Application of New Sodium Vinyl Sulfonate–co-2-Acrylamido-2-methylpropane Sulfonic Acid Sodium Salt-Magnetite Cryogel Nanocomposites for Fast Methylene Blue Removal from Industrial Waste Water

Sami A. Al-Hussain 1, Ayman M. Atta 2,*, Hamad A. Al-Lohedan 2, Abdelrahman O. Ezzat 2 and Ahmed M. Tawfeek 2

1 Department of Chemistry, Faculty of Science, Al Imam Mohammad Ibn Saud Islamic University (IMSIU), Riyadh 11451, Saudi Arabia; sahussain@imamu.edu.sa
2 Surfactants Research Chair, Chemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia; hlohedan@ksu.edu.sa (H.A.A.-L.); ao_ezzat@yahoo.com (A.O.E.); atawfik@ksu.edu.sa (A.M.T.)

* Correspondence: aatta@ksu.edu.sa; Tel.: +966-056-155-7975

Received: 27 September 2018; Accepted: 24 October 2018; Published: 25 October 2018

Abstract: Inorganic nanoparticles based on magnetite were used to improve the mechanical, thermal, and magnetic properties of microporous cryogel polymer composites. Here we report the synthesis of microporous cryogel based on the crosslinked sodium vinyl sulfonate (Na-VS) and 2-acrylamido-2-methylpropane sulfonic acid sodium salt (Na-AMPS). The magnetite nanoparticles were incorporated into Na-VS/Na-AMPS cryogel networks either during its crosslinking polymerization or by the in-situ technique after its crosslinking. The morphology, particle sizes, thermal stability, and magnetite contents of Na-VS/Na-AMPS cryogel and its magnetite composite were investigated. The prepared Na-VS/Na-AMPS cryogel and its magnetite composite were used as adsorbents for methylene blue (MB) cationic dye using optimum conditions. The magnetite Na-VS/Na-AMPS cryogel composite prepared by in-situ technique achieved the best adsorption MB removal capacity for 7 cycles among the other adsorbents via chemical adsorption mechanism at room temperature.

Keywords: methylene blue; water treatment; magnetic nanomaterials; cryogel; nanocomposites

1. Introduction

Ionic hydrophilic crosslinked polymers, as pH sensitive materials, have been used as adsorbents for charged substances and for drug delivery applications [1–4]. The macro-porous cryogels produced from the formation of ice crystals were used as a porogen during the gelation process to form pores [5]. However, the applications of cryogels were limited due to their lack of mechanical strength. Further, the concentration of the crosslinker affected the flexibility of the formed polymeric network chains. The poor mechanical properties of the polymeric cryogels were improved via the formation of cryogel nanocomposites to be applied as effective adsorbents [6,7]. There are many factors based on the cryogelation conditions such as polymerization temperature, freezing time, freezing rate, number of thawing cycles etc. that regulate the micro- and macrostructure of the cryogels [8]. The advanced trend to form cryogels with an internal nano-porosity in the pore walls was a complicated task [9]. In this work, it is proposed that the presence of nanomaterials during the network gelation of the crosslinked cryogels may be used to enhance the mechanical properties and porosity of the...
cryogels. The preparation of ferrogel composites, based on a magnetic oxides polymer matrix, is the target of the present work, owing to their biocompatibility as a drug delivery option [10–12] and as an environmentally friendly effective adsorbent that improves the mechanical properties of the polymer matrix [12].

The magnetic nanomaterials based on the iron oxides polymer composites were used as adsorbents for water purification due to their response in adsorbing both organic and inorganic water pollutants and to be separated and reused by an external magnet [13–17]. The superparamagnetic properties of the iron oxides of the magnetic nanomaterials having sizes ranging between 50 and 180 nm are very important characteristics of magnetic nanomaterials. The sizes between 10 to 50 nm and below 10 nm are called small and very small superparamagnetic iron oxides nanoparticles [18]. The sizes, distribution, and shapes of iron oxides nanomaterials were varied and based on preparation methods such as coprecipitation, thermal decomposition, microemulsion, hydrothermal, sol-gel, flow injection, electrochemical, aerosol/vapor, and the sonolysis syntheses of iron salts [19]. The stability of iron oxides towards environmental oxidation, the formation of mono and highly dispersed nanoparticles, productivity, and energetically favored methods to prepare magnetic nanocomposites are targets for the researchers to increase their activity towards medical and environmental applications [20].

In our previous works [21–26], the dispersion, stability and productivity of magnetite (Fe₃O₄) and magnetite cuprous oxides (Fe₃O₄·Cu₂O·Fe₃O₄) were increased in the polymer composites using the in-situ preparation technique. Moreover, their size distributions and magnetic properties were controlled by the in-situ preparation method. In the present work, sodium vinyl sulfonate (VS) and 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) were selected as ionic monomers that have a strong tendency to link with iron cations to prepare their oxides into their crosslinked polymeric networks as hydrogel and cryogels [27]. The comparison between the abilities of the produced VS/AMPS networks as hydrogels and cryogels to adsorb the water pollutants the aim of the present work. Moreover, the determination of the optimum adsorption parameters for removal of methylene blue cationic dyes from the industrial waste water is another goal of the present work.

2. Materials and Methods

2.1. Materials

All chemicals used in this work were obtained from Aldrich Chemicals Co. The sodium vinyl sulfonate (VS), 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) 50% used as monomers and crosslinked with N,N-methylene bisacrylamide (MBA) as a crosslinker in the presence of ammonium persulfate (APS) and N,N,N′,N′-tetramethylethylenediamine (TEMED) as a radical initiator and activator for crosslinking polymerization at low temperatures. The magnetite nanoparticles were prepared with high yield from the reaction of anhydrous FeCl₃ and KI reagent after iodine removal in the presence of ammonia, as reported in previous work [25]. Methylene blue, produced from Sigma-Aldrich Co (St. Louis, MO, USA). was used to prepare stock solutions of 500–2000 ppm. Buffer solution (H₃PO₄/NaH₂PO₄) was prepared by the titration of 0.1 N of NaH₂PO₄ against 0.1 M HCl (for pH range 2–3) or against 0.1 N NaOH (for pH range 7–12) until the required pH was reached. The pH value was monitored using the pH meter. Milli-Q deionized water (DIW), with resistivity of 18.2 MΩ·cm at 25 °C, was used to prepare the cryogels.

