 3.** SEM (a,b), TEM images (c,d) of Fe- and Copolymergel-NH<sub>2</sub>.

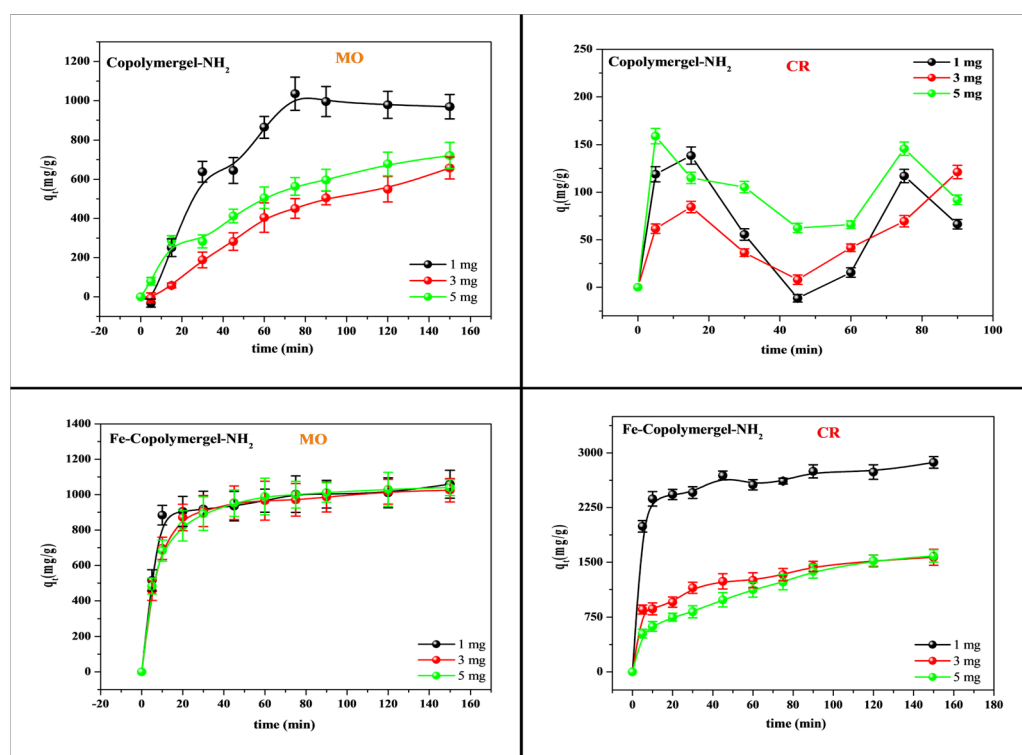
The TEM image of Copolymergel-NH<sub>2</sub> (Figure 3b) shows a relatively low-density internal network with a light, uniform contrast, indicating a standard polymer gel matrix without heavy atom clusters. However, the TEM image of Fe-Copolymergel-NH<sub>2</sub> (Figure 3d) exhibits a more complex internal density. The appearance of dark, speckled regions and increased contrast across the matrix signifies the successful incorporation of Fe<sup>3+</sup> species and the formation of a more rigid, dense network.

The successful incorporation of Fe species and the associated structural rearrangement of the polymer matrix were quantitatively confirmed through XPS and SEM-EDS analyses, and the elemental weight percentages are summarized in Tables S1 and S2, respectively. A consistent decrease in C content was observed across both techniques following the FeCl<sub>3</sub> treatment, with XPS recording a decline from 67.30% to 56.22% and SEM-EDS recording a reduction from 58.32% to 56.22%. This decrease results not from the degradation of the organic skeleton, but rather from the quantitative incorporation of higher-mass Fe and Cl species into the polymer matrix. The appearance of a 4.42 wt.% signal directly confirms Fe loading. Fe signal in SEM-EDS-absent in the pristine sample and indirectly corroborated by the substantial increase in Cl content, which rose from 3.74% to 5.65% in XPS and from 2.19% to 2.88% in SEM-EDS. The redistribution of N (increase from 2.90% to 3.38% in XPS) and O (increase from 22.50% to 27.52% in XPS) further supports the metal-ligand coordination mechanism; it can be said that amine functional units move towards the surface and coordinate with Fe<sup>3+</sup> ions.

The equilibrium water  $S_w$  of the pristine Copolymergel-NH<sub>2</sub> was determined to be approximately 1551.6%, whereas the FeCl<sub>3</sub>-modified Fe-Copolymergel-NH<sub>2</sub> exhibited a substantially higher swelling capacity of 2104.5% (Figure S1). This increase in hydrogel hydrophilicity is attributed to modifications in the polymer network, where the introduction of Fe-coordinated centers creates additional space and enhances the availability of polar active sites for interaction with water molecules [18].

