Research article

Microfluidics combined with ionic gelation method for production of nanoparticles based on thiol-functionalized chitosan to adsorb Hg (II) from aqueous solutions

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ABSTRACT

This work aimed at producing nanoparticles (NPs) based on thiol-functionalized chitosan (CS) using capillary microfluidic (MF) device combined with ionic gelation method to adsorb mercury ion [Hg (II)] from aqueous solutions. In this line, CS was functionalized with epichlorohydrin/cysteaminium chloride (2.73 M ratio) followed by fabricating NPs via MF and bulk mixing (BM) methods. To characterize the morphology, zeta potential, functionality, structure, and magnetic property of the samples, a series of tests such as SEM, TEM, DLS, FTIR, XRD, and VSM were carried out, respectively. The obtained results showed that MF technique was able to produce NPs with a diameter as small as 18 ± 3 nm, and a uniform shape compared to BM method. Thiol groups (−SH) functionalization on CS surface was confirmed by appearing a characteristic peak at 2579 cm\textsuperscript{−1}. Also, the XRD patterns indicated the appropriate synthesis of Fe\textsubscript{3}O\textsubscript{4} (magnetite), and no change in the structure of CS NPs in the presence of magnetite. Moreover, adding the magnetite to thiol-functionalized CS NPs led to suitable saturation magnetization about 26 emu/g to facilitate their separation using a magnetic field. To evaluate the performance of the nanoadsorbent, it has been exposed to Hg (II) in an aqueous solution which in turn the parameters optimization for the adsorption was done via Box-Behnken design (BBD) method, exhibiting the effect of adsorbent dose and the initial concentration of Hg (II) was much more significant than that of pH. Different concentrations of total dissolved solids up to 1000 mg/L had no adverse impact on the adsorption process confirmed by EDAX spectra. The least value of RMSE (5.023) and \(\chi^2\) (0.3) were observed for Redlich-Peterson, Radke-Prausnitz, and UT isotherms. Maximum adsorption capacities calculated using Langmuir and UT models were 1192 mg/g and 1126 mg/g, respectively. Thermodynamic studies demonstrated that the nature of the adsorption process was spontaneous and endothermic. Recovery of nano adsorbent was successfully carried out using HCl 0.5 mol/L. The adsorption studies revealed that the prepared nano adsorbent is promising candidate used in mercury removal from a real wastewater potentially.

1. Introduction

Over the past few decades, the discharge of a large number of heavy metal ions from various sources towards surface, and groundwater has become one of the most important environmental concerns worldwide owing to high toxicity and bioaccumulation. The World Health Organization (WHO) and the US Environmental Protection Agency (EPA) have listed mercury (Hg) as one of the most dangerous elements (Ballav et al., 2018). Based on their report, the maximum contaminant levels of mercury ion in drinking water and discharge standard limit to surface waters are 0.002 and 0.01 mg/L, respectively. This substance is found in the environment in three different forms (elemental, organic, and inorganic) with diverse valence states (0, 1, and 2). Hg (II) is one of the major environmental pollutants and has the potential to transform into methylmercury as a hazardous pollutant (Saleh et al., 2017). Toxic effects of Hg (II) on immune system include neurological disorders, kidney disease and gastrointestinal damage, as well as chromosome breakage (Li et al., 2015; Wang et al., 2016). It can be released to the environment through activities such as coal production, mining, residential heating system, sewage disposal from the dye chemical industry, batteries, and pharmaceutical industries (Holmes et al., 2009; Sun et al., 2018b). Therefore, as a crucial issue, considering the harmful and adverse effects of Hg (II) on human health has led to the development of an efficient method to remove it from pollutants. Various
methods have already been employed for Hg (II) removal, such as ion exchange, photo-reduction, amalgamation, membrane filtration, coagulation, chemical precipitation, reverse osmosis, adsorption, etc. (Luo et al., 2017; Qu et al., 2017). Among these techniques, the adsorption process is more favorable than the other methods due to high efficiency, operational simplicity, low cost, and so forth (Arshadi et al., 2017). Amid the wide range of adsorbents, the development of those based on natural polymers in view of economic feasibility, availability, and non-toxicity has received a great deal of attention (Ge and Hua, 2016).