2.2. Preparation Methods

2.2.1. Preparation of VS/AMPS Cryogel and Its Composite

The Na-VS/Na-AMPS cryogel was prepared in the presence of MBA, APS, and TEMED as crosslinker, initiator and activator, respectively. The monomers concentration in water did not exceed 20 wt% to prepare the cryogel. In this respect, AMPS (2.29 g), VS (2.6 g) and MBA (0.49 g) were mixed with DIW (20 mL) by stirring. APS (0.49 g) dissolved in DIW (2 mL) and TEMED (180 µL) were injected
into the reaction mixture after cooling the solution in an ice bath at 278 K. The reaction mixture was bubbled with nitrogen gas for 30 min. The reaction mixture was cooled to 253 K with a cooling rate of 275 K min\(^{-1}\) and kept constant for 24 h. The crosslinked VS/AMPS cryogel was thawed at room temperature and kept in water for 24 h to remove the unreacted monomers. The produced VS/AMPS cryogel white powder was filtered and dried in a vacuum oven at 318 K. The same procedure was used to prepare the Fe\(_3\)O\(_4\)/VS/AMPS cryogel nanocomposite with the addition of the prepared Fe\(_3\)O\(_4\) (50 wt% related to monomers) to the monomers solution.

2.2.2. In-Situ Preparation of Na-VS/Na-AMPS-Fe\(_3\)O\(_4\) Composite

The iron cations solution was prepared by mixing FeCl\(_3\)·6H\(_2\)O (0.25 g in 20 mL distilled water) with sodium sulfite solution (1 mL of 4.8 wt% aqueous solution) at room temperature under vigorous stirring to reach equilibrium for 1 h under N\(_2\) atmosphere. The Na-VS/Na-AMPS cryogel (1 g) was immersed into iron cation solution for 24 h until it absorbed all aqueous solution. The cryogel was dried in vacuum at 303 K and the ammonium hydroxide solution (5 mL) added to swelled polymer and rinsed for 4 h. The cryogel color changed from yellow to black. The external surface of the cryogels was washed several times with water and ethanol until the filtrate became clear. The black powder washed with water and dried in vacuum over at 303 K to obtain VS/AMPS·Fe\(_3\)O\(_4\).

2.3. Characterization

A Fourier transform infrared (FTIR) spectrometer (FTIR; model Nexus 6700 FTIR, Thermo Scientific, Waltham, MA, USA) was used to elucidate the functional groups of the cryogel and its nanocomposites with a range of 4000–400 cm\(^{-1}\) using KBr pellets. The surface morphologies of Na-VS/Na-AMPS cryogel and its composites were analyzed in a Nova nano SEM 430 (FEI) environmental scanning electron microscope (SEM). The crystal size and crystal structure of the iron composite was determined from X-ray diffraction (XRD) patterns using a (BDX-3300 diffractometer, Beijing University Equipment Manufacturer, Beijing, China) with Cu K\(\alpha\) radiation. Thermogravimetric analysis (TGA) and stability of the nanocomposite, and cryogel was carried out using a TGA-50 SHIMADZU thermogravimetric instrument (SHIMADZU, Tokyo, Japan), with a TA-50 WSI thermal analyzer (SHIMADZU, Tokyo, Japan). Samples (5 mg) were degraded in a nitrogen atmosphere (flow rate 50 mL/min) at a heating rate of 283 K/min.

The concentrations of MB dye in water were measured using a double beam UV–visible spectrophotometer (Shimadzu UV-1208 model at wavelength \(\lambda_{\text{max}}\) equal to 662 nm, SHIMADZU, Tokyo, Japan).

2.4. Application of Na-VS/Na-AMPS Cryogel and Its Nanocomposites for Water Treatment

Various concentrations of MB ranged from 0.01 to 0.1 mmol L\(^{-1}\) in water were used to obtain a standard calibration curve from the relation between MB concentrations and absorbance values. A UV–visible spectrophotometer was used to determine the MB absorbance values at a wavelength of 662 nm. Concentrations of MB dye in aqueous solutions varying from 1.56 to 6.25 mmol L\(^{-1}\) (500 to 2000 mg L\(^{-1}\)) were used to determine the removal efficiencies (%) of the prepared adsorbent at optimum conditions. The adsorption kinetics of MB onto cryogel and its composites were evaluated using different concentrations of MB in 50 mL of aqueous solution in the presence of 0.02 g of the cryogels at 298 K. The MB dye adsorption capacities at equilibrium, \(q_e\) (mg g\(^{-1}\)), and the adsorption efficiency E (%) were calculated as:

\[
q_e = (C_o - C_e) \times \frac{V}{m} \quad (1)
\]

\[
E(\%) = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \quad (2)
\]

\(C_o, C_e, V\) and \(m\) were the liquid phase concentrations of dye initially and at equilibrium (mg L\(^{-1}\)), the volume (L) of the solution and the mass of adsorbent used (g), respectively.
The MB was recovered from the composites by collecting the polymer powder using an external magnet, pressing the gels, followed by treatment with ethanol and 0.5 mol·L⁻¹ HCl and neutralization with 0.1 mol·L⁻¹ NaOH aqueous solutions. The recovered gels were washed with distilled water and dried at room temperature to reuse for several adsorption experiments.

3. Results

The VS/AMPS is selected to prepare crosslinked magnetic cryogel composites either in the presence of magnetite nanoparticles or formation of magnetite cryogel composite using *in-situ* preparation technique as represented in Figure 1.

![Figure 1. Preparation scheme of magnetite Na-VS/Na-AMPS cryogel composites.](image)

3.1. Characterization

The chemical structures of magnetic VS/AMPS cryogel and VS/AMPS-Fe₃O₄ are determined from FTIR spectra represented in the Figure 2a,b.

![Figure 2. Fourier transform infrared (FTIR) spectra of (a) VS/Na-AMPS and (b) VS/AMPS-Fe₃O₄.](image)
The formation of Na-VS/Na-AMPS-Fe₃O₄ cryogel composite using *in-situ* method also elucidated from XRD diffractograms that are represented in Figure 3a,b.

**Figure 3.** X-ray diffraction (XRD) diffractograms of (a) Fe₃O₄·VS/AMPS and (b) VS/AMPS·Fe₃O₄.

Thermogravimetric analysis (TGA) was performed under nitrogen up to 1173 K and under oxygen above 1173 K (Figure 4). The organic polymer segment contents are determined using nitrogen, while the oxidizing segment was used to prove whether the magnetite was still magnetite after modification or using *in-situ* polymerization technique.

**Figure 4.** Thermogravimetric analysis (TGA) thermograms of VS/AMPS cryogel and its magnetite composites.

The surface morphologies of VS/AMPS, Fe₃O₄·VS/AMPS, and VS/AMPS·Fe₃O₄ cryogel composites are investigated from SEM micrographs represented in Figure 5a–c.
3.2. Magnetic Cryogel Composites as MB Dye Adsorbents

The magnetite is selected to reinforce the VS/AMPS cryogel to improve its response to collect from water by an external magnetic field as represented in Figure 6.

