Polyethylenimine-Modified Magnetic Chitosan for the Uptake of Arsenic from Water

Norah Salem Alsaiari 1, Fatimah Mohammed Alzahrani 1,⁎, Khadijah Mohammedsaleh Katubi 1,⁎, Abdelfattah Amari 2,3,⁎, Faouzi Ben Rebah 4 and Mohamed A. Tahoon 5,6

Abstract: The removal of heavy metals from water has become a global environmental problem. Various materials have been applied as adsorbent to remove metals from water. In this field, nanomaterials have been gaining increasing interest due to their exceptional properties. In this work, we discuss the synthesis of a core-shell structure nanocomposite by the modification of magnetic chitosan (CS) (Fe₃O₄/CS) with polyethylenimine (PEI) to produce Fe₃O₄/CS/PEI composite for the adsorption of arsenic ions (As(V) and As(III)) from aqueous solution. The synthesized materials were characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), transmission electron microscope (TEM), and vibrating sample magnetometer (VSM). The results indicated the successful combination of three components of the nanocomposite. The adsorption conditions were optimized by studying the effect of different parameters included pH, contact time, initial concentration, and adsorbent dosage. The optimum adsorption pH was found to be 6.7 while the optimum adsorbent dosage was found to be 2.0 and 1.5 g/L for As(III) and As(V), respectively. The removal efficiency for the uptake of As(III) and As(V) ions over Fe₃O₄/CS/PEI nanocomposite at optimum conditions was found to be 99.5 and 99.7%, respectively. The experimental results were fitted using Freundlich’s and Langmuir’s isotherms. The data were more fitted to Langmuir isotherm providing a suggestion of monolayer adsorption with maximum adsorption capacity equal to 77.61 and 86.50 mg/g for the removal of As(III) and As(V), respectively. Moreover, linear regression coefficient (R²) indicated that the adsorption of arsenic ions over the synthesized magnetic nanocomposite obeyed pseudo 2nd order suggesting the chemisorption process. The reusability of the nanosorbent for arsenic uptake using sodium hydroxide as eluent was also assessed up to five cycles. Interestingly, Fe₃O₄/CS/PEI nanocomposite can be considered as a promising adsorbent for As ions’ removal from water and should be tested for the removal of other pollutants.

Keywords: magnetic nanomaterials; arsenic removal; adsorption; core-shell structures
1. Introduction

The 20th most abundant element on the earth’s crust is arsenic [1], which has become the reason of death in many countries [2]. Arsenic poisoning has claimed the lives of millions of people, and millions more are suffering from its toxicity [3]. Now, the most serious problem is arsenic intake with drinking water [4]. The elevated levels of arsenic in drinking water are associated with several anthropogenic and natural activities [5]. Arsenic is commonly present as arsenite (As(III)) in groundwater while presenting as arsenate (As(V)) in surface water [6]. Arsenite is more poisonous and dangerous to humans than arsenate because of its sensitivity to cell-binding sites [7]. The arsenic limit in drinking water according to WHO is 0.01 ppm [8]. Therefore, the decrease of arsenic concentration in water below this limit is a challenge. Various methods have been applied for the removal of arsenic from water such as the adsorption [9], reverse osmosis [10], ion exchange [11], membrane separation [12], electro-coagulation [13], flocculation [14], and precipitation [15].

The adsorption process has been considered as the commonly used method due to several advantages (eco-friendly, efficient, reversibility, economic, and simplicity) [16–21]. In this context, different materials have been used for arsenic removal from water via adsorption method. These materials include metal oxides [22], agricultural wastes [23], biochar [24], clay-based adsorbents [25], aluminum-based adsorbents [26], commercial activated carbon [27], and many other materials. In recent years, nanomaterials have attracted interest as adsorbents due to their exceptional properties [28–33]. Although adsorption efficiency is offered by the nanomaterials, it is not easy to recollect the used adsorbents after the pollutant adsorption. Interestingly, several magnetic nanomaterials have been used for the adsorption of contaminants from aqueous media due to their ease of separation by an external magnet, large surface area, and simple functionalization [34–39]. By using magnetic nanomaterials, filtration and centrifugation conducted after the adsorption process become unnecessary as they are replaced with an easy magnetic separation. Several reports have described the synthesis and the application of low-cost and eco-friendly magnetic adsorbents for water treatment. Among these adsorbents, Fe₃O₄ nanoparticles are one of the main selected materials due to their high surface area, high saturation magnetization, high affinity, low cost, ease of surface modifiability, biocompatibility, and low toxicity [40]. However, the small size of the magnetic nanoparticles (NPs) is an obstacle to their application in adsorption systems. To overcome this problem, Fe₃O₄ nanoparticles were combined with biopolymeric matrix as a supporting platform. Mainly, chitosan (CS) provides great adsorption ability to different types of pollutants such as heavy metals [41], proteins [42], and dyes [43] because of the presence of high hydroxyl and amino groups in its structure. Additionally, chitosan has many advantages that encourage its application in water treatment such as no harmful by-products, high affectivity, and accessibility. However, the practical applications of chitosan face certain difficulties including its dissolution in acidic medium below pH 5.5, and cannot be recovered. Many materials have been impeded by integration with CS support to overcome this disadvantage by cross-linking (e.g., glutaraldehyde as cross-linker). This integration increases the chitosan adsorption efficiency and decreases its solubility in acidic medium. So, the cross-linked CS can be used as excellent adsorbents for the removal of different types of pollutants including anions [44] and clofibric acid [45] from water, especially if modified with proper amines such as polyethylenimine (PEI). Since the branched amine contains abundant secondary and tertiary amino groups, such modified materials are predicted to have high attraction for arsenic ions in water.

