Ionic gelation synthesis, characterization and adsorption studies of cross-linked chitosan-tripolyphosphate (CS-TPP) nanoparticles for removal of As (V) ions from aqueous solution: kinetic and isotherm studies

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ABSTRACT
The CS-TPP nanoparticles were synthesized and their efficiency for removal of arsenic (V) ions at the optimum conditions was investigated. The optimum conditions for CS-TPP nanoparticles were obtained with the mass ratio of tripolyphosphate to chitosan of 1:2 and pH = 5.0. The experimental data for the adsorption of As (V) ions followed the Freundlich adsorption isotherm and the maximum adsorption capacity was 77 mg/g at pH = 6.0. All isotherm experiments were performed at room temperature (25°C). The crosslinking of sodium tripolyphosphate with the chitosan led to a decrease in crystallinity of the formed particles which then resulted in an improvement in metal ion sorption properties.

1. Introduction
Arsenic is a well-known toxin and carcinogen and its effects on human cells have been studied extensively (Anetor et al. 2007, Stevens et al. 2010, Rostami et al. 2017, Khan et al. 2020). Arsenic is a naturally occurring element found in the environment that originated from natural and anthropogenic sources (Ng et al. 2003, Amaibi et al. 2019, Dousova et al. 2020, Mitra et al. 2020). Acute and chronic exposure to arsenic results in lung cancer, heart attacks, nausea, and gastrointestinal disease (Hopenhayn 2006, WHO, 2010, Abdul et al. 2015, Flora 2020). In natural waters, especially in drinking water, arsenic can be mostly found in trivalent (As³⁺) or pentavalent (As⁵⁺) forms (Boddu et al. 2008). According to WHO and U.S. EPA, the maximum concentration limit (MCL) for As in drinking water is 10 µg/L (Chen and Chung 2006).

The chitosan and chitosan nanoparticles have extensively been used for the removal of heavy metals from contaminated water due to its relatively low cost and availability (Crini and Badot 2008, Abdul et al. 2015, Zafarzadeh and Mehdinejad 2015, Baghanc et al. 2016, Hayatiet al. 2016, Mehdinejad and Bina, 2018, Sanchayanukun and Muncharoen 2019, Salehi et al. 2020, Zubair et al. 2020). Conventional adsorbents used in arsenic removal are activated carbons, alumina, soils, and resins, which can be coated with different materials such as iron or alumina (Adlnasab et al. 2019, Asere et al. 2019, Ghosh et al. 2019, Inchaurreondo et al. 2019, Maghsodi and Adlnasab 2019, Matović et al. 2019). The main disadvantages of those adsorbents being used in water treatment are the difficulty of separating adsorbed contaminants from the adsorbent and formation of the waste stream (Tuutijärvi et al. 2009).

Chitosan is a natural polycationic linear polysaccharide obtained from chitin, which is the principal component of protective cuticles of crustaceans such as crabs, shrimps, prawns, and lobsters (Bina et al. 2009, Cheung et al. 2015, Perini et al. 2020, Zo et al. 2020). It is non-toxic, cost-effective, biodegradable, and bio-compatible adsorbent (Ahmed et al. 2014, Chopra and Ruhi 2016, Bakshi et al. 2020). Chitosan is insoluble in most of the solvents but it is soluble in dilute organic acids such as acetic acid, formic acid, succinic acid, lactic acid, and...
malic acid. This is because chitosan can be considered as a strong base as it possesses primary amino groups with a pKₐ value of 6.3. At low pH values, these amino groups get protonated and become positively charged and that makes chitosan a water-soluble cationic poly-electrolyte. On the other hand, as the pH increases above 6, chitosan’s amino groups become deprotonated and the polymer loses its positive charge and becomes insoluble (Ahmed et al. 2013, Kulkarni et al. 2015). There are several adsorbent synthesis techniques including the ionic gelation technique. This technique has numerous advantages such as (1) use of aqueous media (2) preparation of small and compactly-structured particles; (3) control of colloidal characteristics of the nanoparticles by the variation of formulation and process parameters; (4) the possibility of encapsulation of a wide range of molecules for different intended applications (Hussain and Sahudin 2016).