The optimum conditions to apply Fe\textsubscript{3}O\textsubscript{4}-VS/AMPS and VS/AMPS-Fe\textsubscript{3}O\textsubscript{4} as an adsorbent such as adsorbents concentrations, aqueous solution pH, solution temperature, MB concentrations on the removal of MB from aqueous solutions are investigated in this section.

It is very important to reduce the mass of adsorbents used to remove the pollutants from water. The relations between the mass of VS/AMPS, Fe\textsubscript{3}O\textsubscript{4}-VS/AMPS and VS/AMPS-Fe\textsubscript{3}O\textsubscript{4} cryogel composites (mg of adsorbents dispersed in 100 mL of water) and their efficiencies (E\%) as adsorbents using MB dye solution (1.56 mmol·L\textsuperscript{-1}) under stirring for 10 min using a batch technique are plotted in Figure 7. A range of 20 to 100 mg was added individually to 100 mL of the polluted water.
Figure 7. Effect of VS/AMPS cryogel and its magnetite composite contents on their MB removal efficiencies from water at room temperature.

The effect pH of the aqueous solution (2–10) on the MB adsorption removal capacities of VS/AMPS, Fe₃O₄-VS/AMPS, and VS/AMPS-Fe₃O₄ having 100, 50, and 30 mg adsorbent concentrations at a constant ionic strength of 0.01 M and room temperature is illustrated in Figure 8.

Figure 8. Effect of pH of water on the MB removal capacities of VS/AMPS cryogel and its magnetite composites at room temperature.

The effect of the contact times of the VS/AMPS, Fe₃O₄-VS/AMPS, and VS/AMPS-Fe₃O₄ adsorbents on MB removal efficiencies at their optimum concentrations and pH 7 versus their removal efficiencies MB adsorbate (500 mg·L⁻¹) are illustrated in Figure 9.

Figure 9. Effect of the contact time between VS/Na-AMPS cryogels and the MB aqueous solution on their removal efficiencies at room temperature and pH 7.
The effects of MB concentrations (mmol·L\(^{-1}\)) on the removal efficiencies of the VS/Na-AMPS, Fe\(_3\)O\(_4\)-VS/AMPS, and VS/AMPS-Fe\(_3\)O\(_4\) adsorbents at their optimum conditions are represented in Figure 10.

![Figure 10](image_url)  
**Figure 10.** Effect of the MB concentrations in their aqueous solution on the removal efficiencies of Na- VS/Na-AMPS cryogels at optimum conditions.

3.3. Adsorption Isotherm Modeling of the MB Adsorption

The Langmuir and Freundlich models were selected as the most famous adsorption models used to clarify the homogeneity of the adsorbate surfaces as well as the formation of the MB monolayer and multilayers on the prepared adsorbent surfaces. The Langmuir and Freundlich equations are:

\[
\frac{C_e}{Q_e} = \left[\frac{1}{Q_{\text{max}}} K_l\right] + \left(\frac{C_e}{Q_{\text{max}}}\right)
\]  
(3)

\[
\log (Q_e) = \log (K_l) + \frac{1}{n} \log (C_e)
\]  
(4)

The constants \(n\) (g L\(^{-1}\)), \(K_l\) (L·mg\(^{-1}\)) and \(K_f\) [(mg·g\(^{-1}\)) (L·mg\(^{-1}\))\(^{(1/n)}\)] are the empirical constant, Langmuir and Freundlich constants, respectively. The equilibrium and maximum amount of MB adsorbate are \(Q_e\), and \(Q_{\text{max}}\) (mg·g\(^{-1}\)), respectively. The concentration of MB dye in the aqueous solution at equilibrium is \(C_e\) (mg·L\(^{-1}\)). The linear relation used to fulfill both Equations (3) and (4) with highest linear coefficient (R\(^2\)) is used to explain the surface homogeneity of the adsorbent as well as the monolayer or multilayer adsorption of the MB adsorbate. In this respect, the adsorption parameters of Langmuir and Freundlich were determined and summarized in Table 1.

The chemical interactions between the MB and the prepared adsorbent can be investigated from the effect of temperature on their adsorption efficiencies. In this respect, the MB solution temperatures ranged from 298 to 343 K were used to investigate the effect of the temperature on the adsorption process. The thermodynamic parameters such as change in free energy (\(\Delta G_o\); KJ·mol\(^{-1}\)), change in enthalpy (\(\Delta H_o\); KJ·mol\(^{-1}\)), and changes in entropy (\(\Delta S_o\); J·mol\(^{-1}\)·K\(^{-1}\)) on the adsorbent surfaces were calculated using the following equations:

\[
\Delta G_o = -RT \ln \left(\frac{C_e A}{C}\right)
\]  
(5)

\[
\log \left(\frac{C_e A}{C}\right) = \frac{\Delta S_o}{2.303} R - \frac{\Delta H_o}{2.303 RT}
\]  
(6)

where \(C_e\), \(R\) and \(T\) are the adsorbent concentration (mg·L\(^{-1}\)), gas constant (8.314 J·mol\(^{-1}\)·K\(^{-1}\)) and the aqueous solution temperature (K), respectively. The (CeA/ Ce) is expressed as an equilibrium concentration constant (Kc) between the adsorbent and MB concentrations. The calculated values of \(\Delta G_o\), \(\Delta H_o\), and \(\Delta S_o\) were summarized in Table 2. Moreover, the relations between \(\ln Kc\) and \(1/T\) to remove MB from their aqueous solutions using VS/AMPS, Fe\(_3\)O\(_4\)-VS/AMPS, and VS/AMPS-Fe\(_3\)O\(_4\) adsorbents are represented in Figure 11.
Table 1. Adsorption isotherm parameters of MB dye using VS/AMPS cryogel and its composites at temperature 298 K.