### 3.4. Adsorption Studies

The time variation ( $t$ , min.) of the adsorption capacity ( $q_t$ , mg/g) for MO and CR on pure copolymer gel-NH<sub>2</sub> and Fe-copolymer gel-NH<sub>2</sub> is given in Figure 4. A significant increase in capacity and stability was observed after the modification process, with the equilibrium  $q_t$  value for CR adsorption on Fe-copolymer gel-NH<sub>2</sub> reaching approximately 2800 mg/g at a dosage of 1 mg. In contrast, copolymer gel-NH<sub>2</sub> exhibited significantly lower  $q_t$  with considerable unstable fluctuations. The kinetic curves showed a rapid initial uptake phase, during which 80–90% of the total adsorption occurred within the first 20 min, followed by a gradual approach to an equilibrium plateau between 120 and 180 min; this suggests film diffusion control and intraparticle diffusion within the porous network. Importantly, while pure Copolymergel-NH<sub>2</sub> exhibited irregular  $q_t$ - $t$  due to its smooth, non-porous morphology and insufficient active site density, Fe-Copolymergel-NH<sub>2</sub> formed smooth curves thanks to its highly porous, structurally robust matrix produced by FeCl<sub>3</sub>-mediated coordination crosslinking.



**Figure 4.** MO and CR adsorption-time graphs of Fe- and Coploymergel-NH<sub>2</sub> at different doses.

In Figure 5, the pH zero charge point ( $pH_{PZC}$ ), determined using the pH drift method, corresponds to the pH at which the net electrical charge on the adsorbent surface drops to zero, thereby defining the electrostatic nature of the interface under aqueous conditions [25]. The Copolymergel-NH<sub>2</sub> exhibits a  $pH_{PZC}$  value of 6.67. In contrast, the FeCl<sub>3</sub> treatment elevates this parameter to 8.0 in the resultant Fe-Copolymergel-NH<sub>2</sub>, reflecting an increase of approximately 1.33 pH units driven by the redistribution of surface functional groups and the modulation of protonation equilibria following iron coordination. This  $pH_{PZC}$  value fundamentally determines the surface ionization state: below this threshold, protonation of surface functionalities generates a net positive charge, whereas above it, deprotonation yields a net negative charge [39]. Consequently, Copolymergel-NH<sub>2</sub> exhibits a cationic surface only up to pH 6.67. In contrast, the Fe-Copolymergel-NH<sub>2</sub> counterpart maintains a positive surface potential up to pH 8.0, thereby extending the operational window favorable for electrostatic interactions with target solutes.