The mechanism of As (V) removal using chitosan nanoparticles has been studied by a number of researchers; however, the removal of As (V) by nanoparticles of chitosan powder and application to process design is novel. Furthermore, this study uses nanoparticles of chitosan without chelation with other materials while previous studies used it as a composite of nano chitosan with sodium alginate, chitosan-based nanofibers and metals. Using the ionic gelation technique, the mass ratio of sodium tripolyphosphate solution to chitosan was varied from 1 to 2.5 in order to optimize the arsenic removal despite the previous studies that used a limited range of 1 to 1.5.

2. Materials and methods

2.1. Materials

Chitosan powder (deacetylated chitin; poly- [1–4]-β-glucosamine, deacetylation degree of 85%) was purchased from GMA Chemical Company. The standard solution (1000 mg/L) of As (V) was procured from Chem-lab Company. Acetic acid (99%) from Merck (Darmstadt, Germany) and tripolyphosphate (TPP) from Sigma Aldrich were purchased. Additionally, double-distilled deionized water was used throughout the work. The pH values of the experiments were adjusted by the addition of (0.1 M) HCl (Merck company) and (0.1 M) NaOH (Merck company) solutions.

2.2. Synthesis of chitosan nanoparticles (CS-TPP nanoparticles)

The CS-TPP nanoparticles were synthesized based on the ionic gelation technique (Fernández-Urrusuno et al. 1999, Vimal et al. 2012, Saharan et al. 2013, Vimal et al. 2013, Hashad et al. 2016). First, chitosan solution of 2 mg/mL was dissolved at 0.5% [w/v] acetic acid under magnetic stirring at 800 rpm at room temperature (25°C) for 24 h. Then, 2 mL mL of sodium tripolyphosphate solution (Na₅P₃O₁₀· TPP) (0.25% w/v) was added drop by drop to 5 mL of the chitosan solution (ratio 2.5:1 of CS: TPP) under magnetic stirring at 800 rpm using a titration tube, and mixing was continued to obtain a homogenous colloidal solution. Thereafter, the mixture obtained in the previous step was purified by centrifugation (12000 rpm (35000 G) at 10°C for 30 min). The supernatants were discarded, and the CS-TPP was rinsed with distilled deionized water for further freeze-drying (Alpha1-2ldplus, Martin Christ, Germany) under the following conditions: a primary drying step for 48 h at −30°C and a subsequent drying step while the temperature gradually raised to +20°C. Finally, the dried precipitates were crushed using a mortar and pestle (Fernández-Urrusuno et al. 2019, Vimal et al. 2012, Saharan et al. 2013, Vimal et al. 2013, Hashad et al. 2016). These CS-TPP nanoparticles were kept in a glass tube at a dark place and room temperature until being used. The schematic of CS-TPP nanoparticles synthesis is shown in Figure S1.

2.3. Characterizations of CS-TPP nanoparticles

2.3.1. Morphology

The morphological examination of the CS-TPP nanoparticles was performed by SEM (Scanning Electron Microscopy) at 20 kV, T = 25°C, the mass ratio of 2:1 CS: TPP, and pH = 5. Fourier-transform infrared spectroscopy (FT-IR) was taken on the Shimadzu Spectrum model 4800s in a range of 400–4000 cm⁻¹. The X-ray diffraction (XRD) characterization of chitosan and CS-TPP nanoparticles was done by an X-ray scattering Shimadzu XD-DI diffract meter using Ni filter CuKα (λ = 0.154 nm) radiation. Samples were scanned at a scan rate of 5°/per min.

2.3.2. Zero point of charge (pH_zpc)

The surface chemistry of any material is determined by the acidic or basic character of its surface. Therefore, it is of high importance to know the surface charge of the material in the aqueous media, especially in adsorption studies because particles with the high surface area could be produced; however, if the surface charge of the material is repulsing the adsorption due to possessing the same charge as the adsorbate, then the pH modification is required in order to find the pH range that results in optimal adsorption. It
is also required to find the pH at which the surface charge of the material is zero in the aqueous media or in other words the pH_{zpc} (pH point of zero charges) of the adsorbent material. The pH_{zpc} is the point where the curve pH_{final} vs. pH_{initial} crosses the line pH_{initial} = pH_{final} (Faria et al. 2004). The pH_{zpc} of samples were obtained as follows: 50 mL of 0.01 M NaCl solution was placed in a closed Erlenmeyer flask. The pH was adjusted to a value between 2 and 12 by adding 0.1 M HCl or 0.1 M NaOH solutions. Then, 0.15 g of CS-TPP nanoparticles was added, and the final pH values were measured after 48 h under agitation at room temperature by a pH meter (Metrohm 827, Switzerland).