| Adsorbents      | Langmuir Isotherm Parameters | Freundlich Isotherm Parameters | Exp. Adsorption Capacity |
|-----------------|-------------------------------|--------------------------------|--------------------------|
|                 | $Q_{\text{max}}$ [mg·g$^{-1}$] | $K_l$ [L·mg$^{-1}$] | $R^2$ | $n$ [g·L$^{-1}$] | $K_f$ [(mg·g$^{-1}$)·(L·mg$^{-1}$)(1/n)] | $R^2$ | $Q_{\text{max}}$ [mg·g$^{-1}$] |
| VS/AMPS·Fe$_3$O$_4$ | 788 ± 0.01                    | 0.025 ± 0.001                | 0.991 ± 0.001             | 1.50 ± 0.01 | 23.6 ± 0.01 | 0.932 ± 0.001 | 780 ± 0.03 |
| Fe$_3$O$_4$·VS/AMPS | 748 ± 0.05                    | 0.075 ± 0.002                | 0.987 ± 0.003             | 1.04 ± 0.04 | 21.8 ± 0.04 | 0.929 ± 0.007 | 740 ± 0.01 |
| VS/AMPS          | 626 ± 0.07                    | 0.044 ± 0.001                | 0.995 ± 0.002             | 1.09 ± 0.03 | 33.8 ± 0.05 | 0.921 ± 0.003 | 660 ± 0.02 |

Table 2. Adsorption thermodynamic of MB aqueous solutions using VS/AMPS cryogel and its composites at different temperatures.

| Temp. (K) | Fe$_3$O$_4$·VS/AMPS | VS/AMPS | VS/AMPS·Fe$_3$O$_4$ |
|-----------|----------------------|---------|---------------------|
|           | $-\Delta G_o$ [KJ·mol$^{-1}$] | $-\Delta H_o$ [KJ·mol$^{-1}$] | $\Delta S_o$ [J·mol$^{-1}$·K]$^{-1}$ | $-\Delta G_o$ [KJ·mol$^{-1}$] | $-\Delta H_o$ [KJ·mol$^{-1}$] | $\Delta S_o$ [J·mol$^{-1}$·K]$^{-1}$ | $-\Delta G_o$ [KJ·mol$^{-1}$] | $-\Delta H_o$ [KJ·mol$^{-1}$] | $\Delta S_o$ [J·mol$^{-1}$·K]$^{-1}$ |
| 298       | 21.920 ± 0.01        | 24.202 ± 0.02         | 11.21 ± 0.03          | 31.8 ± 0.01        | 24.97 ± 0.01          | 56.6 ± 0.01          |
| 313       | 22.525 ± 0.03        | 25.292 ± 0.04         | 33.3 ± 0.03           | 32.7 ± 0.01        | 24.97 ± 0.01          | 56.6 ± 0.01          |
| 318       | 22.726 ± 0.02        | 30.074 ± 0.01         | 33.1 ± 0.01           | 32.7 ± 0.01        | 24.97 ± 0.01          | 56.6 ± 0.01          |
| 323       | 22.928 ± 0.02        | 9.901 ± 0.02          | 30.33 ± 0.01          | 33.3 ± 0.03        | 24.97 ± 0.01          | 56.6 ± 0.01          |
| 333       | 23.331 ± 0.02        | 25.292 ± 0.04         | 33.3 ± 0.03           | 33.3 ± 0.03        | 24.97 ± 0.01          | 56.6 ± 0.01          |
| 343       | 23.735 ± 0.01        | 25.728 ± 0.03         | 34.4 ± 0.04           | 33.3 ± 0.03        | 24.97 ± 0.01          | 56.6 ± 0.01          |
3.4. MB Adsorption Kinetics and Reuse of VS/AMPS Cryogel Composites

The adsorption rate of MB removal and the rate-determining step are very important parameters used to determine the MB adsorption mechanism on the surface of the cryogel and its composites. The linear relations of pseudo-first-order and pseudo-second-order kinetic models were used to analyze the MB concentrations with the contact time as expressed in the following equations:

\[
\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (7)
\]

\[
t/q_t = \left(1/k_2 q_e^2\right) + \left(t/q_e\right) \quad (8)
\]

The adsorption capacities of MB on cryogel adsorbents \( q_1 \) (mg/g) and \( q_e \) (mg/g) at time \( t \) (min) and equilibrium respectively are used to investigate the linear relations of the Equations (7) and (8). The constants \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g-mg\(^{-1}\).min\(^{-1}\)) are the kinetic rate of MB adsorption on the surfaces of the cryogels using pseudo-first-order and pseudo-second-order kinetic models, respectively. The values of \( k_1, k_2 \) and their correlation coefficients (R\(^2\)) are determined and summarized in Table 3.

Table 3. Kinetic parameters of VS/AMPS cryogel and its composites for removal of MB from an aqueous solution at temperature 298 K.

| Cryogel Composites | \( q_{exp} \) (mg.g\(^{-1}\)) | Pseudo-first Order Kinetic Parameters | Pseudo-Second-Order Kinetic Parameters |
|--------------------|-------------------------------|--------------------------------------|---------------------------------------|
|                    | \( R^2 \) | \( q_{calc} \) (mg.g\(^{-1}\)) | \( K1 \) (min\(^{-1}\)) | \( R^2 \) | \( q_{calc} \) (mg.g\(^{-1}\)) | \( K2 \) (g-mg\(^{-1}\).min\(^{-1}\)) |
| VS/AMPS            | 0.904 | 261 | 0.033 | 0.997 | 620 | 0.00077 |
| VS/AMPS-\( \cdot \)Fe\(_3\)O\(_4\) | 0.912 | 251 | 0.03 | 0.998 | 740 | 0.06732 |
| Fe\(_3\)O\(_4\)∙VS/AMPS | 0.924 | 251 | 0.03 | 0.997 | 700 | 0.00046 |

The VS/AMPS cryogel and its composites were reused and regenerated for several cycles to remove MB from the aqueous solution using HCl and NaOH as reported in the experimental section. The data of MB removal efficiencies (E\(\%\)) of the VS/AMPS cryogel and its composites for seven cycles were determined and listed in Table 4.

Table 4. Reuse Na-VS/Na-AMPS cryogel and its composites for removal of 1 m mol.L\(^{-1}\) of MB aqueous solution at 298 K.

| Adsorbents | MB Removal Efficiency (%) |
|------------|---------------------------|
|            | Na-VS/Na-AMPS | Fe\(_3\)O\(_4\)∙Na-VS/Na-AMPS | Na-VS/Na-AMPS-Fe\(_3\)O\(_4\) |
| Cycle 1    | 100           | 99.8                           | 99.8                           |
| Cycle 2    | 5.8           | 99.8                           | 99.8                           |
| Cycle 3    | 90.5          | 96.5                           | 99.5                           |
| Cycle 4    | 80.2          | 95.4                           | 99.4                           |
4. Discussion

