Cross-Linked Nano-carboxymethylcellulose, Polyacrylamide, and g-Fe₂O₃-SO₃H to a Hydrophobic Linker: An Organic-Inorganic Hybrid Hydrogel for Dye Removal Adsorption

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Research Article

Keywords: nano-CMC, γ-Fe₂O₃-SO₃H, hydrophobic bis-acrylamide, pH-responsive magnetic hydrogel, methylene blue, adsorption removal

Posted Date: February 25th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1378097/v1>

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Abstract

The pH-responsive magnetic hydrogel bearing hydrophobic chlorophenyl implants was prepared by cross-linking the as-prepared nanocarboxymethylcellulose crystals (NCMCC), $\text{g-Fe}_2\text{O}_3\text{-SO}_3\text{H}$, and polyacrylamide (PAAmide) to the synthesized hydrophobic bis-amide $\text{N,N'-((4-chlorophenyl)methylene) diacrylamide}$ (NNCMDA). $\text{g-Fe}_2\text{O}_3\text{-SO}_3\text{H}$ was either the hydrogel magnetizing agent or the solid acid catalyst for linker synthesis. Carboxymethylation of the cotton-derived nanocellulose was modified to give the NCMCC that cross-linked to the $\text{g-Fe}_2\text{O}_3\text{-SO}_3\text{H}$, and PAAmide by NNCMDA to obtain the NCMCC/PAAmide/ $\text{g-Fe}_2\text{O}_3\text{-SO}_3\text{H}$ /NNCMDA hydrogel. After characterization of the hydrogel by FT-IR, FESEM, TGA, VSM, and XRD, the results of swelling experiments showed a decrease in water absorption and swelling but retained hydrophilic surface of the hydrogel by hosting the hydrophobic cross-linker NNCMDA. Hydrogel revealed good adsorptive dye removal with selectivity to cationic ones, so its adsorption capacity for Methylene blue (MB) and Rhodamine B (RB) were 717.0 mg/g and 61.0 mg/g, respectively. Simultaneous entering of hydrophobic NNCMDA implants and pH-responsive magnetizing agent $\text{g-Fe}_2\text{O}_3\text{-SO}_3\text{H}$ increased the performance of the hydrogel to remove the 74.68% MB and 50.85% RB without matrix change after the fifth recycling run. All results confirmed that NCMCC/PAAmide/ $\text{g-Fe}_2\text{O}_3\text{-SO}_3\text{H}$ /NNCMDA hydrogel is an effective adsorbent for the dye removal from wastewater.

1 Introduction

Due to the serious environmental issues of non-biodegradable organic dyes discharged in hydrosphere by textiles, leather, paper, plastic, food, detergent, polymer, and cosmetic industries [1, 2], various adsorption, oxidation, membrane-filtration, coagulation, and biological methods have been developed for the water-treatment by dye removal [4, 5]. Adsorption is among the most user-friendly removal methods with the advantages of minimal sludge production and simple adsorbent design [6, 7]. Owing to the addition of removal performance to the adsorbent capacity per dye pollutant [8], sorbent tuning is a key object in water-treatment by adsorptive removal.

Hydrogels are three-dimensional hydrophilic networks with high water adsorption capacity [10] that cross-linking increases their mechanical strength, water insolubility, synergistic effects, and performance [11]. The excellent water adsorption and swelling of hydrogels make them promising candidates as food-additives [14], drug-delivers [15], biomedical implants [17], cellular recognition sensors [19], contact lenses [20], wound-dressings [21], and super-absorbents [22]. Despite the wide use of hydrogels in water treatments, high cost, non-adherence, low strength, difficult separation, sterilization limits, and also selectivity for pollutant adsorption versus to huge amount of water are issues. Of the three-dimensional hydrogels, the cross-linked hydrophilic micro/nano cellulose-derivatives to the polyvinylalcohol, polyethyleneglycol, or polyacrylates [23, 24] are advantageous super-absorbents with enormous hydrophilic groups, high swelling/de-swelling ability, biocompatibility, and adjustable physiochemical properties [24]. Carboxymethyl cellulose (CMC) is a high reinforce, surface active, and adhesive cellulose derivative interacted to the in situ polymerized or bulk poly-acrylates and cross-linkers to give hydrogels

[25–27]. Cross-linking of CMC to the synthetic polymers and magnetic nanoparticles (MNPs) has been developed for intelligence hydrogels to the external magnetic field [9, 28]. Recently nano-CMC (NCMC), with the higher surface area and diffusion power than CMC, has cross-linked to the chitosan and alginate in a magnetic hydrogel for drug delivery [29]. However, being the polar negatively-charged COO^- or pH-responsive COOH groups on NCMC makes it smart adsorbent that its high water-solubility can be improved by cross-linking to a hydrophobic linker in a network.