Therefore, we can conclude that the use of modified magnetic chitosan nanocomposite as adsorbent material for water treatment purposes can enhance the adsorption power of the materials toward pollutants such as arsenic ions. In this study, we aim to synthesize and characterize magnetic chitosan modified with polyethylenimine nanocomposite (Fe₃O₄/CS/PEI) for the application as adsorbent for the removal of arsenic ions from water. The magnetic, structural, and physicochemical properties of the synthesized nanocomposite were investigated. The arsenic adsorption using synthesized nanocomposite was
determined with the investigation of different parameters’ effect on the adsorption process such as arsenic initial concentration, pH, adsorbent dose, and contact time. The nanocomposite regeneration for several times of use in arsenic ions’ adsorption was investigated, since the nanocomposite has the advantage of magnetic separation that makes simple its separation and reuse. The current study approved that the fabricated Fe$_3$O$_4$/CS/PEI nanocomposite is a promising adsorbent for water treatment.

2. Materials and Methods

2.1. Chemicals and Reagents

All supplied chemicals were analytical grade and used without any modification. Sodium arsenite (NaAsO$_2$, 98.0%), sodium arsenate dibasic heptahydrate (Na$_2$HAsO$_4$·7H$_2$O, 98.0%), branched polyethylenimine (PEI), CS, sodium tripolyphosphate (TPP), epichlorohydrin as a cross-linking agent, ferric chloride hexahydrate (FeCl$_3$·6H$_2$O), and ferrous chloride tetrahydrate (FeCl$_2$·4H$_2$O) were supplied from Sigma-Aldrich. Isopropanol as a solvent was supplied from Al-Nasr Co., Helwan, Egypt. All solutions were prepared using distilled water.

2.2. Synthesis of Fe$_3$O$_4$ Magnetic Nanoparticles

The common co-precipitation chemical method was used for the synthesis of Fe$_3$O$_4$ magnetic nanoparticles as described in the literature [46]. Under nitrogen atmosphere, deionized H$_2$O (200.0 mL) was used for the dissolving of 4.75 g of ferric chloride hexahydrate and 1.747 g of ferrous chloride tetrahydrate, and this mixture was stirred vigorously and heated up to 60 °C. During the stirring process, approximately 7.5 mL of ammonium solution (33% v/v) was added drop-wise. The reaction was kept for 1.0 h at 60 °C to occur and the black product was obtained. Then, deionized H$_2$O was used for the washing of the product until the neutral filtrate was obtained. A vacuum oven was used for drying the product at 60 °C up to 12 h. Importantly, all steps were performed under nitrogen atmosphere to prevent the transformation of the product from one phase to another in air (i.e., from magnetite to maghemite).

2.3. Synthesis of CS-Modified Fe$_3$O$_4$ Magnetic Nanoparticles

Firstly, 0.01 g of CS powder was used for the preparation of CS solution by dissolution in 11.0 mL of acetic acid (2.0%). After that, the CS solution was mixed with 0.26 g of previously prepared magnetic nanoparticles with the sonication up to half an hour to reach the complete dispersion of the nanoparticles. Then, the mixture was vigorously shaken at 600.0 rpm and 60.0 °C with a drop-wise of 50 mL TPP solution (0.02 g/50.0 mL H$_2$O) for the cross-linking of chitosan on the surface of magnetic nanoparticles [47]. The synthesized core-shell nanocomposite (Fe$_3$O$_4$/CS) was filtered and dried using a freeze dryer for 36.0 h at −20 °C.