The VS/AMPS cryogel was formed through the crystallization of water solvent during the crosslinking polymerization at a cooling temperature of 253 K (Figure 1). The non-frozen liquid micro-phase based on VS/AMPS among the growing contact ice crystals is polymerized using the crosslinking radical polymerization technique in the presence of MB, KPS, and TEMED as a crosslinker, initiator and activator, respectively. The ice crystal was used as a porogen during the crosslinking gelation process and melted after thawing to produce macro-porous networks have interconnected pores structure. The FTIR spectra (Figure 2a,b) elucidated the crosslinking polymerization of VS and AMPS monomers from the disappearance of vinyl = CH stretching, C=C stretching, and =CH out of plan bending absorption bands at 3100–3000 cm$^{-1}$, 1550 cm$^{-1}$ and 900–1000 cm$^{-1}$, respectively. The appearance of a new strong band at 3462 cm$^{-1}$, NH stretching of MBA, and AMPS amides with strong absorption in VS/AMPS-Fe$_3$O$_4$ spectrum (Figure 2b) elucidates the formation of magnetite nanoparticles surrounded by hydroxyl groups [28]. The interaction between magnetite and amide groups of MBA and AMPS is confirmed from the formation of strong intense CONH at band 1666 cm$^{-1}$ (Figure 2b), which has a lower intensity at 1697 cm$^{-1}$ for VS/AMPS (Figure 2a). Moreover, the interaction of magnetite with sulfonate groups of VS/AMPS is elucidated from the S=O asymmetric stretching and symmetric S=O stretching at 1400 and 1043 cm$^{-1}$, respectively (Figure 2b). The appearance of absorption bands at 580 cm$^{-1}$ (attributed to Fe-O bond vibration band) elucidates the presence of Fe$_3$O$_4$ nanoparticles. The disappearance of strong absorption bands at 650 and 750 cm$^{-1}$ (Figure 2b) confirms the formation of magnetite without the formation of the other iron oxides such as maghemite, and α-Fe$_2$O$_3$ (hematite) nanoparticles [29]. Moreover, the presence of the magnetite characteristic peaks and their crystal dimensions at 2θ = 37.53° (311), 43.53° (400), 54.51° (422), 57.27° (511), and 63.88° (440), and 77.00° (511) in the VS/AMPS-Fe$_3$O$_4$ diffractogram (Figure 3b) confirms the encapsulation of pure magnetite in a cubic phase (Fe$_3$O$_4$, JCPDS No. 89-3854). The broad peaks at 2-theta values ranging from 15 to 30° (Figure 3b) elucidates the amorphous structure of VS/AMPS-Fe$_3$O$_4$ cryogel polymers. The disappearance of peaks as topotactic with the [111] and [110] axes of the maghemite corresponding to the [001] and [110] axes of hematite [29] confirm the absence of maghemite and hematite to elucidate the ability of VS/AMPS to protect the magnetite from oxidation to other iron oxides such as; maghemite (γ-Fe$_2$O$_3$), hematite (α-Fe$_2$O$_3$), and the two oxyhydroxides, lepidocrocite (γ-FeOOH), and goethite (α-FeOOH). The good interaction of magnetite among cryogel matrices also elucidated from the right shifts of 2θ values of pure magnetite (Fe$_3$O$_4$, JCPDS No. 89-3854) as compared with VS/AMPS-Fe$_3$O$_4$ diffraction peaks (Figure 3b). The XRD diffractograms of magnetite and VS/AMPS-Fe$_3$O$_4$ cryogel (Figure 3a,b) show low intense and broad peaks, which assume the small crystallite size of magnetite into the VS/AMPS-Fe$_3$O$_4$ cryogel. The diffracting domain size (d$_{xrd}$) of the magnetite nanoparticles encapsulated into the VS/AMPS cryogel networks are automatically calculated from the width of the XRD peak under the Scherrer approximation as $d_{xrd} = k\lambda/\beta \cos \theta$; where $k = 0.9$ is the Scherrer constant, $\lambda = 0.154$ nm is the X-ray wavelength, $\theta$ is the diffraction angle in degrees (2θ = 37.53°) and $\beta$ is the peak width at half maximum height of the peak. The (d$_{xrd}$) crystallite sizes of magnetite and magnetite encapsulated into VS/AMPS-Fe$_3$O$_4$ cryogel are 12.32, and 8.73 nm, respectively. These data elucidate the increasing interaction between iron cations with the amide and sulfonate groups of VS/AMPS matrices and reduces the aggregation of magnetite that reduces their sizes into the VS/AMPS cryogel. Furthermore, the free volume in the highly crosslinked VS/AMPS cryogels reduces the growing of magnetite to produce ultrafine nanoparticles [11,29–32]. The thermal stability of the cryogel and its composites with magnetite is investigated from the TGA curves (Figure 4). The thermograms elucidate the increasing of VS/AMPS thermal stability with incorporation of magnetite either during crosslinking polymerization or using the in-situ technique. The higher contents of the remaining residual for VS/AMPS-Fe$_3$O$_4$ more than Fe$_3$O$_4$.VS/AMPS indicate that an oxidation from Fe$_3$O$_4$ to Fe$_3$O$_3$ has occurred [32]. This means that the binding of the Fe$_3$O$_4$ nanoparticles with VS/AMPS during their crosslinking polymerization protected the magnetite from the oxidation more...
the than *in-situ* technique [32]. The VS/AMPS-Fe$_3$O$_4$ shows two decomposition steps beginning at approximately 623 K and 773 K were detected within the nitrogen segment, resulting from the decomposition of polymer chains. The higher magnetite contents for VS/AMPS-Fe$_3$O$_4$ (55 wt%) confirms that the *in-situ* method is efficient to incorporate the magnetite into the Na-VS/Na-AMPS networks. The morphology of VS/AMPS cryogel (Figure 5a) shows a spongy morphology with higher wall density and large pore sizes when compared with VS/AMPS-Fe$_3$O$_4$ cryogel composite (Figure 5b). This observation elucidates that the presence of magnetite nanomaterials during the freezing of VS and AMPS monomers brings about the formation of small ice crystals. Moreover, as a consequence the pore sizes of VS/AMPS-Fe$_3$O$_4$ cryogel composite (Figure 5b) is small with the formation of continuous channels. The presence of magnetite changes the nature of bound water into the VS/AMPS hydrophilic gel [33,34]. The morphology of the VS/AMPS-Fe$_3$O$_4$ micrograph (Figure 5c) elucidates that the formed magnetite into VS/AMPS networks is distributed either inside the pores or more densely among the composite pores. It was also observed that there are highly dispersed magnetite nanoparticles on the surfaces of the cryogels and their pores and channels, which referred to the electrosteric stabilization of the magnetite nanoparticles with sulfonate and amide groups of VS/AMPS [35].