Polyacrylamide (PAAmide) is a sterilize-able synthetic polymer, with excellent water absorptivity, for preparing the hydrogels applied in cell-adhesives, ophthalmic operations, drug delivery, food packing, and also water-treatments [9, 25]. PAAmide contributes in hydrogel matrixes by either the in situ polymerized acrylamide [30] or the native polymer [31, 32]. Accordingly, the magnetic PAAmide-chitosan microspheres [33], PPAamide-composites [34], and PAAmide-CMC hydrogels [9, 25] have been used for adsorptive removal of the cationic dyes and heavy metal ions from the wastewater. However, fabrication of a new magnetically separable hydrogel from PAAmide and NCMC crystals (NCMCC) is highly anticipated.

Due to the critical role of cross-linker to bind the hydrogel's components in three dimensional networks [32], the *N,N*-methylene bis-acrylamide and radical initiator ammonium per-sulfate (APS) were co-operatively applied for free-radical cross-linking of a Fe_3O_4 -based hydrogel [35]. However, hydrophobic reinforced bis-acrylamides are awaited cross-linkers to protect the hydrogels in swelling/de-swelling processes.

Magnetization of hydrogels by magnetic nanoparticles (MNPs) of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ makes them simply separable and increases their reusability impacts [15]. Therefore, magnetic hydrogels [36] and especially CMC/nano Fe_3O_4 -based hydrogels have been developed for various purposes [3]. Because of the instability of nano Fe_3O_4 phase by possible oxidation of the surface Fe^{2+} ions [37, 38], the more stable $\gamma\text{-Fe}_2\text{O}_3$ phases [39] or pH-sensitive polar $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H}$ are much reliable magnetizing agents for hydrogels. The $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H}$, prepared by functionalization of $\gamma\text{-Fe}_2\text{O}_3$ with chloro-sulfonic acid, is a reusable solid acid catalyst for some organic transformations [37, 40]. However, magnetization of hydrogels by $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H}$ MNPs can be resulted to the pH-smartness hydrogels with easy magnetically separation.

The objects of this work were dual applying the $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H}$ MNPs as the hydrogel magnetizing agent and the solid acid catalyst for synthesis of the hydrophobic cross-linker *N,N'*-((4-chlorophenyl)methylene) di-acrylamide (NNCMDA). The second aim was converting the cotton-derived nanocellulose crystals (NCC) to the nano-CMC crystals (NCMCC) bearing sensitive- COOH groups and link affinity to the $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H}$ and polyacrylamide. The latter step was cross-linking the $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H}$ MNPs, NCMCC, and PAAmide to the hydrophobic bisacrylamide NNCMDA by radical initiator APS to give the magnetic hydrogel $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H/NCMCC/PAAmide/NNCMDA}$. After characterization, the swelling changes, surface hydrophobicity, and efficiency of this newly prepared hydrogel for adsorptive removal of five cationic, anionic, and neutral organic dyes from wastewater were validated.

2 Materials And Methods

2.1 Materials

Nanocellulose crystals (NCCs) were from the cotton (Dima Co. Mybood-Yazd-Iran) following a previous experience [41] were converted to the NCMCC by carboxymethylation with the in situ formed sodium chloroacetate from the chloro-acetic acid and sodium carbonate. Cross-linker was synthesized based on our previous experience [42] using γ -Fe₂O₃-SO₃H as catalyst, while PAAmide, FeCl₃·6H₂O, FeCl₂·4H₂O, 4-chlorobenzaldehyde, APS, solvents, and all other chemicals were purchased in analytical grade from the Merck Company (Germany).