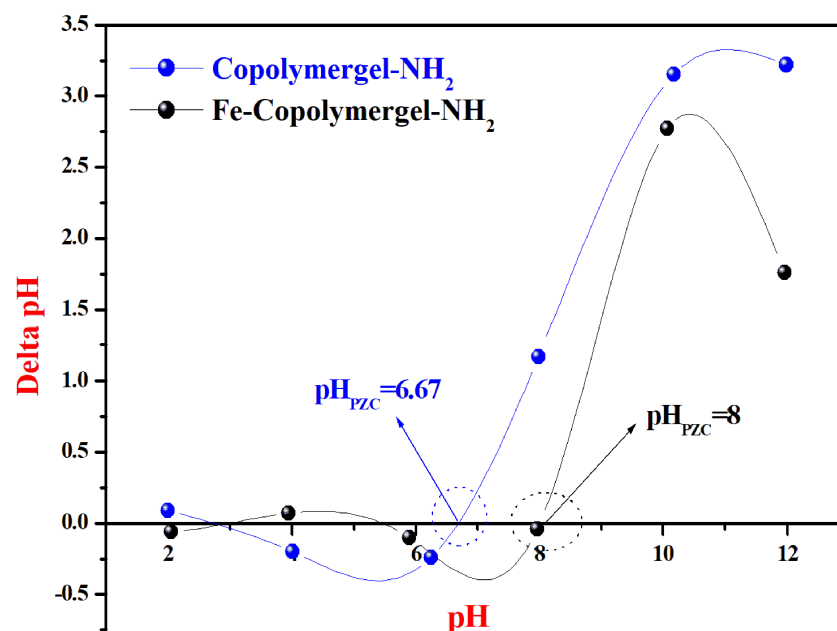


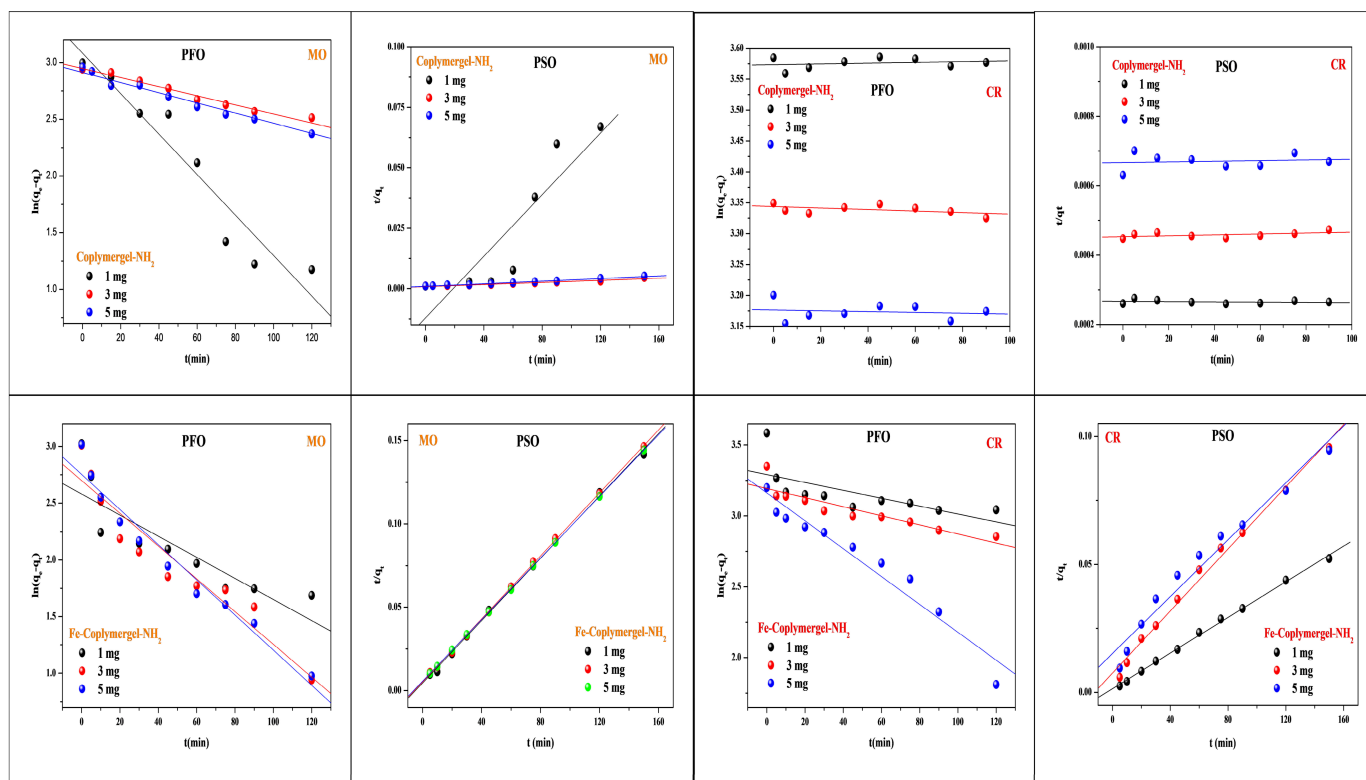
Figure 5. Determination of  $\text{pH}_{\text{PZC}}$  for Fe- and Copolymergel- $\text{NH}_2$ .

### 3.5. Kinetic Studies of Adsorption Processes

The PFO and PSO kinetic modelling results are summarized in Table 2 and Figure 6. Because both kinetic models are empirical rate laws, neither is, in isolation, evidence of a particular adsorption mechanism; PSO nonetheless localizes the rate-limiting step at the adsorption sites, while PFO localizes it at film diffusion within the bulk solution. For Fe-Copolymergel- $\text{NH}_2$ , the PSO model provided near-perfect fits ( $R^2 = 0.968$  for CR and  $R^2 = 0.999$  for MO) with calculated equilibrium capacities close to experiment ( $q_{\text{e,exp}} = 2870 \text{ mg g}^{-1}$  vs.  $q_{\text{e,cal}} = 2872 \text{ mg g}^{-1}$  for CR). Mechanistically, the highly porous and therefore interacting Fe-copolymergel- $\text{NH}_2$  reflects synergistic interactions, including electrostatic attraction between protonated  $-\text{NH}_3^+$  sites and anionic dye  $-\text{SO}_3^-$  groups, and inner sphere complexation occurring via added  $\text{Fe}^{3+}$  centers [40].