The selection of VS and AMPS to prepare ionic cryogel contain sulfonate and amide group aims to use as adsorbents for charged water pollutants such as the MB dye. It was noticed that the weak mechanical properties of the VS/AMPS cryogels was due to its swelling in water, which affects their application as adsorbents. For these reasons Fe$_3$O$_4$·VS/AMPS and VS/AMPS-Fe$_3$O$_4$ cryogel composites are selected to apply as adsorbents because they reduce the swelling characteristics and improve the stability of cryogel in the aqueous medium. The data (Figure 7) confirms that the optimum adsorbent concentrations for VS/AMPS, Fe$_3$O$_4$·VS/AMPS, and VS/Na-AMPS-Fe$_3$O$_4$ to remove 100% of MB are 100, 50, and 30 mg, respectively. These data elucidate that the presence of magnetite either during the cryogelation (Fe$_3$O$_4$·VS/AMPS) or using the *in-situ* method after cryogelation (Fe$_3$O$_4$·VS/AMPS) improves the electrostatic interactions of the polymer networks with the positive charges of MB [36–38]. This interaction increases the diffusion of MB into the cryogel matrices in the presence of a low amount of magnetite cryogel composites [36]. It is also noticed that the increasing magnetite particle sizes of VS/AMPS-Fe$_3$O$_4$ as elucidated from XRD and TEM data (Figures 3 and 5) increases the adsorption of MB. It is noticed (Figure 8) that the optimum pH for MB removal adsorption capacities is pH 7. The lower MB removal adsorption capacities of the cryogel and their composites in acidic pH (2–5) are referred to the protonation of sulfonate groups of VS/AMPS cryogel [36]. It is also noticed that the presence of magnetite into VS/AMPS cryogels reduces the MB removal into acidic medium more than free VS/AMPS cryogel without magnetite. This means that the presence of magnetite nanoparticles during the cryogelation of VS/Na-AMPS cannot protect the sulfonate groups of cryogels from protonation [36]. The formation of magnetite after cryogel formation (Fe$_3$O$_4$·VS/AMPS) protects the protonation of sulfonate anions in acidic pH and increases MB removal in acidic medium (Figure 8). The stability of MB removal from their aqueous solution at pH 7 without improvement at pH above 7 can be attributed to the blocking of cryogel pore sizes in alkaline medium due to the presence of sodium salts of AMPS and VS, which inhibited the cryogel MB dye uptakes [37]. The data (Figure 9) elucidate that the effective contact times of VS/AMPS, Fe$_3$O$_4$·VS/Na-AMPS, and VS/AMPS-Fe$_3$O$_4$ adsorbents to remove MB from aqueous solution are 50, 40 and 20 min, respectively. These data mean that the microporous morphology of VS/AMPS-Fe$_3$O$_4$ adsorbents, beside the good dispersion of magnetite into the VS/AMPS networks, facilitate the diffusion and interaction of MB with the cryogel composites. The presence of magnetite into the cryogel pores produces interconnected networks (Figure 5b,c) of highly adsorbed MB amounts [38]. The data (Figure 10) elucidate that the VS/AMPS-Fe$_3$O$_4$ achieves higher removal efficiencies (above 99.5%) at MB concentrations than other adsorbents up to MB 3.12 mmol·L$^{-1}$. It can be concluded that the presence of highly dispersed magnetite nanoparticles into the cryogel matrices and interconnected pores produced facilitate the adsorption of MB dye in short time.
The homogeneity of the adsorbent surfaces, good dispersion of the nanomaterials in the polymer composites beside the porosity of cryogel composites are the important factors to investigate the adsorption rate of the adsorbate on the surfaces of the prepared adsorbents. The chemical, physical, and physico-chemical mechanisms for the adsorption of MB from aqueous solution using VS/AMPS, Fe₃O₄/VS/AMPS and VS/AMPS-Fe₃O₄ adsorbents can be estimated from the adsorption isotherm models and kinetics study. It is noticed that (Table 1) all VS/AMPS, Fe₃O₄/VS/AMPS and VS/AMPS-Fe₃O₄ adsorbents obey the Langmuir adsorption isotherm more than the Freundlich model as elucidated from their higher coefficient (R²). These data elucidate the homogeneity of all adsorbent surfaces with the formation of a monolayer MB layer onto all the prepared cryogel composites. The data (Table 2 and Figure 10) indicate that the Kc values increase with an increase in temperature for all the cryogel and their magnetite composites. Moreover, it is also observed that only VS/AMPS-Fe₃O₄ have more negative ΔH° than −20 KJ.mol⁻¹ to confirm the spontaneous chemical adsorption of MB on its surfaces. The proposed mechanism for removal of MB using VS/AMPS and Fe₃O₄/VS/AMPS is physical or physico-chemical adsorption mechanisms. This means that the in-situ technique used to insert the magnetite into VS/AMPS facilitates both the interactions of MB with the cryogel and the formation of interconnected pores. The negative values of ΔG°, ΔH° (Table 2) elucidate the exothermic nature of the MB adsorption process using VS/AMPS cryogel and its composites. The negative values of ΔS°, (Table 2) indicate the increasing degree of freedom of the adsorbed MB dye molecules and elucidate that the increasing concentration of MB dye molecules in a solid-liquid interface increases the adsorption onto the cryogel surfaces. It can be concluded that the increasing of MB dye concentrations in the aqueous solution will increase their adsorption on the cryogel surfaces in the order VS/AMPS-Fe₃O₄ > VS/AMPS > Fe₃O₄-VS/AMPS. The VS/AMPS-Fe₃O₄ cryogel composite adsorbs the MB with an ion exchange mechanism and the presence of the sulfonate and amide group forms a complex with the MB pollutant via a chemical bond [39]. The linear and nonlinear relations of the pseudo-second-order and pseudo-first-order model, respectively, are confirmed from the low value of R² (Table 3). These results confirm the pseudo-second-order chemical adsorption of MB on the cryogels [39]. The agreement of the calculated values (qₑ,cal, Table 3) and the experimental values (qₑ,exp) elucidates the chemisorption of MB on the cryogels using the pseudo-second-order model [40,41]. The k₂ values (Table 3) arrange the increasing order of the MB removal rate from aqueous solutions as VS/AMPS-Fe₃O₄ > VS/AMPS > Fe₃O₄-VS/AMPS. The recyclability of VS/AMPS cryogel (Table 4) is reduced after two cycles to confirm its low mechanical properties. The VS/AMPS-Fe₃O₄ are stable for five cycles without significant reduction to elucidate its good mechanical and chemicals resistances. Therefore, the VS/AMPS-Fe₃O₄ shows higher thermal stability, porosity, faster dye removal and excellent mechanical and chemical stability and is recommended to be applied as an effective adsorbent to remove cationic pollutants from industrial waste water.