Chitosan (CS) as a well-known natural polymer, because of its unique properties such as biocompatibility and biodegradability, availability, and appropriate for adsorption process. The presence of functional groups as active sites on CS surface allows this polymer to consider as a raw material for the preparation of adsorbents extensively (Wang et al., 2013). Despite the unprecedented characteristics of this polymer, its structural modification chemically is an inevitable issue because of some drawbacks such as the high tendency for aggregation, low chemical resistance in acidic environments, and low amounts of active sites on CS surface for the adsorption. It has been found that the chemical treatment can enhance the performance of adsorbents based on CS in water treatment processes (Fithikar et al., 2018). According to hard and soft acids and bases (HSAB) theory, mercury is classified as a soft acid, which tends to interact with sulfur as a soft base. Also, nitrogen is suitable for chelating with Hg (II); so, materials including these functional groups are promising candidates for the chemical treatment of CS to remove this ion effectively (Sun et al., 2018a). Recently, some researches have been reported on the adsorbents based on the modified CS including CS/amine modified diatomite composites (Fu et al., 2018), polyamine-co-thiourea inarched CS gel (Li et al., 2018), CS flakes coated ethylenediaminetetraacetic-disodium (Ferrah, 2018), aminothiourea-functionalized magnetic carbon nanobiosorbent (Hou et al., 2018), and CS-graft-polyacrylamide (Li et al., 2015). With regard to the materials containing sulfur and nitrogen elements, cysteamine as an aminothiol substance is the appropriate nominee for CS functionalization to increase the efficacy of Hg (II) adsorption.

Generally, in comparison with the conventional adsorbents such as beads, flakes, and microparticles, those which are made based on nanoscaled particles exhibit a much better performance due to the high surface area and lack of an intrinsic molecular diffusion resistance. Although one of the limitations of polymeric nanoadsorbents is the separation/recovery process, it can be overcome using magnetic nanoparticles (NPs), e.g., magnetite (Fe₃O₄), thereby collecting by an external magnetic field (Galhoum et al., 2015). Different methods have been used for the synthesis of CS NPs, such as emulsion (Ge et al., 2017), reverse micelles (Orellano et al., 2017), precipitation (Agnihotri et al., 2004), spray drying (Asada et al., 2004), ionic gelation (Koukaras et al., 2012; Manikandan and Sathiabama, 2016), etc. Among them, the ionic gelation technique has attracted much attention because of the non-toxicity of crosslinking agent, the absence of organic solvents, and the chemical functionalization of CS using cysteaminium chloride as a crosslinking agent and modified CS to synthesize uniform nanoadsorbent with an average particles size of approximately 378 nm using a T-junction MF system for copper ion removal. Their results exhibited the adsorption capacity around 149 mg/g.

By following up the literature, rare publications have been reported on the synthesis of CS NPs using the ionic gelation combined with MF technique. For example, Pessoa et al. (2017) examined various parameters such as the effect of mixing within MF pattern and the volume ratio of ATP to CS through ionic gelation method for CS NPs production. The average NPs size obtained by employing dynamic light scattering (DLS) was calculated to be 85 ± 15 nm. Also, the synthesis of CS/TPP NPs with the size of 550–700 nm using an MF system has been briefly reported (Cetin et al., 2013a, 2013b). Therefore, based on our knowledge, the chemical functionalization of CS using cysteaminium chloride followed by its NPs fabrication by means of capillary MF device combined with ionic gelation method to investigate the metal ion adsorption has not been reported.

The objective of this work is MF fabrication of the nanoadsorbent based on thiol-functionalized CS in the presence of TPP as ionic crosslinker for Hg (II) removal. For this purpose, the effects of initial adsorbent dosage, the concentration of heavy metal ion, and pH on the adsorption process will be investigated via the design of experiments. Moreover, the adsorption equilibrium and thermodynamic studies, as well as the recovery capability of the nanoadsorbent for the ion removal, will be assessed, and the obtained results will be discussed in detail.

2. Experimental

2.1. Materials

Chitosan (CS, a biological macromolecule, and random copolymer of D-glucosamine and N-acetyl-D-glucosamine, the average molecular weight of 37,000 Da and deacetylation degree of 85%), epichlorohydrin, and TPP were purchased from Sigma-Aldrich Co., (Pillsburg, The Netherlands). Cysteaminium chloride (synthesis grade, C₉H₁₂ClN₂S, the molecular weight of 113.61 g/mol) was supplied from
Merck Millipore (Germany). The other chemicals were also provided from Merck and used without further purification. Sodium hydroxide (NaOH), iron (II) chloride (FeCl₂·4H₂O), iron (III) chloride (FeCl₃·6H₂O) were used for the preparation of Fe₃O₄ NPs. A stock solution of TDS (total dissolved solid) was prepared using MgSO₄, CaCl₂, NaHCO₃, and KNO₃. Also, mercury nitrate (II) was used for the preparation of a stock solution of mercury (1000 mg/L), from which working solutions with different concentrations were provided for batch experiments. The pH value of each solution was adjusted with hydrochloric acid (HCl) and NaOH by a pH meter.