2.4. Synthesis of Polyethylenimine-Modified Fe$_3$O$_4$/CS

Firstly, 30.0 mL of isopropanol alcohol was used for washing of 0.250 g of Fe$_3$O$_4$/CS nanocomposite. After that, isopropanol containing epichlorohydrin (25.0 mL) was used to suspend this washed Fe$_3$O$_4$/CS nanocomposite with the continuous shaking of the suspension (3.0 h at 70 °C and 150.0 rpm) for the activation reaction between CS’ hydroxylmethyl groups and epichlorohydrin’s epoxy group. Until being washed three times with deionized water to extract unreacted epichlorohydrin, the Fe$_3$O$_4$/CS nanocomposite had been modified with 25.0 mL of polyethylenimine solution for 5.0 h at 90 °C and 150 rpm. Finally, Fe$_3$O$_4$/CS/PEI nanocomposite was washed by distilled water to remove unattached polyethylenimine and dried at 65.0 °C up to 12.0 h. The Fe$_3$O$_4$/CS/PEI nanocomposite became ready for the investigation and adsorption studies.
2.5. Batch Adsorption Experiment

For the study of the adsorption of arsenic ions (As(III) and As(V)) over the surface of synthesized adsorbents, 500.0 mL stock solutions of both ions were prepared by dissolving Na$_2$HAsO$_4$·7H$_2$O (2.080 g) and NaAsO$_2$ (0.8670 g) in distilled water to reach the concentration of 1000.0 mg/L. Then, these stock solutions were diluted using deionized water to acquire the required concentration for the batch adsorption experiment. After each experiment, the adsorbent was separated using an external magnet and the solution was examined for the presence of arsenic ions using an atomic absorption spectrometer. The effect of different parameters on the adsorption process was studied including pH, adsorbent dosage, initial concentration, and contact time. The pH effect was studied by changing the pH value in the range of 3.0 to 11.0 by using an initial concentration of arsenic ions of 10.0 mg/L, 0.50 g/L of adsorbent, and solution volume of 100.0 mL. The effect of adsorbent dosage was also studied in the range of 0.50 to 2.50 g/L at pH of 6.70, 30.0 °C, 150 rpm of shaking for 1.0 day, and solution volume of 100.0 mL. The initial concentration effect was studied in the range of 10.0 to 500.0 mg/L at pH of 6.70, 30.0 °C, 150 rpm of shaking for 1.0 day, solution volume of 100.0 mL, and adsorbent dosage of 2 and 1.5 g/L for As(III) and As(V), respectively. Additionally, the contact time effect was studied by varying the time in the range of 5.0 to 60.0 min at the same experimental conditions. The removal efficiency can be calculated using Equation (1):

$$\text{Removal efficiency (\%) } = \left(\frac{C_i - C_e}{C_i}\right) \times 100, \quad (1)$$

The symbols $C_i$ and $C_e$ denote the initial and equilibrium concentrations of arsenic ions, respectively.

The adsorption capacity can be calculated using Equation (2):

$$\text{Adsorption capacity } (q_e) = \left(\frac{C_i - C_e}{W}\right) \times V, \quad (2)$$

The symbols $W$ and $V$ denote mass of adsorbent (g) and volume of solution (L), respectively.

The adsorption rate was investigated using the kinetic models of pseudo 1st order and pseudo 2nd order according to Equations (3) and (4), respectively:

$$\ln \left(\frac{q_e}{q_t}\right) = \ln q_e - k_1 t, \quad (3)$$

$$\frac{t}{q_e} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right), \quad (4)$$

where $k_1$ (min$^{-1}$) and $k_2$ (g mg$^{-1}$ min$^{-1}$) denote the equilibrium rate constants and $q_t$ denotes the adsorption capacity at $t$ time.

The adsorption mechanism was investigated using the linearized form of Freundlich’s isotherm that can be represented by Equation (5):

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e, \quad (5)$$

The symbols $1/n$ and $K_F$ denote adsorption intensity and Freundlich’s constant, respectively.

Additionally, the adsorption mechanism was investigated using the linearized form of Langmuir’s isotherm that can be represented by Equation (6):

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{\text{max}} 1/C_e}\right) + \left(\frac{1}{q_{\text{max}}}\right), \quad (6)$$

The symbols $K_L$ and $q_{\text{max}}$ denote Langmuir’s constant and maximum adsorption capacity, respectively.

The regression coefficient $R^2$ value was used to determine the best fitting between experimental data and isotherm that determines the mechanism of adsorption.
2.6. Regeneration and Reusability Study

The reusability of synthesized adsorbent was studied up to five successive cycles. In each cycle, the adsorbent was mixed with the arsenic solution (10.0 mg/L, 100.0 mL) followed by the magnetic separation using an external magnet, and the filtrate was examined for the presence of arsenate and arsenite. The separated adsorbent was desorbed and dried at 55 °C for 2 h. The desorption process was achieved by immersing the adsorbent in 0.10 M of sodium hydroxide as eluent, and the mixture was shaken for 3.0 h at 30 °C and 150.0 rpm. Then, the adsorbent was washed several times with deionized H2O and dried in an oven to be ready for the next adsorption-desorption cycle. The removal efficiency of arsenic ions over the studied adsorbent was determined in each cycle to evaluate the ability to reuse the adsorbent material for the uptake of arsenic ions from water several times.