2.2 Measurement and characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer in the range of 4000 – 400 cm⁻¹ using KBr discs. The surface morphologies of the dried hydrogel and its components were studied by field emission scanning electron microscopy (FESEM) images (TESCAN-MIRA III). Thermo gravimetric analyses (TGAs) were performed by a thermo gravimetric analyzer TA Q600 in the temperature ranging 25–600°C under an air atmosphere at a heating rate of 20°C/min. The magnetic properties of the fabricated hydrogel were analyzed by Vibrating-sample magnetometer (VSM) model Lake Shore Cryotronics 7407. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra of the cross-linker were recorded in DMSO-*d*₆ using a 500 MHz NMR spectrometer (Bruker). Dye concentration was determined by measuring absorbance at λ_{max} of each dye using a UV-Vis spectrometer (AvaSpec-2048).

2.3 Preparation of the hydrogel NCMCC/PAAmide/ γ -Fe₂O₃-SO₃H/NNCMA

The hydrogel was prepared by one-pot free-radical cross-linking of the gemini bisamide NNCMA and APS with the native PAAmide and the as-prepared components in the following steps.

2.3.1 Preparation of nano-cellulose crystals (NCC)[41]

To prepare the NCC, the cotton-derived micro-cellulose (MC) (2 g) was added to the sulfuric acid solution (35% v/v, 20 mL) and stirred at 50°C for 3 h. Then, ice water was added to stop the reaction, and the NCCs were collected after repeating the centrifugation and decantation of the aqueous phase for three times.

2.3.2 Conversion of NCC to nano-carboxymethyl cellulose crystals (NCMCC)

Firstly, alkalization pretreatment was performed by vigorously stirring of NCC (2 g) in a 250 mL flask containing 2-propanol (50 mL) and addition of aqueous NaOH (25 mL, 20% w/v) at 20°C. After 2 h stirring, etherification of alkaline NCC was done by adding sodium monochloroacetate (SMCA) (4.3 g), stirring the mixture at 80°C for 4 h, and filtering the solid product. Aqueous methanol (100 mL) and acetic

acid were then added to neutralize the NCMCC (pH 6–8), which was then filtered, washed three times with aqueous ethanol, and dried at 40°C for 24 h. The degree of substitution (DS) for the prepared NCMCC was determined by conductometric titration method as 0.78 and more than the previously reported method for the NCMC fibers [29].

2.3.3 Preparation of the γ -Fe₂O₃-SO₃H nanoparticles

γ -Fe₂O₃-SO₃H MNPs was prepared following a modified version of the previous method [40]. Briefly, the γ -Fe₂O₃ prepared by our previous co-precipitation method [41] was collected using a magnet, washed several times with distilled water, and dried in oven 70°C. Then, chlorosulfonic acid (0.14 mL) was added drop wise to γ -Fe₂O₃ (0.6 g) under solvent-free conditions, the mixture was stirred at room temperature for 30 min, the brownish solid was collected on the flask wall, washed with EtOH, and dried at 70°C for 2 h.

2.3.4 Synthesis of cross-linker N,N'-((4-chlorophenyl)methylene)bisacrylamide (NNCMDA)

γ -Fe₂O₃-SO₃H (60 mg) as a solid acid catalyst was added to a mixture of 4-chlorobenzaldehyde (2 mmol) and acrylamide (4 mmol), and the resulting mixture was stirred at 80°C for 20 min. After completion of the reaction (TLC monitoring), hot acetone (10 mL) was added, γ -Fe₂O₃-SO₃H separated by an external magnet, and the precipitated product after the addition of ice water was filtered. The physicochemical and spectral data containing melting point, FT-IR, ¹H NMR, and ¹³C NMR [42] confirmed the structure of the given cross-linker by new method.

2.3.5 Cross-linking of NCMCC, PAAmide, and γ -Fe₂O₃-SO₃H by NNCMDA to give hydrogel

To prepare the hydrogel NCMCC/PAAmide/ γ -Fe₂O₃-SO₃H/NNCMDA, NCMCC (2.0 g), PAAmide (0.5 g), and Fe₂O₃-SO₃H (0.5 g) were added to a flask containing H₂O (50 mL) and the mixture was homogenized by 30 min stirring. The flask was placed in an 80°C water bath, the solution of cross-linker NNCMDA (0.05 g) in NaOH (5 mL, 5% w/v) was added, then the APS solution in water (0.1 g in 5 mL) added drop-wise into the mixture and vigorously stirred for 2 h. The hydrogel was precipitated immediately as a dark brown solid and collected by an external magnet, washed with deionized water three times, and dried at 70°C for 24 h. The schematic procedure for the preparation of NCMCC/PAAmide/ γ -Fe₂O₃-SO₃H/NNCMDA hydrogel is illustrated in Scheme 1.