5. Conclusions

The incorporation of magnetite nanoparticles either during crosslinking or after polymerization of VS/AMPS cryogel modified its micro-porosity and mechanical properties. The in-situ preparation of the magnetite nanoparticles among VS/AMPS cryogel networks produced effective, highly dispersed and low particle sizes composites more than introducing magnetite during crosslinking polymerization at a lower temperature. The MB removal rate using VS/AMPS-Fe₃O₄ prepared by in-situ method is greater than VS/AMPS and Fe₃O₄-VS/AMPS. The VS/AMPS-Fe₃O₄ adsorbs the MB from their aqueous solutions with the ion exchanges mechanism and via a complex formation between their sulfonate and the amide groups with MB pollutant.

Author Contributions: Methodology, investigation, writing—review and editing A.M.A. and S.A.A.-H.; supervision H.A.A.-L.; revision and resources A.O.E.; methodology A.M.T.

Funding: This research was funded by Al Imam Mohammad Ibn Saud Islamic University (IMSIU), Deanship of Scientific Research (project 371224).
Acknowledgments: The project 371224 was financially supported by Al Imam Mohammad Ibn Saud Islamic University (IMSIU), Deanship of Scientific Research.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Abdel-Azim, A.A.A.; Farahat, M.S.; Atta, A.M.; Abdel-Fattah, A.A. Preparation and properties of two-component hydrogels based on 2-acrylamido-2-methylpropane sulphonic acid. Polym. Adv. Technol. 1998, 9, 282–289. [CrossRef]

2. Bajpai, A.K.; Sandeep, K.S.; Bhanu, S.; Kankane, S. Responsive polymers in controlled drug delivery. Prog. Polym. Sci. 2008, 33, 1088–1118. [CrossRef]

3. Atta, A.M.; Abdel-Azim, A.A.A. Effect of Crosslinker Functionality on Swelling and Network Parameters of Copolymeric Hydrogels. Polym. Adv. Technol. 1998, 9, 340–348. [CrossRef]

4. Gupta, P.; Vermani, K.; Garg, S. Hydrogels: From controlled release to pH-responsive drug delivery. Drug Discov. Today 2002, 7, 569–579. [CrossRef]

5. Atta, A.M.; Arndt, K.F. Synthesis of charged linear and crosslinked maleic diester polymers with electron-beam irradiation. Polym. Int. 2003, 52, 389–398. [CrossRef]

6. Lozinsky, V.I.; Galaev, I.Y.; Plieva, F.M.; Savina, I.N.; Jungvid, H.; Mattiasson, B. Polymeric cryogels as promising materials of biotechnological interest. Trends Biotechnol. 2003, 21, 445–451. [CrossRef] [PubMed]

7. Tekin, K.; Uzun, L.; Sahin, C.A.; Bektas, S.; Denizli, A. Preparation and characterization of composite cryogels containing imidazole group and use in heavy metal removal. React. Funct. Polym. 2011, 71, 985–993. [CrossRef]

8. Dainiak, M.B.; Kumar, A.; Plieva, F.M.; Galaev, I.Y.; Mattiasson, B. Integrated isolation of antibody fragments from microbial cell culture fluids using supermacroporous cryogels. J. Chromatogr. 2004, 1045, 93–98. [CrossRef]

9. Lozinsky, V.I. Cryogels on the basis of natural and synthetic polymers: Preparation, properties and application. Russ. Chem. Rev. 2002, 71, 489–511. [CrossRef]

10. Kennedy, S.; Roco, C.; Deleris, A.; Spoerri, P.; Cezar, C.; Weaver, J.; Vandenburgh, H.; Mooney, D. Improved magnetic regulation of delivery profiles from ferrogels. Biomaterials 2018, 161, 179–189. [CrossRef] [PubMed]

11. Blyakhman, F.A.; Buznikov, A.N.; Sklyar, F.T.; Safronov, P.A.; Golubeva, V.E.; Svalov, V.A.; Sokolov, Y.S.; Melnikov, Y.G.; Orue, I.; Kurylyandskaya, F.G. Mechanical, Electrical and Magnetic Properties of Ferrogels with Embedded Iron Oxide Nanoparticles Obtained by Laser Target Evaporation: Focus on Multifunctional Biosensor Applications. Sensors 2018, 18, 872. [CrossRef] [PubMed]

12. Blyakhman, F.A.; Buznikov, A.N.; Sklyar, F.T.; Safronov, P.A.; Golubeva, V.E.; Svalov, V.A.; Sokolov, Y.S.; Melnikov, Y.G.; Orue, I.; Kurylyandskaya, F.G. Mechanical, Electrical and Magnetic Properties of Ferrogels with Embedded Iron Oxide Nanoparticles Obtained by Laser Target Evaporation: Focus on Multifunctional Biosensor Applications. Sensors 2018, 18, 872. [CrossRef] [PubMed]

13. Kirsebom, H.; Elowsson, L.; Berillo, D.; Cozzi, S.; Inci, I.; Piskin, E.; Galaev, I.Y.; Mattiasson, B. Enzyme-Catalyzed Crosslinking in a Partly Frozen State: A New Way to Produce Supermacroporous Protein Structures. Macromol. Biosci. 2013, 13, 67–76. [CrossRef] [PubMed]

14. Ambasha, R.D.; Sillanpää, M. Water purification using magnetic assistance: A review. J. Hazard. Mater. 2010, 180, 38–49. [CrossRef] [PubMed]

15. Ozay, O.; Ekici, S.; Baran, Y.; Aktas, N.; Sahiner, N. Removal of toxic metal ions with magnetic hydrogels. Water. Res. 2009, 43, 4403–4411. [CrossRef] [PubMed]

16. Hua, M.; Zhang, S.; Pan, B.; Zhang, W.; Lv, L.; Zhang, Q. Heavy metal removal from water/wastewater by nanosized metal oxides: A review. J. Hazard. Mater. 2012, 211–212, 317–331. [CrossRef] [PubMed]

17. Oliveira, L.C.A.; Rios, R.V.R.A.; Fabris, J.D.; Garge, V.; Sapag, K.; Lago, R.M. Activated carbon/iron oxide magnetic composites for the adsorption of contaminants in water. Carbon 2002, 40, 2177–2183. [CrossRef]

18. Teka, A.S.; Koh, P.Y. Synthesis, properties, and applications of magnetic iron oxide nanoparticles. Prog. Cryst. Growth Charact. Mater. 2009, 55, 22–45. [CrossRef]