3. Results and Discussion

3.1. The Characterization of Synthesized Nanomaterials

The synthesized nanomaterials of magnetic Fe3O4 nanoparticles, Fe3O4/CS nanocomposite, and Fe3O4/CS/PEI nanocomposite were characterized using different techniques included Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), transmission electron microscope (TEM), and vibrating-sample magnetometer (VSM). For the characterization of the presented functional groups, FT-IR spectra were performed for Fe3O4 nanoparticles, Fe3O4/CS nanocomposite, and Fe3O4/CS/PEI nanocomposite as shown in Figure 1a. For Fe3O4 NPs, Fe–O bond vibration, and O–H bending vibration of absorbed H2O molecules have two significant bands at 622 cm⁻¹ and 3402 cm⁻¹, respectively [48,49]. Additionally, the significant bands of CS were recognized at 1082 cm⁻¹, 1662 cm⁻¹, 2882 cm⁻¹, and 3402 cm⁻¹ corresponding to the axial bending vibration of C-N, C=O stretching of amide I of CS, C-H vibrations of aliphatic –CH2 hydrocarbon stretch, and OH besides NH stretching vibration, respectively [50].

For the nanocomposite Fe3O4/CS/PEI, the C–N–C asymmetrical stretch and the C–N vibration in PEI were represented by the two bands at 447 cm⁻¹ and 1072 cm⁻¹, respectively [51]. Additionally, the branched polymer was indicated by two characteristic bands at 1632 cm⁻¹ and 3422 cm⁻¹ corresponding to N-H deformation and N-H stretch, respectively. Moreover, the secondary amine group of the polymer was represented by 1142 cm⁻¹ and 1312 cm⁻¹ small band. The band at 1462 cm⁻¹ was related to the CH2 deformations. Finally, the clear band at 622 cm⁻¹ approved the presence of Fe-O group. So, the FT-IR results indicated the successful implantation of Fe3O4/CS skeleton by the branched polymer PEI.

Figure 1. FT-IR (a) and XRD (b) of the synthesized Fe3O4, Fe3O4/CS, and Fe3O4/CS/PEI magnetic nanomaterials.

(a)

(b)
The crystalline structure of synthesized nanomaterials was studied using XRD as shown in Figure 1b. For Fe$_3$O$_4$ NPs, the six characteristic crystal planes (440), (551), (422), (400), (311), and (220) were represented by the reflexes at $2\theta = 62, 57, 53, 43, 36$, and $30^\circ$, respectively, and indicated the spinel structure of pristine Fe$_3$O$_4$. It can be viewed that Fe$_3$O$_4$ NPs have inverse spinel structure without another phase, only magnetite [46,49]. XRD patterns of Fe$_3$O$_4$/CS and Fe$_3$O$_4$/CS/PEI nanocomposites were found to be similar to that of pure Fe$_3$O$_4$ indicating the retention of Fe$_3$O$_4$ crystal forms, and the reflex positions were unchanged (i.e., the surface modification of Fe$_3$O$_4$ by CS or polymer did not change the phase or crystalline structure of the magnetic nanoparticles). This may be related to the preparation method of the composite that allowed the coating of chitosan on iron oxide nanoparticles [46]. The average size of synthesized nanomaterials was determined using the Debye-Scherrer Equation:

$$D = \frac{\kappa \lambda}{\beta \cos \theta},$$  

where $\beta$, $\theta$, $\lambda$, $\kappa$, and $D$ denote the full-width half-maximum (FWHM), diffraction angle, wavelength of X-ray beam, Scherrer constant (0.89), and the particle size, respectively. The average size of synthesized Fe$_3$O$_4$/CS/PEI, Fe$_3$O$_4$/CS, and Fe$_3$O$_4$ magnetic nanomaterials was 12.1 ± 0.2 nm, 10.2 ± 0.4 nm, and 9.2 ± 0.3 nm, respectively. This indicated the higher size of Fe$_3$O$_4$/CS/PEI and Fe$_3$O$_4$/CS nanocomposites than that of pure Fe$_3$O$_4$, similar to other results reported in the literature [49]. The morphology of synthesized nanomaterials was also studied by the TEM analysis as shown in Figure 2.