2.4. Batch adsorption experiments

Isotherm experiments and adsorption kinetics were performed by addition of a specific amount of CS-TPP nanoparticles in a series of 250 mL Erlenmeyer flasks containing a known amount of As (V) ions and then flasks were agitated on a laboratory shaker at 150 rpm and room temperature (25°C). The effect of contact time on the sorption capacity of CS-TPP nanoparticles was studied in the range 0 – 150 min. For optimal pH selection, a constant dose of CS-TPP nanoparticles was added to the sample and the jar tests were performed at various pH (4, 5, 6, 7, and 8). Based on the optimal pH, the effect of the initial concentration of As (V) on the adsorption was studied by varying C_0 of As (V) ions from 0.05 to 4 mg/L. Then, the concentration of CS-TPP nanoparticles was varied from 0.1 to 1 mg/mL in order to find the optimal As (V) removal.

At the end of each experiment, the obtained suspensions were centrifuged at 3000 rpm for 15 min in order to separate the insoluble matter from the suspensions. The solution obtained from the centrifuge was then filtered by Whatman paper (45 μm) and analyzed for As (V) using Atomic Absorption Spectrometer 8020. The removal efficiency of As (V) ions (R%) and the amount of adsorbed arsenic (q_e) were calculated according to the equations presented in Table S1.

3. Results and discussion

3.1. Adsorbent characterization

Sodium tripolyphosphate (TPP) is the most widely used ion crosslinking agent owing to its nontoxic properties (Fan et al. 2012). The structure of the chitosan nanoparticles being formed from the cross-linking of chitosan and TPP agent are shown in Figure S2. As shown in Figure S2, cross-linking was induced by electrostatic ad sorption reaction between the protonated amino acid groups in the chitosan and the negative charge on the P-O groups in the TPP. SEM analysis of CS-TPP nanoparticles is shown in Figure 1. As shown in Figure 1, synthesized CS-TPP nanoparticles have a homogeneous morphology and a rough surface that exhibits a well-developed open pore structure (Kalkan et al. 2012).

The particle size of a material is a highly important component in understanding its physiochemical properties. The specific surface area increases as the particle size decrease. It also increases if the particle is porous. So, it is important to acquire the average particle size as well as the specific surface area to evaluate the activity and adsorption capacity of the synthesized material (Ikenyiri and Ukpaka 2016). The mean particle size of CS-TPP nanoparticles (D) was acquired using XRD analysis via Debye–Scherrer’s equation as follows (Kalkan et al. 2012, Baghani et al. 2016):

\[ D = \frac{K\lambda}{b\cos \theta} \]

where D is the thickness of CS-TPP nanoparticles (nm), \( \lambda \) is the X-rays wavelength (0.15406 nm), \( \theta \) is the Bragg angle, K is the Debye–Scherrer constant (0.9), and \( b \) is the corrected full width. Applying the Equation (1) to the result of the size distribution illustrated that the size of the synthesized nanoparticles was under 24.9 nm at 2\( \theta \) and \( b \) of 29.359\(^\circ\) and 3.029\(^\circ\), respectively.

The X-ray diffraction profile of chitosan powder and CS-TPP nanoparticles are shown in Figure 2(a,b), respectively. As shown in Figure 2(a), for chitosan powder, the crystalline regions correspond to the peaks at 10.186\(^\circ\) and 20.182\(^\circ\) on the XRD spectrum. Previous studies have also shown the presence of two
strong peaks at the $2\theta$ range of 10 to 22 on the XRD spectrum (Qi et al. 2004, Kwok et al. 2014). These peaks have shown that the chitosan powder has a characteristic peak of an allomorphic crystalline form. Figure 2(b) shows a number of sharp peaks at $2\theta$ of 29.359°, 35.912°, 39.361°, 44.345°, 47.345°, 48.549°, and 57.563° for CS-TPP nanoparticles. The decrease in the chitosan peak and the appearance of less intense peaks in the XRD spectra of the CS-TPP nanoparticles (Figure 2(b)) indicated a decrease in crystallinity of chitosan which is due to the reduction of the polymer chain size that is better suited for the adsorption purposes (highly amorphous nature) (Qi et al. 2004). Furthermore, it could be deduced from Figure 2(b) that the structure of CS-TPP nanoparticles is comprised of a dense network of interconnecting polymer chains cross-linked to each other by the TPP counter ions.