Table 2. PFO and PSO kinetic model parameters of CR and MO adsorption onto Fe- and Copolymergel- $\text{NH}_2$ .

| Adsorbents                          | Adsorbent Dosage (mg) | $q_{\text{e}} [\text{exp}]$ (mg/g) | PFO                                |        |        | PSO                                |                     |       |
|-------------------------------------|-----------------------|------------------------------------|------------------------------------|--------|--------|------------------------------------|---------------------|-------|
|                                     |                       |                                    | $q_{\text{e}} [\text{cal}]$ (mg/g) | $k_1$  | $R^2$  | $q_{\text{e}} [\text{cal}]$ (mg/g) | $k_2$ ( $10^{-5}$ ) | $R^2$ |
| Copolymergel- $\text{NH}_2$ (MO)    | 1                     | 995                                | 134,028                            | 0.011  | 0.395  | 258                                | 43.76               | 0.945 |
|                                     | 3                     | 875                                | 311.19                             | 0.012  | 0.968  | 403                                | 7.37                | 0.989 |
|                                     | 5                     | 914                                | 257.5                              | 0.010  | 0.874  | 353                                | 8.59                | 0.889 |
| Copolymergel- $\text{NH}_2$ (CR)    | 1                     | 219                                | -                                  | -0.009 | 0.050  | -                                  | 5.67                | 0.053 |
|                                     | 3                     | 121                                | -                                  | 0.001  | 0.261  | -                                  | 3.77                | 0.263 |
|                                     | 5                     | 92                                 | -                                  | 0.001  | 0.0215 | -                                  | 1.29                | 0.019 |
| Fe-Copolymergel- $\text{NH}_2$ (CR) | 1                     | 2870                               | 1958                               | 0.006  | 0.472  | 2872                               | 8.54                | 0.998 |
|                                     | 3                     | 2236                               | 1561                               | 0.007  | 0.809  | 1649                               | 4.87                | 0.991 |
|                                     | 5                     | 1586                               | 1454                               | 0.023  | 0.947  | 1800                               | 2.03                | 0.968 |
| Fe-Copolymergel- $\text{NH}_2$ (MO) | 1                     | 1059                               | 381                                | 0.021  | 0.74   | 1070                               | 19.25               | 0.999 |
|                                     | 3                     | 1025                               | 501                                | 0.033  | 0.911  | 1059                               | 17.12               | 0.999 |
|                                     | 5                     | 1040                               | 568                                | 0.036  | 0.96   | 1083                               | 15.07               | 0.999 |



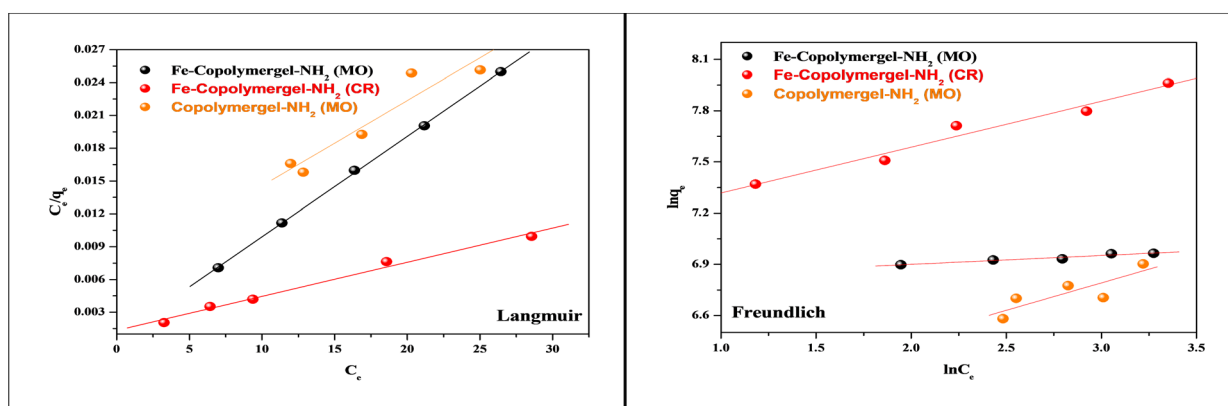
**Figure 6.** PFO and PSO kinetic models of MO and CR adsorption onto Fe- and Copolymergel-NH<sub>2</sub> at different doses.

In contrast, the low-porosity Copolymergel-NH<sub>2</sub> exhibited nonphysical compatibility, confirming the structural inadequacy of the unmodified matrix for effective dye uptake. The relatively low CR uptake of pure Copolymergel-NH<sub>2</sub>, despite a certain level of MO adsorption was due to the inability of CR molecules to penetrate the inner parts of the gel because of their larger molecular structure compared to MO, due to its low porosity, and the low level of interaction being solely due to surface interaction. The kinetic graphs in Figure 6 show well-defined linearity for the PSO model and a pronounced curvature for the PFO model, reinforcing that Fe-functionalization successfully establishes a robust chemisorption-driven mechanism.