**Figure 2.** TEM images of Fe$_3$O$_4$ nanoparticles (a), Fe$_3$O$_4$/CS nanocomposite (b), Fe$_3$O$_4$/CS/PEI nanocomposite (c), and the particle size distribution of the nanocomposite Fe$_3$O$_4$/CS/PEI (d).
According to the TEM image of Fe₃O₄ NPs (Figure 2a), the particles are homogenous with spherical shape, and the nanoparticles are also aggregated. The TEM image of the Fe₃O₄/CS nanocomposite (Figure 2b) showed a higher particle size of the nanocomposite than that of magnetite, which is compatible with the results of XRD. Additionally, the TEM image of Fe₃O₄/CS/PEI (Figure 2c) showed an increase in the particles' size after the polymer was grafted on the magnetic chitosan. Figure 2b,c showed the core-shell structure of the nanocomposites of Fe₃O₄/CS and Fe₃O₄/CS/PEI, respectively, that can be seen at the boundary of magnetite spherical NPs. This core-shell structure was reported in many previously synthesized magnetic nanomaterials [52–54]. Figure 2d showed the particle size distribution of the nanocomposite Fe₃O₄/CS/PEI that equals to 12 nm, similar to the results of XRD. The most important characteristic of magnetic adsorbents are their magnetic separation from the experimental solution. Therefore, the magnetization curves of the synthesized Fe₃O₄, Fe₃O₄/CS, and Fe₃O₄/CS/PEI are shown in Figure 3.

![Magnetization curves](image)

**Figure 3.** Magnetization curves (inset: magnetic separation of Fe₃O₄/CS/PEI nanocomposite) of the synthesized Fe₃O₄ NPs, Fe₃O₄/CS, and Fe₃O₄/CS/PEI nanomaterials.

According to Figure 3, all synthesized nanomaterials are ferromagnetic with saturation magnetization (Mₛ) of 71, 62, and 51 emu g⁻¹ for Fe₃O₄, Fe₃O₄/CS, and Fe₃O₄/CS/PEI, respectively. The clear drop of saturation magnetization by the modification of magnetite with chitosan was attributed to the non-magnetic properties of chitosan. Similarly, the drop occurred when the PEI was added. This was attributed to the diamagnetic properties of the polymer. The drop of magnetic properties after the modification of magnetite NPs was reported in previous studies [55,56]. This order of magnetism of the three synthesized nanomaterials was reflected on their time of separation with an external magnet that was found to equal 69 s, 93 s, and 119 s for Fe₃O₄, Fe₃O₄/CS, and Fe₃O₄/CS/PEI, respectively. Figure 3 (inset) showed the magnetic separation of Fe₃O₄/CS/PEI nanocomposite with an external magnet. The synthesized nanomaterials have excellent magnetic properties sufficient for their application in water treatment with the benefit of the adsorbent magnetic separation. Moreover, Brunauer–Emmett–Teller surface area (S_BET) was analyzed for the three synthesized nanomaterials as shown in Figure 4. The S_BET values were found to equal 82.5, 83.1, and 74.6 m² g⁻¹ for Fe₃O₄, Fe₃O₄/CS, and Fe₃O₄/CS/PEI, respectively. The results indicated the small difference in the S_BET value between Fe₃O₄ and Fe₃O₄/CS while the value was decreased by the addition of branched PEI indicating the effect of PEI on the surface properties of magnetic chitosan. This means that the core-shell structure of Fe₃O₄/CS/PEI nanocomposite was formed by the adsorption of PEI on the surface of magnetic chitosan that will save additional capturing sites for arsenic ions in water.
3.2. The Effect of Adsorbent Dosage

The effect of Fe₃O₄/CS/PEI nanocomposite’s amount on the adsorption of As(V) and As(III) ions from water was studied in the range of 0.50 g/L to 2.50 g/L as shown in Figure 5a. During the study of adsorbent dosage effect, the other factors which were kept constant included the initial adsorbate concentration, temperature, and pH value that were 10 mg/L, 30 °C, and 6.7, respectively. According to Figure 5a, the increased amount of adsorbent from 0.50 g/L to 2.0 g/L caused an increase in the removal efficiency of As(III) from 52.0% to 99.5% while the dosage increase from 0.50 g/L to 1.5 g/L caused an increase in the removal efficiency of As(V) from 95.5% to 99.7%. This relation between adsorbent dosage and the increased removal efficiency was attributed to the vacant adsorption sites that increase by the addition of more adsorbent dosage.

Figure 5. The adsorbent dosage effect (a) and pH value effect (b) on the adsorption of As(III) and As(V) ions over the surface of Fe₃O₄/CS/PEI nanocomposite.
As shown in Figure 5a, there was no increase in the removal efficiency of As(III) and As(V) when the dosage of Fe$_3$O$_4$/CS/PEI nanocomposite was increased from 2.0 g/L to 2.50 g/L and from 1.50 g/L to 2.0 g/L, respectively, meaning that the equilibrium has been reached. So, these values were selected as the optimum adsorbent dosages.