2.4 Hydrogel hydrophobicity and swelling

To determine the surface hydrophobicity, affinity of the hydrogel to water and octane as a hydrophobe solvent was evaluated at 25°C and 40°C by immersing the NCMCC/PAAmide/ γ -Fe₂O₃-SO₃H/NNCMDA powder (0.2 g) in excess deionized water or octane (200 mL) and stirring for 2 h. Then hydrogel was separated, extra solvent was removed, and weighted. For accuracy, experiments were repeated for the three times.

For swelling test, solid NCMCC/PAAmide/ γ -Fe₂O₃-SO₃H/NNCMA (0.2 g) was immersed in excess deionized water (200 mL) at room temperature and allowed to swell by stirring for 2 h. After equilibrium, extra water was removed from the separated hydrogel by an external magnet and weighted in triplicate experiments at room temperature. The swelling capacity was then calculated based on the Eq. (1):

$$\text{Swelling capacity (SC)} = (W_s - W_{\text{dry}}) / W_{\text{dry}} \quad (1)$$

where W_{dry} and W_s are the dried and swelled hydrogel weights after the t time.

2.5. Dye adsorption experiments

The adsorption proficiency of the prepared hydrogel was evaluated for the two different cationic dyes (Methylene blue (MB) and Rhodamine B (RB)), two anionic dyes (Eriochrome black T (EBT) and Methyl orange (MO)), and a neutral dye (Methyl red (MR)). Typically, the hydrogel (50 mg) was immersed into the 30 mL of each stirring dye solution (200 mg/L, except for MB (200–1800 mg/L)) at different pHs. After approximately 2 h contact time to reach equilibrium, the magnetic hydrogel was removed, and the dye concentration was determined by measuring supernatant absorbance at λ_{max} of each dye using a UV–Vis spectrophotometer.

The equilibrium adsorption capacity (Q_e , mg/g) of the hydrogel was calculated based on the changes in dye concentration before and after adsorption, according to Eq. (2):

$$Q_e = \frac{(C_0 - C_e)V}{m}$$

2
The removal percentage of dyes was also calculated from Eq. (3):

$$\text{Removal\%} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3)$$

where C_0 (mg/L) and C_e (mg/L) are dye concentrations at the initial time and equilibrium point, respectively, V (L) is the dye solution volume, and m (g) is the dried hydrogel weight.

2.5.1 Hydrogel performance for MB adsorption

To investigate the superiority of the prepared hydrogel, MB as a cationic dye was selected and the hydrogel adsorption capacity for MB was determined at various pHs. The selectivity of the MB adsorption was also investigated in the MB/MR mixture at different pHs, and the decreased dye concentration in the mixture was evaluated at λ_{max} of each dye.

2.5.2 Desorption experiments

For the desorption test, the MB-adsorbed hydrogel was magnetically separated from the solution after reaching the equilibrium and the dye concentration in the supernatant was measured. Reusability of the hydrogel was investigated by its recycling through 5 separate MB sorption-desorption cycles by adding desorbing agent EtOH to the hydrogel-adsorbed dye, stirring the mixture, magnetically separation and rinsing the hydrogel by DI water, and freeze-drying for the further adsorption experiment. In a typical experiment, 50 mL of an aqueous dye solution was mixed with 50 mg of hydrogel powder and stirred magnetically for 2 h at room temperature. Then the adsorbed MB was eluted from the hydrogel by EtOH addition (10 mL) and the collected hydrogel by magnet was prepared for the subsequent sorption experiment.

3 Results And Discussion

3.1 Hydrogel preparation

The three-step strategy for the preparation of hydrogel NCMCC/PAAmide/ γ -Fe₂O₃-SO₃H/NNCMA is illustrated in Scheme 1. In the first step, γ -Fe₂O₃-SO₃H MNPs were prepared and used as either a solid Bronsted acid catalyst in the one-pot synthesis of the cross-linker NNCMA or as the hydrogel magnetizing agent. Secondly, NCMCC with DS = 0.78 was prepared from the cotton-derived nanocellulose crystals (NCC) and sodium chloroacetate. The NCMCC, PAAmide, and γ -Fe₂O₃-SO₃H were cross-linked by free-radical reaction of the as-prepared NNCMA and the in situ released sulfate anion radical from APS decomposition. During the cross-linking, the double vinyl groups of NNCMA act as the covalently bonding sites to either the NH₂ ends of PAAmide or OHs of NCMCC, although additional hydrogen-bonding between the -SO₃H, -OH, CONH₂, and -COOH groups finalized the cross-linking of hydrogel (Scheme1).