19. Thorek, D.L.J.; Chen, A.K.; Czupryn, J.; Tsourk, A. Superparamagnetic Iron Oxide Nanoparticle Probes for Molecular Imaging. Ann. Biomed. Eng. 2006, 34, 23–38. [CrossRef] [PubMed]

20. Kammari, R.; Das, N.G.; Das, S.K. Nanoparticulate Systems for Therapeutic and Diagnostic Applications, Emerging Nanotechnologies for Diagnostics, Drug Delivery and Medical Devices. Micro/Nano Technol. 2017, 6, 105–144.
21. Wu, W.; He, Q.; Jiang, C. Magnetic Iron Oxide Nanoparticles: Synthesis and Surface Functionalization Strategies. Nanoscale Res. Lett. 2008, 11, 397–415. [CrossRef] [PubMed]

22. Atta, A.M.; Al-Hussain, S.A.; Al-Lohedan, H.A.; Ezzat, A.O.; Tawfek, A.M.; Al-Otabi, T. In situ preparation of magnetite/cuprous oxide/poly (AMPS/NIPAm) for removal of methylene blue from waste water. Polym. Int. 2018, 67, 471–480. [CrossRef]

23. Al-Hussain, S.A.; Ezzat, A.O.; Gaffer, A.K.; Atta, A.M. Removal of organic water pollutant using magnetite nanomaterials embedded with ionic copolymers of 2-acrylamido-2-methylpropane sodium sulfonate cryogels. Polym. Int. 2018, 67, 166–177. [CrossRef]

24. Atta, A.M.; Al-Hussain, S.A.; Al-Lohedan, H.A.; Ezzat, A.O.; Tawfek, A.M.; Ahmed, M.A. In situ preparation of magnetic Fe₃O₄Cu₂OFe₂O₄/cryogel nanocomposite powder via a reduction–coprecipitation method as adsorbent for methylene blue water pollutant. Polym. Int. 2018, 67, 925–935. [CrossRef]

25. Atta, A.M.; Abdel Hameed, R.S.; Al-Lohedan, H.A.; Ezzat, A.O.; Hashem, A.I. Magnetite doped cuprous oxide nanoparticles as modifier for epoxy organic coating. Prog. Org. Coat. 2017, 112, 295–303. [CrossRef]

26. Akl, Z.F.; El-Saeed, S.M.; Atta, A.M. In-situ synthesis of magnetite acrylamide amino-amidoxime nanocomposite adsorbent for highly efficient sorption of U(VI) ions. J. Ind. Eng. Chem. 2016, 34, 105–116. [CrossRef]

27. Atta, A.M.; Al-Lohedan, H.A.; Ezzat, A.O.; Eissa, Z.; Oumi, A.B. Synthesis and application of magnetite polyacrylamide amino-amidoxime nano-composites as adsorbents for water pollutants. J. Polym. Res. 2016, 23, 69. [CrossRef]

28. Nguyen, T.H.; Paluck, S.J.; McGahran, A.J.; Maynard, H.D. Poly(vinyl sulfonate) Facilitates bFGF-Induced Cell Proliferation. Biomacromolecules 2015, 16, 2684–2692. [CrossRef] [PubMed]

29. Atta, A.M.; Al-Lohedan, H.A.; Al-Hussain, S.A. Synthesis of Stabilized Myrrh-Capped Hydrocolloidal Magnetite Nanoparticles. Molecules 2014, 19, 11263–11278. [CrossRef] [PubMed]

30. Bucak, S.; Yavuzturk, B.; Sezer, A.D. Magnetic Nanoparticles: Synthesis, Surface Modifications and Application in Drug Delivery. IntechOpen 2012. [CrossRef]

31. Novoselova, I.P.; Safronov, A.P.; Samatov, O.M.; Beketov, I.V.; Medvedev, A.I.; Kurylandskaya, G.V. Water based suspensions of iron oxide obtained by laser target evaporation for biomedical applications. J. Magn. Magn. Mater. 2016, 415, 35–38. [CrossRef]

32. The’venot, J.; Oliveira, H.; Sandre, O.; Lecommandoux, S. Magnetic responsive polymer composite materials. Chem. Soc. Rev. 2013, 42, 7099–7116. [CrossRef] [PubMed]

33. Kozlovskaya, V.; Kharlampieva, E.; Chang, S.; Muhlbauer, R.; Tsukruk, V.V. pH-Responsive Layered Hydrogel Microcapsules as Gold Nanoreactors. Chem. Mater. 2009, 21, 2158–2167. [CrossRef]

34. Okoroafor, E.U.; Newborough, M.; Highgate, D.; Augood, P. Effects of thermal cycling on the crystallization characteristics of water within crosslinked hydroactive polymeric structures. J. Phys. D Appl. Phys. 1998, 31, 3130–3138. [CrossRef]

35. Patil, R.D.; Mark, J.E.; Apostolov, A.; Vassileva, E.; Fakirov, S. Crystallization of water in some crosslinked gelatins. Eur. Polym. J. 2000, 36, 1055–1061. [CrossRef]

36. Liang, Y.N.; Hu, J.; Tam, M.K.C.; Hu, X. CuO nanotubes via an unusual complexation induced block-like self-assembly of poly(acrylic acid). RSC Adv. 2012, 2, 9531–9537. [CrossRef]

37. Nart, Z.; Apohan, N.K. Preparation, characterization and drug release behavior of poly (acrylacid-co-2-hydroxyethyl ethacrylate-co-2-acrylamido-2-methyl-1-propanesulfonylic acid) microgels. J. Polym. Res. 2011, 18, 869–874. [CrossRef]

38. Ng, L.T.; Ng, K.S. Photo-cured pH-responsive polyampholyte-coated membranes for controlled release of drugs with different molecular weights and charges. Radiat. Phys. Chem. 2008, 77, 192–199. [CrossRef]

39. Sahiner, N.; Sagbas, S. Sucrose based ionic liquid colloidal microgels in separation of biomacromolecules. Sep. Purif. Technol. 2017, 196, 191–199. [CrossRef]

40. Ho, Y.S.; McKay, G. Pseudo-second order model for sorption processes. Process Biochem. 1999, 34, 451–465. [CrossRef]

41. Zhu, H.; Fu, Y.; Jiang, R.; Yao, J.; Liu, L.; Chen, Y.; Xiao, L.; Zeng, G. Preparation, characterization and adsorption properties of chitosan modified magnetic graphitized multi-walled carbon nanotubes for highly effective removal of a carcinogenic dye from aqueous solution. Appl. Surf. Sci. 2013, 285, 865–873. [CrossRef]