### 3.6. Adsorption Isotherms

The Langmuir and the Freundlich isotherm plots for CR and MO are presented in Figure 7, and the parameters derived from these plots are summarized in Table 3. The higher  $R^2$  observed for the Langmuir model, particularly for the Fe-modified adsorbent, suggests that the adsorption process is primarily governed by monolayer coverage on a structurally homogeneous surface with a uniform distribution of active sites. Furthermore, the high  $n$  values obtained from the Freundlich model indicate strong, favorable adsorption intensity, confirming the energetic heterogeneity of the surface sites facilitated by the Fe<sup>3+</sup> modifications [41]. This alignment with the Langmuir isotherm underscores the prevalence of localized chemical interactions where dye molecules occupy specific, equivalent coordination centers. These results reflect a monolayer-type chemisorption process in which the saturation of these high-affinity Fe-based sites effectively restricts multilayer deposition. The findings demonstrate that the Fe-functionalized gel possesses one of the highest reported monolayer capacities for CR, with  $q_0$  reaching 3201.9 mg/g alongside  $K_L$  of 0.23 L/mg, and similarly elevated Langmuir parameters for MO. In contrast, the pristine Copolymergel-NH<sub>2</sub> yielded only a moderate MO fit and failed to converge for

CR, confirming the indispensable role of  $\text{Fe}^{3+}$  in establishing well-defined coordination sites. Parallel examination of the Freundlich constants corroborates this conclusion:  $K_F$  rose from 338.9 for the unmodified matrix to 894.6 for Fe-Copolymergel- $\text{NH}_2$  toward MO, and from a non-convergent value for CR to  $K_F = 1150.8$  with  $n = 3.72$  for the dye on the Fe-modified gel, where  $n > 1$  throughout signals spontaneous and energetically favorable sorption across both substrates [25]. Comparable trends in the energetic favorability of the adsorption process, as indicated by these intensity parameters, align with findings observed in similar metal-doped porous adsorbents such as CoMgAl-LDH and  $\alpha\text{-Mn}_2\text{O}_3$  architectures, where  $\text{Fe}^{3+}$ - or transition-metal-mediated coordinative anchoring dictates the partitioning of anionic contaminants [42,43]. Moreover, the Fe-Copolymergel- $\text{NH}_2$  exhibits a higher adsorption capacity for CR compared to MO, which is attributed to the larger molecular size of the CR molecule in conjunction with the high porosity of the Fe-Copolymergel- $\text{NH}_2$  matrix [44]. As summarized in Table 4, Copolymergel- $\text{NH}_2$  and Fe-Copolymergel- $\text{NH}_2$  exhibit superior CR and MO adsorption capacities compared to many previously reported adsorbents [44–59].



**Figure 7.** Langmuir and Freundlich isotherms for Fe- and Copolymergel- $\text{NH}_2$  adsorption of MB and MO at different doses.

**Table 3.** Langmuir and Freundlich adsorption isotherm parameters of Fe- and Copolymergel- $\text{NH}_2$ .

| Adsorbent        | Copolymergel- $\text{NH}_2$ |    | Fe-Copolymergel- $\text{NH}_2$ |        |
|------------------|-----------------------------|----|--------------------------------|--------|
|                  | MO                          | CR | MO                             | CR     |
| Langmuir Model   |                             |    |                                |        |
| $q_0$ (mg/g)     | 1281.6                      | -  | 1089.8                         | 3201.9 |
| $K_L$            | 0.12                        | -  | 1.25                           | 0.23   |
| $R^2$            | 0.90                        | -  | 0.999                          | 0.989  |
| Freundlich Model |                             |    |                                |        |
| $K_F$            | 338.9                       | -  | 894.6                          | 1150.8 |
| $n$              | 3.11                        | -  | 19.25                          | 3.72   |
| $R^2$            | 0.71                        | -  | 0.951                          | 0.968  |

**Table 4.** Adsorption capacities of CR and MO on different adsorbents.

| Adsorbents                | $q_{\max}$ (CR) (mg/g) | $q_{\max}$ (MO) (mg/g) | Ref. |
|---------------------------|------------------------|------------------------|------|
| $\text{CoFe}_2\text{O}_4$ | 162.68                 | 94.46                  | [44] |
| PMMA-Na-MT                | 355.5 mg/g             | -                      | [45] |
| EDA-PAN                   | 130                    | -                      | [46] |