3.2 Characterization of hydrogel and its components

Figure 2 shows the overlaid FT-IR spectra of the NCMCC, PAAmide, γ -Fe₂O₃-SO₃H, cross-linker NNCMA, and hydrogel. In NCMCC spectrum, the vibrational modes observed at 3419 cm⁻¹, 2921 cm⁻¹, 1601 cm⁻¹, and 1063 cm⁻¹ were attributed to the O-H, C-H, C = O, and C-O stretching. In the γ -Fe₂O₃-SO₃H spectrum, acidic OH stretching, asymmetrical and symmetrical stretching of O = S = O, and the lattice Fe/O stretching are characteristic vibrational absorptions observed at 3000–3300 cm⁻¹, 1350 – 1100 cm⁻¹, and 625 cm⁻¹, respectively. For the cross-linker NNCMA, the peaks observed at 3275 cm⁻¹, 1669 cm⁻¹, 1626 cm⁻¹, 1559 – 1411 cm⁻¹, and 1087 cm⁻¹ were assigned to the NH stretching, amide -C = O stretching, aromatic ring skeletal bands, overlapped NH-bending with the vinyl C = C stretching, and C-N groups. In the FT-IR spectrum of PAAmide, peaks at 3427 cm⁻¹, 1619 cm⁻¹, 1385 cm⁻¹, and 1002 cm⁻¹ are related to the N-H stretching, C = O stretching, NH-bending, and C-N stretching, respectively. The appearance of the vibrational absorption bands at 625 cm⁻¹, 1411 cm⁻¹, 1326 cm⁻¹, 1668 cm⁻¹, and 3000–3300 cm⁻¹ due to the Fe/O, SO₃, para substituted aromatic ring, carboxamide, carboxylate, and

overlapped acidic OH/amide-NH groups in the FT-IR spectrum of the hydrogel are evidences for the entering the NCMCC, PAAmide, $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H}$, and NNCMDA in the hydrogel matrix.

Due to the critical role of surface morphology in the adsorption behavior of hydrogel, FESEMs of the NCMCC gel, PAAmide gel, and hydrogel were compared in Figs. 2A-C.

Based on the FESEM images, NCMCC gel has a regular distribution of rump wrinkles in surface, gel of PAAmide has a cracked and wrinkled surface with the rugged-shape particles (Fig. 2C), and the hydrogel NCMCC/PAAmide/ $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H}$ /NNCMDA has a different morphology with densely distributed uniform granular particles. These changes in surface morphology can be attributed to the linking of the agglomerated $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H}$ MNPs to the densely cross-linked NCMCC/PAAmide by hydrophobic NNCMDA implants and also hydrogen bonding interactions between hydrogel functional groups. These overall changes led to a granular surface for hydrogel to facilitate the pollutant adsorption during the water-treatment. Based on the histogram of size distribution of particles in Fig. 2D, the hydrogel has granular particles with average diameters in 15 nm-50 nm.

With no hysteresis loop, the magnetization saturation (M_s) of the hydrogel was 14.58 emu/g, lower than $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H}$ (28.00 emu/g) and $\gamma\text{-Fe}_2\text{O}_3$ (60.02 emu/g) [41]. Such decrease in M_s of hydrogel is due to the coating of the $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H}$ MNPs by the non-magnetic matrix hydrogel.

The comparative XRD patterns of $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H}$, NCMCC, and hydrogel in Fig. 3 (left) show similarity between the reflection phases of the hydrogel and its components at most 2θ s, although a little broadening in all XRD peaks of hydrogel indicate the little influence of cross-linking on the crystalline phases of the $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H}$ and NCMCC as hydrogel's components.

Comparative TGA curves of the components and hydrogel exhibits higher thermal stability and less weight loss of hydrogel than NCMCC and PAAmide in the temperature range 30–600°C, presumably due to the $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H}$ animation and cross-linking of hydrogel matrix in a three-dimensional network. Besides, the two degradation stages with 14% and 16% weight loss at $\sim 250^\circ\text{C}$ and $\sim 450^\circ\text{C}$ for the hydrogel are due to the water and SO_3H removing, and further decomposition of NCMCC/PAAmide polymer chains (Fig. 3 (right)).