3.3. The Effect of PH Value

The effect of pH value on the adsorption of As(V) and As(III) ions from water over the surface of Fe$_3$O$_4$/CS/PEI nanocomposite was studied in the range of 3.0 to 11.0 as shown in Figure 5b. The pH effect is known to be a very important factor due to its dual effect on ionic form of the adsorbate and the surface charge of the adsorbent. According to Figure 5b, the adsorption of As(III) ions was decreased from pH > 9.0. While in the pH range of 5.0 to 9.0, there was no significant pH effect on their removal. This behavior could be described according to the ionic form of As(III) ions at different pH values. At pH < 9.0, As(III) ions were present in the forms of HAsO$_4^{2-}$ and H$_2$AsO$_3^{-}$ that allow their maximum adsorption via H-bonding and Van der Wall’s forces. Thus, the maximum removal of As(III) ions was reached at pH (6.0 to 8.0). Additionally, the pH increase caused an increase in the removal of As(V) ions over the surface of Fe$_3$O$_4$/CS/PEI nanocomposite until the value of pH (6.7), then the removal decreased with the pH increase. This behavior could be also explained according to the change of ionic form with pH change. At pH of 6.0 to 8.0, the As(V) ions were present as HAsO$_4^{2-}$ and HAsO$_4^{-}$. At pH of 8.0 to 10.0, the As(V) ions were present as HAsO$_4^{2-}$. However, at pH of 3.0 to 6.0, As(V) ions were present as HAsO$_4^{-}$ making the maximum removal reached at pH of 6.7. These results clarify that the pH value is a key parameter for the removal of arsenic ions over the studied magnetic nanocomposite.

3.4. The Adsorption Kinetics

The effect of contact time was studied for the removal of As(V) and As(III) ions on the surface of Fe$_3$O$_4$/CS/PEI nanocomposite as shown in Figure 6a. The effect of time on the adsorption process was studied in the range of 5.0 to 60.0 min. According to Figure 6a, the maximum and rapid capturing of both arsenic ions was achieved in the first 5.0 min and when the time increased, there was no significant increase in the adsorption capacity of the nanosorbent toward the As(V) and As(III) ions. The adsorption equilibrium was achieved during the first 30.0 min. The large number of available and vacant adsorption sites over the surface of the nanocomposite adsorbent is responsible for this rapid kinetic action. After the equilibrium is reached, all adsorption sites were occupied by the pollutants’ ions and the contact time had no effect on the adsorption process. The kinetic behavior of arsenic removal over Fe$_3$O$_4$/CS/PEI nanocomposite was studied using the pseudo 1st order and the pseudo 2nd order equations as shown in Figure 6b,c, respectively. According to Figure 6b,c, the pseudo 2nd order showed better fit to the adsorption kinetics for the uptake of both arsenic ions over Fe$_3$O$_4$/CS/PEI nanocomposite than the pseudo 1st order and this was clear from the value of the regression coefficient ($R^2$). $R^2$ value is 0.999 for As(V) and As(III) ions in the case of pseudo 2nd order fit, while it is 0.630 and 0.603 for As(V) and As(III) ions, respectively, in case of pseudo 1st order fit. The pseudo 1st order and the pseudo 2nd order kinetic parameters for the uptake of arsenic ions over the studied magnetic nanocomposite were introduced in Table 1.
Table 1. Kinetic parameters for the uptake of arsenic ions over the studied magnetic nanocomposite Fe₃O₄/CS/PEI.

| Item               | Coefficient | Pollutant | Pollutant |
|--------------------|-------------|-----------|-----------|
|                    |             | As(III)   | As(V)     |
|                    |             | 0.603     | 0.630     |
| Pseudo 1st order   |             | k₁        | -7.90 × 10⁻⁴ | -7.70 × 10⁻⁴ |
|                    |             | qₑ (mg/g) | 5.1       | 6.1       |
| Pseudo 2nd order   | R²          | 0.999     | 0.999     |
|                    | K₂          | 0.43      | 0.35      |
|                    | qₑ (mg/g)  | 15.90     | 23.70     |
| Freundlich's isotherm | R²        | 0.938     | 0.943     |
|                    | 1/n         | 0.5563    | 0.5200    |
|                    | Kᵥ          | 2.46      | 4.54      |
| Langmuir's isotherm | R²         | 0.999     | 0.999     |
|                    | Rᵢ          | 0.5649    | 0.4249    |
|                    | Kᵥ (L/mg)  | 0.0158    | 0.0394    |
|                    | qₑ max (mg/g) | 77.61     | 86.50     |

The agreement between the experimental data and the pseudo 2nd order kinetic model indicated that the capturing of arsenic ions over this polymer-modified magnetic chitosan happened via the chemisorption mechanism. Additionally, the chemical interaction between the arsenic ions and the adsorbent surface was the rate-limiting step [57].