Table 4. Cont.

| Adsorbents                      | q <sub>max</sub> (CR) (mg/g) | q <sub>max</sub> (MO) (mg/g) | Ref.       |
|---------------------------------|------------------------------|------------------------------|------------|
| PDA@PCL/PEO                     | -                            | 60.2                         | [47]       |
| PMMA/zeo                        | -                            | 95.33                        | [48]       |
| PVDF@CoAl-LDH                   | -                            | 621.17                       | [49]       |
| PAN-g-HPEI                      | -                            | 194                          | [50]       |
| PPy@PVDF/PDA                    | 384.6                        | -                            | [51]       |
| AOPAN                           | -                            | 68.07                        | [52]       |
| PHMG-OCS-PVA                    | 289                          | -                            | [53]       |
| MIEX resin                      | 254.58                       | 607.68                       | [54]       |
| Fe-Mg LDH                       | 894.17                       | 370.36                       | [55]       |
| CS-A nanofiber pads             | 1140.70                      | 505.31                       | [56]       |
| Chitosan/PVA/TiO <sub>2</sub>   | 131                          | 314                          | [57]       |
| cLDH                            | 584.56                       | 451.2                        | [58]       |
| GO-NiFe LDH                     | 450                          | 403                          | [59]       |
| Copolymergel-NH <sub>2</sub>    | -                            | 1281.6                       | This study |
| Fe-Copolymergel-NH <sub>2</sub> | 3201.9                       | 1089.8                       | This study |

### 3.7. Thermodynamic Studies

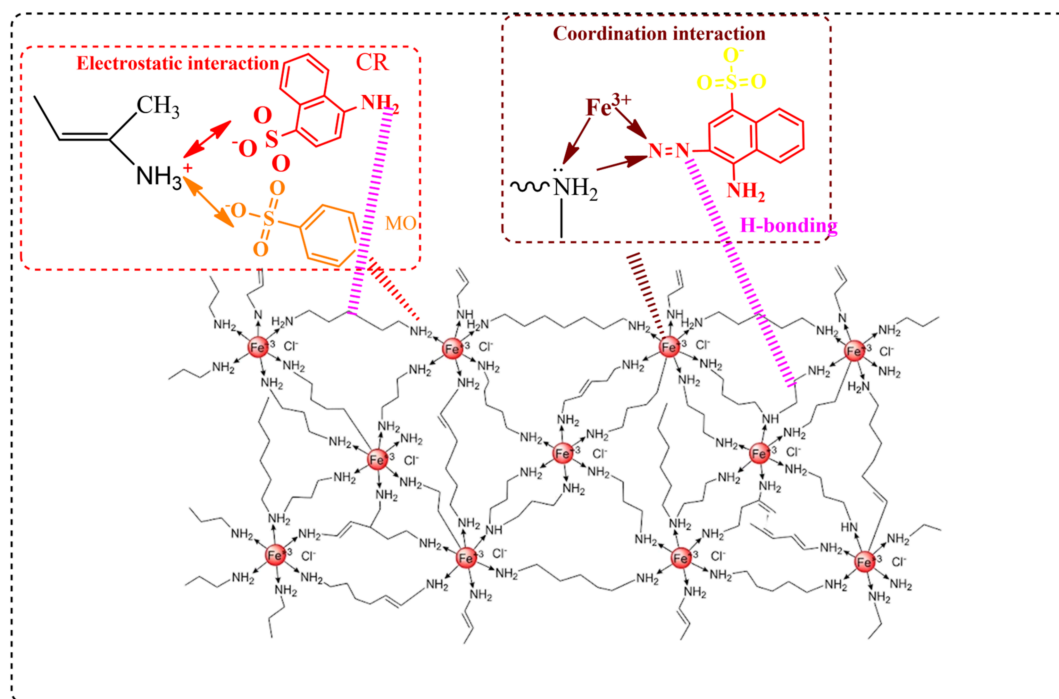
The thermodynamic parameters for the adsorption of CR and MO onto pristine Copolymergel-NH<sub>2</sub> and FeCl<sub>3</sub>-mediated Fe-Copolymergel-NH<sub>2</sub> are compiled in Table 5. These values reveal four distinct thermodynamic behaviors that clarify the impact of the Fe<sup>3+</sup>-amine coordination chemistry. For CR on the pristine Copolymergel-NH<sub>2</sub>,  $\Delta H^0 = +15.09 \text{ kJ mol}^{-1}$  and  $\Delta S^0 = +58.78 \text{ J mol}^{-1} \text{ K}^{-1}$  together drive an endothermic, entropy-controlled process in which the increasingly negative  $\Delta G^0$  values ( $-2.14$ ,  $-2.73$ ,  $-3.32$  and  $-3.91 \text{ kJ mol}^{-1}$  at 293, 303, 313 and 323 K, respectively) reflect the dominant contribution of the positive entropy term as temperature rises, consistent with the release of ordered hydration water molecules from the dye and polymer interface upon adsorption on a structurally under-activated, low-affinity matrix [60]. In contrast, the MO/Copolymergel-NH<sub>2</sub> system is exothermic and exhibits low entropy ( $\Delta H^0 = -1.50 \text{ kJ mol}^{-1}$ ,  $\Delta S^0 = -3.91 \text{ J mol}^{-1} \text{ K}^{-1}$ ). This confirms the unmodified matrix's limited capacity for MO adsorption. In contrast, Fe-Copolymergel-NH<sub>2</sub> exhibits a fundamental thermodynamic shift. CR adsorption becomes strongly exothermic ( $\Delta H^0 = -34.60 \text{ kJ mol}^{-1}$ ), with significantly lower  $\Delta G^0$  values ( $-11.29$  to  $-8.91 \text{ kJ mol}^{-1}$ ). Since  $|\Delta H^0| \gg |T\Delta S^0|$ , the rate-limiting step is governed by valence-strength bond formation; this is the electrostatic attraction between  $-\text{NH}_3^+$  and  $-\text{SO}_3^-$  groups, reinforced by the internal structure  $\text{Fe}^{3+} \leftarrow \text{:N}$  coordination [61]. A negative  $\Delta S^0 = -79.50 \text{ J/mol} \cdot \text{K}$  value indicates that the dye molecules have lost rotational and translational freedom within these coordination structures, consistent with results for similar metal-coordinated hydrogels [60,62].