3.3 Hydrogel swelling and dye adsorption

3.3.1 Swelling of hydrogel

Due to the hosting of hydrophobic cross-linker NNCMDA in the hydrogel matrix, its sympathy to water and octane as a hydrophobic solvent was evaluated at 25°C and 40°C (Table 1).

Table 1
Hydrogel swelling capacity (SC) in water and octane at 25 °C and 40 °C.

Entry	Temp. (°C)	SC in Water	SC in Octane	Water/Octane adsorption ratio
1	25	54.45	0.003	18150
2	40	75.05	0.005	14010

The very little swelling capacity of hydrogel in octane and SC = 50–75 in water at 25°C and 40°C indicated no added hydrophobic properties of hydrogel by entering the hydrophobic cross-linker NNCMDA in hydrogel matrix. By performing the swelling experiment via the immersing of NCMCC/PAAmide/ γ -Fe₂O₃-SO₃H/NNCMDA in excess deionized water and following the Eq. 1, the swelling capacity of hydrogel calculated as 54.45. Comparison of this amount with the swelling capacity ~150 for a similar hydrogel bearing a higher hydrophilic linker [26] shows the impact of hydrophobic cross-linker NNCMDA to reduce the hydrogel swelling in water.

3.3.2 Comparative adsorption of cationic, anionic, and neutral dyes

To evaluate the efficiency of the prepared hydrogel NCMCC/PAAmide/ γ -Fe₂O₃-SO₃H/NNCMDA for dye sorption, adsorption experiments were performed for MB, RB, EBT, MO, and MR as cationic, anionic, and neutral dyes (Fig. 4). At first, based on the dye concentration changes before and after adsorption, the equilibrium adsorption capacity (Q_e , mg/g) of the hydrogel for all five dyes at neutral pH = 7 was calculated according to Eq. (2) and compared in Fig. 4A. Then the removal percent of dyes at this pH were specified following Eq. (3) as 61.97%, 50.85%, 40.66%, 26.67%, and 12.5% for MB, RB, EBT, MO, and MR, respectively, although removal% for MB enhanced to 74.68% at pH = 9 in further experiments.

Consistent with the given data, at pH = 7, hydrogel adsorbed anionic dyes EBT and MO with the adsorption capacities of 50 mg/g and 32 mg/g that are higher than 15 mg/g for the neutral dye MR. The Q_e for the two cationic dyes MB and RB were 595 mg/g and 61 mg/g. The hydrogel performance for dye sorption with the order of MB > RB > EBT > MO >> MR reveals much hydrogel attraction to the charged ionic dyes (especially cationic dyes) versus the neutral MR in which dye adsorbed by only hydrogen-bonding. Correspondingly, the trend of adsorption capacity order cationic > anionic > neutral dyes directs us to its higher affinity for selective adsorption of cationic dyes versus the other ones. Generally, surface pores, hydrogen-bonding, and the abundant of polar functional groups including -OH, -COOH, -SO₃H, and -CONH₂ are responsible for diffusion and adsorption of dyes into this hydrogel matrix. The higher Q_e of hydrogel toward MB is due to the strong electrostatic interactions between MB and the deprotonated anionic groups of -SO₃⁻ and -COO⁻ in the hydrogel surface at pH 7. Due to the highest Q_e of hydrogel for MB adsorbing, further studies were followed by this cationic dye, which is used in printing, food, textiles, plastic, wood, and paper industries as well as methemoglobinemia treatment [43]. It is notable that >15%

remaining of this non-biodegradable pollutant in industrial wastewaters leads to the serious environmental problems [44, 45].

3.3.2.1 Effect of initial MB concentration on adsorption capacity of the hydrogel

Evaluation of the effect of initial MB concentration (from 200 ppm to 1800 ppm) on the adsorption capacity of hydrogel displays Q_e growth by the initial MB concentration increasing (Fig. 4B), although more escalation in the MB concentration beyond 1600 mg/L was not effective. This manner is due to the higher availability of dye molecules in the locality of the adsorbent at MB concentrations lower than 1600 mg/L and saturation of the hydrogel adsorption sites by MB molecules at higher concentrations than 1600 mg/L.