The agreement between experimented data and the pseudo 2nd order for the treatment of aqueous arsenic ions was previously reported in the literature using another magnetic nanocomposite [58].

Figure 6. The contact time effect (a), pseudo first order plot (b), and pseudo second order plot (c) for the adsorption of As(III) and As(V) ions over the surface of Fe₃O₄/CS/PEI nanocomposite.
The agreement between the experimental data and the pseudo 2nd order kinetic model indicated that the capturing of arsenic ions over this polymer-modified magnetic chitosan happened via the chemisorption mechanism. Additionally, the chemical interaction between the arsenic ions and the adsorbent surface was the rate-limiting step [57]. The agreement between experimented data and the pseudo 2nd order for the treatment of aqueous arsenic ions was previously reported in the literature using another magnetic nanocomposite [58].

3.5. The Adsorption Isotherm

The effect of arsenic initial concentration on their adsorption over the surface of Fe₃O₄/CS/PEI nanocomposite was studied as shown in Figure 7a. According to Figure 7a, the increased initial concentration of arsenic caused an increase of the adsorption capacity indicating the high affinity between As(III) and As(V) ions and the nanosorbent.

![Figure 7a](image)

![Figure 7b](image)

![Figure 7c](image)

**Figure 7.** The arsenic initial concentration effect (a), Freundlich’s isotherm fitting (b), and Langmuir’s isotherm fitting (c) for the adsorption of As(III) and As(V) ions over the surface of Fe₃O₄/CS/PEI nanocomposite.

This behavior was attributed to the availability of ions to be adsorbed. To understand the adsorption mechanism of arsenic ions over the Fe₃O₄/CS/PEI nanocomposite, the
information related to the binding affinity and adsorption capacity must be obtained and thus achieved via the study of adsorption isotherm. As mentioned in the experimental section, the two classical isotherm models (Freundlich and Langmuir) were used to fit the experimental data of the arsenic ions’ adsorption over the synthesized nanosorbent as shown in Figure 7b,c. The parameters of Freundlich and Langmuir were also presented in Table 1. According to Figure 7b,c, and the R² values, the experimental data was more fitted to Langmuir’s isotherm than Freundlich’s isotherm. R² values are 0.999 for both ions of arsenic in case of Langmuir’s fit while equal to 0.94 in case of Freundlich’s fit. Freundlich’s isotherm suggests the heterogeneous adsorption of adsorbates over energetically dissimilar adsorption sites while Langmuir’s isotherm suggests the homogeneous adsorption of adsorbates over energetically equal sites. Thus, the adsorption of As(III) and As(V) ions occurred as a monolayer over Fe₃O₄/CS/PEI nanocomposite. The calculated maximum adsorption capacity (qₘₐₓ) was found to equal 86.50 and 77.61 mg/g for the uptake of As(V) and As(III), respectively. These values were compared to previous results in the comparative study section. Moreover, the adsorption process of arsenic ions is favorable due to the value of Rₑ that was less than 1.0.

3.6. Regeneration and Reusability Study

The reusability of any adsorbent is a key factor determining its sustainability, effectiveness, and applicability for real samples treatment. The reusability of Fe₃O₄/CS/PEI nanocomposite for the uptake of As(III) and As(V) ions was studied up to five sequential cycles as shown in Figure 8. Each cycle included the adsorption of polluted ions followed by desorption of adsorbed ions using alkaline solution (0.1 M of NaOH) as eluent. Herein, the magnetic separation was used to collect the adsorbent to be washed and dried for the next cycle.

![Figure 8](image-url)

**Figure 8.** The reusability of Fe₃O₄/CS/PEI magnetic nanomaterials for the removal of As(V) and As(III) ions up to five successive cycles.

According to Figure 8, the removal efficiency of As(III) and As(V) ions using Fe₃O₄/CS/PEI nanocomposite was dropped from 99.5% to 92.0% and from 99.7% to 94.0%, respectively, after the 5th cycle. The literature reported the use of Fe₃O₄/CS for the uptake of As(III) and As(V) ions from water with the retention of only 76.0% and 88.0% of the initial efficiency after the 5th cycle [59]. The small drop of the removal efficiencies of As(III) and As(V) ions over Fe₃O₄/CS/PEI nanocomposite was attributed to the damaged adsorption sites after each cycle. However, the removal efficiencies for the uptake of both ions over Fe₃O₄/CS/PEI nanocomposite remain over 90.0% after the 5th cycle indicating the ability to reuse this synthesized adsorbent to remove arsenic ions for several times. As a result,
the Fe$_3$O$_4$/CS/PEI nanocomposite can be used for real water treatment with a low cost of processing due to the excellent results of reusability.