MO adsorption on Fe-Copolymergel-NH<sub>2</sub> also shifts to an exothermic, enthalpy-controlled process ( $\Delta H^0 = -16.23 \text{ kJ mol}^{-1}$ ,  $\Delta S^0 = -22.67 \text{ J/molK}$ ). The systematically more negative  $\Delta G^0$  values demonstrate the effectiveness of the Fe<sup>3+</sup>-induced coordination. The smaller  $\Delta H^0$  value of MO compared to CR can be attributed to its smaller molecular size and lower charge density. Finally, the temperature dependence confirms that room temperature is optimal for adsorption on the Fe-modified gel, as predicted by the Gibbs–Helmholtz relation. Together, these thermodynamic signatures confirm that FeCl<sub>3</sub>-mediated coordination successfully establishes a high-affinity chemisorption mechanism, validating the structural and kinetic evidence presented in earlier sections. As shown in Figure 8, the uptake of CR and MO onto Fe-Copolymer Gel-NH<sub>2</sub> is governed by three synergistic interactions: electrostatic, coordination, and H-bonding interactions, which operate in parallel at the dative  $\text{Fe}^{3+} \leftarrow \text{:NH}_2$  coordination nodes placed during the FeCl<sub>3</sub>-catalyzed cross-linking step. In the electrostatic interaction, both CR and MO are dianionic azo dyes

bearing  $\text{SO}_3^-$  ends, and the protonated  $\text{NH}_3^+$  sites formed in the 2-AEMA segments below  $\text{pH\_PZC}$  7.22 provide a net positive surface charge [4]. Within the Fe-copolymer gel- $\text{NH}_2$  framework,  $\text{Fe}^{3+}$  centers doubly chelated by  $\text{NH}_2$  donors exhibit  $\text{Fe}^{3+} \leftarrow \text{:NH}_2$  coordination interactions. Unprotonated  $\text{NH}_2$  groups in the gel structure can donate  $\text{N-H}\cdots\text{N}$  H bonds to dye guests. CR's higher aromatic ring density and larger molecular footprint compared to MO may allow for stronger  $\pi$ - $\pi$  stacking and H-bonding with the polymer, supporting the systematically higher uptake of CR compared to MO.