3.3.2.2 Effect of contact time on the hydrogel adsorption capacity for MB

Figure 5C shows the effect of contact time from 0-200 min on the efficiency of the hydrogel for MB removal. Based on the results, the Q_e of hydrogel increased by the increase in the contact time with MB, although through a fast slope during the first 60 min and with a slow slope at equilibrium point and > 120 min contact time. The enhancement of Q_e in the first slope is due to the available vacant sites of hydrogel to accommodate the dye molecules by electrostatic cationic-anionic interactions. At the equilibrium state, the hydrogel's anionic sites were occupied by the cationic MB molecules and mass transfer of the pollutant to the adsorbent is possible by only hydrogen-bonding.

3.3.2.3 The pH effect on MB adsorption capacity

Figure 4D demonstrates the pH effect (varied from 2 to 12) on the adsorption performance (Q_e) of the NCMCC/PAAmide/ γ -Fe₂O₃-SO₃H/NNCMA hydrogel. While the results reveal a gradual increase in Q_e of hydrogel to adsorb MB by pH rising, the maximum 717 mg/g adsorption capacity of hydrogel for MB sorption occurs at pH = 9. This trends is due to the pH-sensitivity of hydrogel, neutral surface charge by protonated -OH, -SO₃H, and -COOH groups at high acidic pHs, competition of H⁺ with the MB cations, and dye adsorption by the only hydrogen-bonding. By pH increasing to 7 and 9, the hydrogel takes a negatively charged surface with the -SO₃⁻ and -COO⁻ groups that facilitate higher MB adsorption by strong electrostatic cationic-anionic interactions besides to hydrogen-bonding (Scheme 1, last picture).

3.3.2.4 Kinetic study of the MB adsorption on hydrogel

As shown in Fig. 5C, the amount of adsorbed MB increased by time elongation and reached to equilibrium within 1.5 h. To investigate the kinetics of MB adsorption by hydrogel, pseudo-first- and pseudo-second-order models were applied [46]. The pseudo-first order model expressed by the following Eq. (4):

$$\ln(Q_e - Q_t) = \ln Q_{e1} - k_1 t \quad (4)$$

where Q_e and Q_t (mg/g) are the MB adsorbed by hydrogel at equilibrium and t time (min), respectively. The theoretical amount of adsorbed MB at equilibrium (Q_{e1} (mg/g)) and the rate constant (k^1 (min^{-1})) were calculated from the intercept and slope of a plot of $\ln(Q_e - Q_t)$ versus t , respectively. The applied pseudo-second-order model was Eq. (5):

$$t/Q_t = 1/k_2 Q_{e2}^2 + t/Q_{e2} \quad (5)$$

where k_2 (g/mg h) is the rate constant of the pseudo-second-order model, and Q_{e2} (mg/g) is the theoretical adsorption calculated from the plot of t/Q_t versus t . The honest lines with high correlation coefficients ($r^2 = 0.99$) for the MB adsorption by hydrogel was well fitted with the pseudo-second-order model (Fig. 5A and B).

3.3.2.5 Isotherms of MB adsorption on the hydrogel

To examine the dye concentration effect on MB adsorption by hydrogel, adsorption experiments were conducted by changing the dye concentrations from 200 to 2000 mg/L. The adsorption capacity of hydrogel for MB increased by the increasing in concentrations and reached an equilibrium at a concentration more than 1600 mg/L. The MB adsorption data were analyzed by Langmuir and Freundlich models (Fig. 5C and D). The Langmuir equation and Freundlich model were applied by equations 6 and 7 [46]:

$$C_e/Q_e = C_e/Q_m + 1/Q_m^b \quad (6)$$

where C_e (mg/L) is the equilibrium dye concentration in solution; Q_e (mg/g) is the adsorbed dye at equilibrium; Q_m (mg/g) is the theoretical maximum adsorption capacity; and b (L/mg) is the Langmuir constant.

$$\log Q_e = \log k_f + 1/n \log C_e \quad (7)$$

where k_f (mg/g) and n are the adsorption capacity and the adsorption intensity Freundlich constants.

The correlation coefficient values (r^2) for MB adsorption by hydrogel in the Langmuir model and Freundlich models were 0.99 and 0.94, respectively. This results takes the best correlation of the kinetic model to the Langmuir and monolayer adsorption isotherm.