The Fourier Transform Infrared Spectroscopy (FTIR) spectra of chitosan and CS-TPP nanoparticles are shown in Figure 3(a,b), respectively. The peaks at 3395.29 cm$^{-1}$ in chitosan and 3394.24 cm$^{-1}$ in CS-TPP nanoparticles are due to the NH$_2$ and OH stretching vibrations. A shift from 3395.2 to 3394.2 cm$^{-1}$ and a sharper peak in the CS-TPP nanoparticles indicates that the hydrogen bonding is enhanced due to arsenic adsorption. The band at 1608.25 cm$^{-1}$ is attributed to the CONH$_2$ group. The peak at 1516 cm$^{-1}$ for chitosan is sharper than the peak at 1608.2 cm$^{-1}$ for the CS-TPP nanoparticles which shows a high degree of deacetylation of the chitosan. This is in accordance with the findings of a previous study (Boddu et al. 2008). In CS-TPP nanoparticles, two sorption bands appeared at 1607.61 and 1516.88 cm$^{-1}$ which indicates that the ammonium groups were cross-linked with tripolyphosphate molecules (Figure 3(b)). The
absorption bands observed at 1055.3 and 859.98 cm$^{-1}$ for the CS-TPP nanoparticles were due to the stretching vibration of the P=O and P–O of the tripolyphosphate ion, respectively. TPP is a polyfunctional cross-linking agent and can create five ionic cross-linking points with amino groups of chitosan. Chitosan nanoparticles prepared by TPP as an anionic crosslinker are homogeneous, and possess a positive surface charge that makes them suitable for heavy metals adsorption applications.

### 3.2. Effect of initial pH of the solution

The removal of heavy metals from aqueous solution using adsorption processes depends on the pH of the solution (Baghani et al. 2016, Baimenov et al. 2020, 

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**Figure 3.** The FTIR spectra of chitosan (a) and CS-TPP nanoparticles (b).
Kuczajowska-Zadrożna et al. (2020). The effect of pH on the As (V) adsorption is shown in Figure 4(a). According to Figure 4(a), the highest As (V) removal was achieved at pH = 6. The increase in the pH of the solution from 4 to 6 increased the arsenate adsorption and the removal efficiency was increased from 55% to 75%. This could be due to the fact that at low pH values, the amine group and tripolyphosphate group of chitosan nanoparticles are protonated to varying degrees, leading to a reduction in the number of binding sites and therefore, the As ion uptake is low. Because arsenic is an anionic in nature which leads to higher degrees of protonation when the pH is increased above neutral, competitor effect between the chitosan nanoparticles and arsenic ions is decreased leading to electrostatic repulsion, thus when the pH is increased above 6, the precipitation of arsenic trioxide occurs leading to a decrease in sorption of chitosan nanoparticles. Another reason could be due to the positive chitosan charge having a greater tendency to adsorb anions. According to a previous study, this increase in As (V) removal could be due to the release of hydroxide ions (OH\(^-\)) in the protonation process of free amine groups (NH\(_2\)) present in the CS-TPP nanoparticles (Wang et al. 2006). Moreover, the amine groups on chitosan are strongly reactive with arsenate ions due to the free-electron doublets of the nitrogen atoms (Kwok et al. 2014). The pH\(_{zpc}\) of CS-TPP nanoparticles was equal to 6.5, indicating that below this pH value, the CS-TPP nanoparticles have a positive charge whereas the surface of the adsorbent is negatively charged at pH values higher than pH\(_{zpc}\). The adsorption rate decrease at high pH values is due to the repulsive electrostatic forces in the solution (Tuutijärvi et al. 2009).

### 3.3. Effect of contact time on As (V) removal by CS-TPP nanoparticles

Figure 4(b) shows the effect of contact time on the adsorption of arsenate ions onto the CS-TPP nanoparticles. As shown in Figure 4(b), the arsenate ions
removal rate was increased when the contact time was increased from 30 to 90 min which could be due to the availability of adsorption sites on the adsorbent. The maximum adsorption capacity of arsenate was obtained at 90 min. Moreover, a rapid and high arsenate ions adsorption onto the adsorbent occurred within the first 30 min. This behavior is due to the fact that all the active adsorption sites are unoccupied at the start of the reaction and this results in an initially high adsorption rate which goes down after most of the active sites on the CS-TPP nanoparticles are occupied by arsenate ions (Kwok et al. 2014).