**Table 5.** Thermodynamic parameters of CR and MO adsorption onto Fe- and Copolymergel- $\text{NH}_2$  at different temperatures.

| Copolymergel- $\text{NH}_2$    |                       |                       | $\Delta G^0$ (kJ/mol) |       |       |       |
|--------------------------------|-----------------------|-----------------------|-----------------------|-------|-------|-------|
| Dyes                           | $\Delta H^0$ (kJ/mol) | $\Delta S^0$ (J/Kmol) | 293 K                 | 303 K | 313 K | 323 K |
| CR                             | 15.09                 | 58.78                 | −2.14                 | −2.73 | −3.32 | −3.91 |
| MO                             | −1.5                  | −3.91                 | −0.35                 | −0.31 | −0.28 | −0.24 |
| Fe-Copolymergel- $\text{NH}_2$ |                       |                       | $\Delta G^0$ (kJ/mol) |       |       |       |
| Dyes                           | $\Delta H^0$ (kJ/mol) | $\Delta S^0$ (J/Kmol) | 293 K                 | 303 K | 313 K | 323 K |
| CR                             | −34.6                 | −79.5                 | −11.29                | −10.5 | −9.7  | −8.91 |
| MO                             | −16.23                | −22.67                | −9.58                 | −9.36 | −9.13 | −8.9  |



**Figure 8.** Proposed adsorption mechanism of CR and MO onto Fe-Copolymergel- $\text{NH}_2$ .

### 3.8. Reusability Studies

The reusability of Fe-Copolymergel- $\text{NH}_2$  is a crucial parameter for evaluating its industrial viability. To assess this, 3 mg of the adsorbent underwent CR adsorption, followed by regeneration with 0.1 M NaOH (10 min), centrifugation, and drying at 70 °C. Five successive adsorption–desorption cycles were performed, as shown in Figure S2. As illustrated in the bar graph, the material achieved near-quantitative initial CR removal. However, the capacity declined consistently across the five cycles, with removal percentages dropping to roughly 78%, 64%, 51%, and 38% in cycles 2 through 5, respectively.

This represents a consistent decrease of approximately 14–17 percentage points per cycle, resulting in ~40% residual activity by the fifth cycle. This disadvantageous performance degradation is attributed to alkali-induced leaching of  $\text{Fe}^{3+}$ - $\text{NH}_2$  coordination crosslinks formed during  $\text{FeCl}_3$ -mediated processing, progressive erosion of the mesoporous skeleton, and irreversible accumulation of CR residues at high-affinity  $\text{Fe}^{3+}$ -amine nodes.

#### 4. Conclusions

This study demonstrated that coordination crosslinking of copolymergel- $\text{NH}_2$ , containing primary amine groups, with  $\text{FeCl}_3$  produced a mesoporous adsorbent (Fe-Copolymergel- $\text{NH}_2$ ) with high affinity for anionic azo dyes, especially MO and CR. FTIR-ATR, XPS, and SEM-EDS confirmed the characterization of the copolymer gels.  $\text{FeCl}_3$  treatment resulted in a significant increase in the mesoporous properties and surface area (BET, from 8.11 to 12.55  $\text{m}^2 \text{g}^{-1}$ ) of Fe-Copolymergel- $\text{NH}_2$ . These structural changes led to Langmuir maximum capacities  $Q_0 = 3201.9 \text{ mg g}^{-1}$  and 1089.8  $\text{mg g}^{-1}$  for CR and MO in Fe-Copolymergel- $\text{NH}_2$ , respectively. Kinetic modeling revealed that Fe-Copolymergel- $\text{NH}_2$  exhibits PSO behavior governed by chemisorption of Copolymergel- $\text{NH}_2$ . Thermodynamically, the adsorption of CR and MO is exothermic, facilitating the spontaneous, self-initiated adsorption of Fe-Copolymergel- $\text{NH}_2$ . The reported findings demonstrate that the synthesized Fe-Copolymergel- $\text{NH}_2$ , with its improved pore structure, has significant potential as an effective adsorbent for the removal of anionic dyes such as CR and MO from textile wastewater.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/polym18151838/s1>, Figure S1: Swelling degree of Fe- and Copolymergel- $\text{NH}_2$  in water; Figure S2: Fe-Copolymergel- $\text{NH}_2$  CR reusability; Table S1: Elemental composition of Fe- and Copolymergel- $\text{NH}_2$  by XPS analysis; Table S2: SEM-EDS analysis of Fe- and Copolymergel- $\text{NH}_2$ .

**Author Contributions:** Conceptualization, A.T., Ş.G. and B.H.; methodology, A.T., Ş.G. and B.H.; software, A.T.; validation, A.T., Ş.G. and B.H.; formal analysis, A.T. and Ş.G.; investigation, A.T., Ş.G. and B.H.; resources, A.T.; data curation, A.T. and Ş.G.; writing—original draft preparation, A.T. and Ş.G.; writing—review and editing, A.T. and Ş.G.; visualization, A.T.; supervision, A.T. and B.H.; project administration, A.T. and B.H.; funding acquisition, A.T., Ş.G. and B.H. All authors have read and agreed to the published version of the manuscript.

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