3.3.2.6 Performance of hydrogel for MB adsorption

To show the hydrogel performance, its adsorption capacity (Q_e) for MB adsorption, initial concentration (IC), sorbent dosage, and pH was compared with some corresponding reported adsorbents [3, 9, 12, 13, 16, 18] (Fig. 6A). The results indicate the advanced adsorption capacity of the as-prepared hydrogel for

MB removal and thus its high adsorbent performance for the water-treatments by efficient adsorption removal.

3.3.2.7 MB desorption and reusability tests

Due to the eco-environmentally importance of the sorbent in practical water treatments, five times desorption-adsorption rounds were performed for MB sorption by hydrogel at room temperature and pH = 9 by ethanol washing the hydrogel. The only 4.75% decrease in efficiency of the recycled hydrogel after the fifth round revealed the reusability of the hydrogel for MB removal, although no significant changes in FT-IR and FESEM of the regenerated NCMCC/PAAmide/ γ -Fe₂O₃-SO₃H/NNCMA described no structural change for this new adsorbent after reusing (Fig. 6B-D).

Moreover, the advantages of this hydrogel than our previously reported nano-alkaline cellulose carboxylates for MB adsorption [45] are easy magnetically separation, simple reusing, and 50% lower decrease in adsorption capacity of hydrogel adsorbent after five round adsorption-desorption processes.

4 Conclusion

In this study, NCMCC was prepared by carboxymethyl etherification of NCC, the hydrophobic cross-linker NNCMA synthesized using solid acid catalyst γ -Fe₂O₃-SO₃H that is also hydrogel magnetizing agent, and hydrogel NCMCC/PAAmide/ γ -Fe₂O₃-SO₃H/NNCMA was prepared by cross-linking of the components in a three-dimensional network. Structural analysis of hydrogel showed characteristic FT-IR vibrational modes, granular shape particles in the range of 15–41 nm, similar crystallinity with γ -Fe₂O₃-SO₃H, magnetization saturation 14.58 emu/g, and thermal stability. This hydrogel exhibited different swelling and adsorption properties for the cationic, anionic, and neutral dyes as well as selectivity for cationic dyes, so this hydrogel shows a remarkable performance to adsorb MB with a high adsorption capacity. We developed herein a smart pH-sensitive and three-dimensional hydrogel to adsorb all types of organic dye contaminants and selective adsorption of methylene blue (MB) as a cationic dye. Multi-active sites, biocompatibility, magnetically separation, versatility for removing of various dye-pollutants, and high selectivity for MB removal by altering the pH are advantages of this hydrogel.

Declarations

Acknowledgments We gratefully thank the Yazd University Research Council for some financial support.

Author contributions Fatemeh Tamaddon: Conceptualization, supervision, validation, project administration. Ehsan Ahmadi-AhmadAbadi: Methodology, investigation, validation, formal analysis, software, and visualization. Ehsan Khoje-neamah: Synthesis of cross-linker.

Funding There is no financial sources funding regarding of this study.

Conflict of interest Authors declare that they have no competing interests and non-financial competing interests.

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Figures

Figure 1

FT-IR spectra of NCMCC, g-Fe₂O₃-SO₃H, NNCMDA, PAAmide, and hydrogel.

Figure 2

FESEM images of NCMCC gel (A), PAAmide gel (B), and hydrogel in 100 nm resolution (C), and histogram of particle size distribution of hydrogel.

Figure 3

XRD patterns of $\gamma\text{-Fe}_2\text{O}_3\text{-SO}_3\text{H}$, MNCMC, and hydrogel (left), TGA curves of PAAmide, MNCMC, and hydrogel (right).

Eriochrome black T, MW: 1058.01, λ_{max} = 527 nm

Rhodamine B, MW: 443.56, λ_{max} = 557 nm

Methyl orange, MW: 596.63, λ_{max} = 463 nm

Methylene blue, MW: 319.85, λ_{max} = 664 nm

Methyl red, MW: 269.30, λ_{max} = 443 nm

Figure 4

Structure and properties of the organic dyes. Dye adsorption capacities of the prepared hydrogel to various dyes (A), effect of initial dye concentration (B), contact time (C), and pH (D) MB adsorption capacity.

Figure 5

Kinetics and isotherms of MB adsorption on hydrogel

Figure 6

Performance of the hydrogel based on the adsorption capacity for MB (A). MB adsorption-desorption cycles and hydrogel reusability tests (B); FT-IR (C) and FESEM (D) analyses for the recovered hydrogel after the fifth round.

Supplementary Files

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- [Scheme1.png](#)