3.4. Effect of initial concentration on As (V) removal by CS-TPP nanoparticles

Figure 4(c) demonstrates the effect of initial concentrations on As (V) on the adsorption of arsenate ions using the CS-TPP nanoparticles. It is shown that the removal percentage was increased from 21 to 61% with increasing the arsenate concentration from 0.05 to 0.5 mg/L, respectively. After that, with increasing the concentrations of As (V) beyond 0.5 mg/L, the removal percentage decreased until dropping down to 33.5% for the initial concentration of 4 mg/L for As (V). The main reason for the reduction in removal percentage is the limited number of active sites on the adsorbent surface due to being saturated by As (V). The results of this work showed that the As (V) removal efficiency decreased with the increase in initial As (V) concentration. In low concentrations, the ratio of the initial number of moles of As (V) ions to the available surface area of adsorbent is large and subsequently, the fractional adsorption becomes independent of initial concentration. Increasing adsorption capacity could be related to the reactions between the metal ion molecules and the adsorbent surface or due to the increased repulsion between the molecules, which is consistent with the results of a previous study conducted by Soltani et al. (2017). However, at higher concentrations, the removal percentage decreases from 61 to 33.5% because the available sites of adsorption become fewer, and hence the percentage removal of metal ions which depends upon the initial concentration, decreases. Our finds were according to the obtained results by Sivakami (Sivakami et al. 2013).

3.5. Effect of CS-TPP nanoparticles dosage on As (V) removal

Figure 4(d) demonstrates the effect of different doses of CS-TPP nanoparticles on As (V) removal. As shown in Figure 4(d), increasing the adsorbent dose from 0.1 to 0.5 g/L increased the removal efficiency from 13 to 57%. This increase in As (V) removal could be explained by the increase in available sites on the surface of adsorbent at higher doses of CS-TPP (Ehrampoush et al. 2015). This finding is in accordance with a previous study that was conducted on arsenic adsorption from aqueous solution using chitosan nanoparticles (Anto and Annadurai 2012).

3.6. Adsorption isotherm and kinetics

The equilibrium data were collected at various initial As (V) concentrations in the range of 0.05 to 4 mg/L. A 0.1 g of adsorbent was added to 100 mL of arsenic solution with different As (V) concentrations and was shaken until equilibrium. Then, the equilibrium concentration of arsenic was determined and fitted to Langmuir, Freundlich, and Temkin isotherms. The Langmuir, Freundlich, and Temkin isotherms are summarized in Table 1. The values of the constants were obtained from the Freundlich, Langmuir and Temkin isotherms linear plots as shown in Figure S3.

Freundlich’s model illustrates adsorption within heterogeneous systems. According to Table 1, where: $q_e = \text{Amount adsorbed per unit weight of adsorbent at equilibrium (mg/g)}$, $C_e = \text{equilibrium concentration of adsorbate in solution after adsorption (ppm)}$, $K_l = \text{empirical Freundlich constant or capacity factor (L/g)}$, $n = \text{Freundlich’s exponent which demonstrates the severity of adsorption}$. The experimental data for the

| Table 1. The parameters of isotherm and kinetic models for Arsenic (V) adsorption using CS-TPP nanoparticles. |
|----------------------------------------|------------------------------------------|----------------------------------|
| Isotherm models                       | Langmuir                                 | Freundlich                       | Temkin                           |
| $R^2$                                 | $q_{max}$ (mg/g)                         | $K_l$ (L/mg)                     | $n$                              | $R^2$                                    | $b_l$ | $K_t$ |
| 0.988                                 | 21.3                                     | 0.63                            | 0.991                            | 1.14                          | 1.25       | 0.883 | 0.27 | 24.03 |
| Kinetic models                        | Pseudo-first-order                       | Pseudo-second-order             |                                  |
| $K_1$ (min⁻¹)                        | $q_{e, exp}$ (mg/g)                     | $q_{e, calc}$ (mg/g)            | $R^2$                            | $K^2$ (g/mg) (min⁻¹)            | $q_{e, calc}$ (mg/g) | $R^2$ |
| 0.014                                 | 0.09                                     | 0.1                              | 0.945                            | 0.23                          | 0.11       | 0.998 |
adsorption of As (V) on the CS-TPP nanoparticles showed that the process followed the Freundlich isotherm \( R^2 = 0.991 \) and is a better fit for the data acquired from the experiments compared to the Langmuir \( R^2 = 0.988 \) and Temkin \( R^2 = 0.883 \) models. In fact, it showed that both mono-layer and multi-layer adsorptions may have occurred for As (V) adsorption on the CS-TPP nanoparticles. This is consistent with the findings of previous studies (Saha and Sarkar 2012, Sivakami et al. 2013). Furthermore, the maximum sorption capacity of As (V) ions on the CS-TPP nanoparticles was 21.3 mg/g and achieved at pH = 6.