3.7. Comparative Study

The maximum adsorption capacity and pH value for the removal of arsenic ions (As(V) and As(III)) were compared with previously studied adsorbents as tabulated in Table 2. According to Table 2, the adsorption capacities in the current study are comparable to the values reported in the literature indicating the affinity of the Fe$_3$O$_4$/CS/PEI nanocomposite for arsenic ions. However, the difference in the adsorbent efficiency between materials can be explained by the applied operating conditions and the variability of the interactions between pollutants and the material functional groups. Generally, strong interactions with the specific functional groups of the adsorbent surface permitted high adsorption capacity. Subsequently, the synthesized Fe$_3$O$_4$/CS/PEI nanocomposite can be considered as a promising nanosorbent for water treatment that must be investigated for the capturing of additional metals, dyes, and pharmaceuticals in the future. However, the complete view about the treatment study should be obtained by the determination of the thermodynamic parameters [60–62] of the adsorption process.

| Adsorbent                                | pH Value | Removal Capacity (mg/g) | Ref.         |
|------------------------------------------|----------|-------------------------|--------------|
|                                          |          | As(V) | As(III) |          |
| Fe$_3$O$_4$/CS/PEI                      | 6.70     | 86.50 | 77.61   | This study|
| Fe–Mn binary oxide-impregnated granular activated carbon | 4.0      | 16.0  | 18.0    | [63]       |
| Egg shell                                | 4.10     | 8.0   | 12.0    | [64]       |
| Tea waste                                | 7.0      | 5.0   | 7.30    | [64]       |
| MnO$_2$-impregnated alginate beads       | 6.50     | 6.50  | -       | [65]       |
| PEI-coated bacterial biosorbent          | 4.0      | 63.0  | -       | [66]       |
| Magnetic pinecone biomass                | 8.0      | -     | 18.0    | [67]       |
| Turbinaria vulgaris sp.                  | 4.0      | 26.0  | -       | [68]       |
| Iron oxide/nanoporous carbon             | 8.0      | -     | 6.69    | [69]       |
| MIL-53(Al)-GO nanocomposites             | 9.0      | -     | 65.0    | [70]       |
| Dust ferric hydroxide                    | 7.9      | 6.90  | 3.50    | [71]       |
| Micro-sized tetravalent manganese feroxyhyte | 8.0      | 15.4  | -       | [72]       |
| Micro-sized granular ferric hydroxide    | 8.0      | 22.4  | -       | [72]       |

4. Conclusions

The present study discussed the successful fabrication of magnetic chitosan modified with polyethylenimine to produce core-shell structure nanocomposite defined as Fe$_3$O$_4$/CS/PEI. As described in the experimental section, chitosan and magnetite nanoparticles were cross-linked using Na$_5$P$_3$O$_10$ while the modification of the magnetic chitosan using PEI was achieved using epichlorohydrin. The successful combination between three parts of the nanocomposite (Fe$_3$O$_4$, CS, and PEI) was confirmed by using different characterization techniques including XRD, FT-IR, TEM, and VSM. Additionally, the spinel structure of magnetite was not changed by the modification process as shown from XRD. The synthesized nanocomposite was investigated for the adsorption of arsenic ions (As(V) and As(III)) from aqueous solution. Different parameters such as pH, contact time, adsorbent dosage, and initial concentration were examined to define the optimum conditions of adsorption. The arsenic adsorption over the Fe$_3$O$_4$/CS/PEI magnetic nanocomposite
was found to be pH dependent and the optimum pH was detected to be 6.7. The arsenic removal over Fe$_3$O$_4$/CS/PEI nanocomposite according to the adsorption isotherm results occurred as a monolayer over energetically symmetrical adsorption sites. Moreover, the experimental data was better fitted with the pseudo 2nd order kinetics indicating the chemisorption uptake of arsenic ions over the nanocomposite. The magnetic separation of the synthesized nanocomposite enhanced their reusability for arsenic removal up to five successive cycles by using sodium hydroxide as eluent solution. The results indicated the ability to reuse the nanocomposite for arsenic removal with high efficiency that reduces the overall cost of water purification. All results indicated that Fe$_3$O$_4$/CS/PEI nanocomposite can be considered as a promising adsorbent for the removal of As(V) and As(III) ions from aqueous solution, and must be examined in the near future for the removal of additional pollutants.

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