The affinity to the adsorption sites between As (V) and CS-TPP nanoparticles is determined by separation factor \( (R_L) \) (Equation (8) in Table S1). The \( R_L \) value above 1 indicates unfavorable adsorption while the \( R_L \) values between 0 and 1 indicate a favorable reaction. \( R_L \) value of zero hints at an irreversible reaction while \( R_L \) value of 1 demonstrates a linear reaction (Baghani et al. 2017, Khouzani et al. 2018, Azari et al. 2019). In the present study, the value of \( R_L \) calculated is less than 1, which means, the adsorption of As (V) on CS-TPP is a favorable process. The Langmuir \( K_L \) constant is a measure of the metal ions' affinity to the adsorption sites. Therefore, the higher value of \( K_L \) indicates better adsorption. The value of \( K_L \) (L/mg) (Langmuir constant) calculated for this study was 0.63. It means that the adsorption process was achieved to equilibrium point in 0.63 L/mg of adsorbent surface.

In the Temkin isotherm model, \( b_1 \) constant is connected to the heat of sorption (J/mol). If the \( b_1 \) exceeds 1 \( (b_1 > 1) \), it indicates rapid sorption of adsorbate at the initial stages of the adsorption process (Soori et al. 2016). In this study, the \( b_1 \) value was equal to 0.27 demonstrating an exothermic adsorption process. The obtained results showed that the removal of As (V) ions from aqueous solutions was not achieved in a short contact time which is in accordance with the \( b_1 \) value of lower than 1. Moreover, a low value for \( K_t \) \( (K_t \leq 1) \) is related to weak bonding between adsorbate and the medium (Soori et al. 2016). In this study, the \( K_t \) value was calculated to be 24.03 which shows strong bonding between arsenate ions and CS-TPP nanoparticles.

As shown in Table 1, the equilibrium data were fitted onto both kinetic models: pseudo-first-order and pseudo-second-order. The pseudo-second-order (PSO) model had a higher correlation coefficient \( R^2 = 0.998 \) than the pseudo-first-order (PFO) model \( R^2 = 0.945 \). The values of \( K_1 \) and \( K_2 \) were determined from the slope of the linear plots of log \( (q_e - q_t) \) versus time and the slope of the linear plot \( q_t \) versus time, respectively. The calculated value of \( q_e \) in pseudo-second-order model \( (q_{e \text{cal.}} = 0.11 \text{mg/g}) \) is in agreement with the experimental values \( (q_{e \text{exp.}} = 0.09 \text{mg/g}) \).

Table 2 compares the maximum adsorption capacity of arsenic ions \( q_{\text{max}} \) (mg/g), the kinetic and isotherm models this study with other adsorbents.

| Adsorbent                        | pH  | Isotherm | Kinetic   | \( q_{\text{max}} \) (mg/g) | Ref               |
|----------------------------------|-----|----------|-----------|-----------------------------|------------------|
| Chitosan-red scoria              | 7   | Langmuir | PSO       | 0.72                        | (Asere et al. 2017) |
| Chitosan–pumice blends           | 7   | Langmuir | PSO       | 0.71                        | (Asere et al. 2017) |
| KMnO₄ modified clinoptilolite     | 7   | Langmuir | PSO       | 0.15                        | (Massoudinejad et al. 2015) |
| Iron-oxide coated sands           | 5   | Langmuir | –         | 0.022                       | (Hsu et al. 2008) |
| Chitosan-modified diatomite       | 7   | Langmuir | PSO       | 11.95                       | (Yang et al. 2020) |
| Bituminous iron-modified activated carbon (AC) (CF-MP) | 7   | Langmuir | –         | 2.45                        | (Arcibar-Orozco et al. 2014) |
| Wood-based activated carbon (AC) (CW-MP) | 7   | Langmuir | –         | 2.28                        | (Arcibar-Orozco et al. 2014) |
| Activated carbons with iron hydro (oxide) nanoparticles (F400-M) | 7   | Langmuir | PSO       | 0.847                       | (Vitela-Rodriguez and Rangel-Mendez 2013) |
| Porous iron oxide on activated carbon (AC-3) | 7   | Langmuir | PSO       | 15.34                       | (Yüreğ et al. 2014) |
| Copper exchange zeolite-a (CEZ)  | 7   | Langmuir | PSO       | 1.48                        | (Pillewein et al. 2014) |
| Magnetite-graphene oxide and magnetite-reduced graphene oxide composite (M-rGO) | 4   | Freundlich | PSO       | 12                          | (Yoon et al. 2016) |
| Graphene modified by iron–manganese binary oxide (FeMnO x/RGO) | 7   | Langmuir | PSO       | 11                          | (Zhu et al. 2015) |
| Magnetic biochar                 | 2   | Langmuir | PSO       | 3.1                         | (Baig et al. 2014) |
| Chitin-TiO₂                      | 3   | Langmuir | Elovich   | 3.1                         | (Ramos et al. 2016) |
| CNT/CuO                          | 5   | Langmuir | PSO       | 2.4                         | (Singh et al. 2016) |
| Metal-organic framework2ZrO₂(OH)₄(btc)₂(HCOO)₆ (MOF-808) | –   | –        | PSO       | 24.83                       | (Li et al. 2015) |
| Chitosan magnetic graphene oxide  | 7.3 | Langmuir | PSO       | 4.5                         | (Sherlala et al. 2019) |
| Nano alumina nanoparticles in chitosan-graftpolyacrylamide (CTS-g-PA) | 7.2 | Freundlich | –         | 6.56                        | (Saha and Sarkar 2012) |
| CS-TPP nanoparticles             | 6   | Freundlich | PSO       | 21.3                        | This study       |
with other studies using different adsorbents. Comparing the As (V) adsorption capacity of CS-TPP nanoparticles with other adsorbents, it is evident that this process results in a high $q_{\text{max}}$ value ($q_{\text{max}} = 21.3 \text{ mg/g at pH } = 6$). As shown in Table 2, the CS-TPP nanoparticles after Zr$\text{O}_4$ (OH)$\text{₄}(\text{btc})_2$(HCOO)$\text{₆}$ (MOF-808) (Li et al. 2015) adsorbent have the highest $q_{\text{max}}$ among all the tested adsorbents. However, the synthesis of CS-TPP nanoparticles is simple compared to the adsorbent of that study. In addition, based on Table 2, most of the experimental data for the adsorption of As (V) ions onto different adsorbents demonstrated that the process followed the Langmuir isotherm and PSO model.

4. Conclusion

In this work, the chitosan-tripolyphosphate nanoparticles (CS-TPP nanoparticles) were synthesized based on the ionic gelation technique for removal of As (V) ions from aqueous solution and characterized by SEM, FTIR and XRD. The FT-IR results showed that the larger adsorption capacity of CS-TPP nanoparticles is connected to the decrease of the chitosan crystallinity by the decrease of the polymer chain. The effects of pH, initial concentrations of As (V) ions, contact time, adsorbent dosage and adsorption isotherm were investigated, as well. Using the ionic gelation technique, this study was able to synthesize CS-TPP nanoparticles with an average size of 24.9 nm. The highest adsorption capacity was about 77 mg/mg and obtained at pH = 6. By increasing the adsorbent dosage, the adsorption performance increased and then decreased. This can be attributed to the increased adsorbent surface area and availability of many adsorption sites for the As (V) ions. Among the 3 isotherms investigated in this study, the Freundlich model showed to be the best fit for the experimental data with an $R^2$ value of 0.991. The adsorption kinetic data for As (V) ions were according to the assumption of a PSO model and the maximum sorption capacity was 21.3 mg/g at pH = 6. Simple preparation and high adsorption capacity of CS-TPP nanoparticles compared to other adsorbents such as chitosan-modified diatomite, porous iron oxide on activated carbon (AC-3) and graphene-modified by iron-manganese binary oxide (FeMnO x/RGO) presents a potential for using these nanoparticles for As (V) removal.

Disclosure statement

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