2.2. Preparation of thiol-functionalized CS NPs

The chemical modification of CS was carried out according to (Galhoum et al., 2015). Hereby, to optimize the molar ratio of epichlorohydrin to cysteamine chloride for the maximum adsorption of Hg (II), a series of different ratios including 0.91, 1.82, 2.73, and 3.64 were investigated. For this purpose, the amounts of 0.5, 1, 1.5, and 2 mL of epichlorohydrin were added to 1 g of cysteamine chloride in the presence of 200 mL of ethanol: water with a ratio of 1: 1, and the mixtures were stirred under a reflux system at pH of 10 for 6 h. Then, 100 mL of CS solution (4 g/L concentration) was added to the mixtures and stirred overnight. Finally, the mixtures were precipitated using NaOH solution, and the precipitates were washed three times with ethanol/water for impurities removal. After the samples were dried in a vacuum chamber at ambient temperature for 48 h, thiol-functionalized CS powder was attained.

The next step was the preparation of thiol-functionalized CS NPs using ionic gelation method. In this line, MF and bulk mixing (BM) methods were separately used for the formation of the samples. Toward the NPs based on MF technique, a glass capillary with an inner diameter of 0.5 cm and an outer diameter of 1 cm was used as the main channel for the continuous flow. The dispersed phase flow entered the main channel by using a stainless steel needle, which was coaxially embedded in the main channel, and the two channels were connected to peristaltic pumps to inject the solutions. One of the crucial factors in the synthesis of NPs based on ionic gelation method in MF device is to adjust the mass ratio of CS to TPP. Hereby, it was investigated by changing the volume flow rate of TPP, and also the effect of CS/TPP mass ratio on different flow rates of CS was studied. For this purpose, according to the literature (Dima et al., 2015), CS and TPP solutions were selected at concentrations of 0.8 g/L and 0.96 g/L, respectively at pH of 5. To investigate the effect of the mass ratio of CS to TPP, TPP solution was injected into the system with volume flow rates of 2, 3, 4, and 5 mL/min with different volume flow rates of CS solution (18, 20, 22, and 24 mL/h). The amount of mass ratio was calculated based on Eq. (1):

\[
\text{Mass ratio of CS to TPP} = \frac{Q_{CS}}{Q_{TPP}} \times \frac{C_{CS}}{C_{TPP}},
\]

where “QCS” and “QTPP” are the volume flow rates of CS and TPP solutions, respectively. Also, “Ccs” is the concentration of CS solution, and “Ctpp” is the concentration of TPP solution. The NPs were synthesized using different mass ratios of CS to TPP to determine the optimal conditions for their synthesis in the MF system. In this step, three different states through the visual analysis of NPs can be observed: (1) clear solution, (2) opalescent suspension, and (3) aggregates, which opalescent suspension is associated with the presence of appropriate NPs based on the ionic gelation method (Dima et al., 2015). Regarding the NPs production using BM method, TPP solution was added drop wise to CS solution at a vigorous stirring under the optimum condition of TPP/CS molar ratio obtained from MF technique. Finally, the obtained suspensions were freeze-dried to form a powder for further evaluation.

2.3. Characterization

To characterize the polymeric NPs, the following tests were carried out: (1) elemental composition using a CHNS analyzer (Flash EA 1112 series, Thermo Finnigan, United States) for the confirmation of chemical functionalization, (2) a dynamic light scattering (DLS, Malvern ZEN 3600, United Kingdom) and zeta potential analyzer (Zeta plus, Brookhaven, United States) were utilized to determine the NPs size and the size distribution and their surface charge, (3) a field emission-scanning electron microscopy (FE-SEM, NanoSEM 450, FEI Nova, United States) with 60,000× , and 150,000× magnifications and transmission electron microscopy (TEM, CM120, Philips Co., The Netherlands) were applied to observe the morphology of the samples, (4) a Fourier transform infrared spectroscopy (FTIR, Spectrum Two, PerkinElmer Inc., United States) was used to study the variations of chemical groups before and after functionalization of CS, (5) a vibrating sample magnetometer (VSM, Kavir Magnetic, Iran) and X-ray diffraction spectroscopy (XRD, Equinox 3000, Inel, France) were utilized to measure the magnetic properties and the structure of the nanoadsorbents, respectively. Also, an energy-dispersive X-ray analyzer (EDAX, SEM equipped with EDAX, CamScan MV2300, Oxford) was employed to investigate the elemental spectra of the nanoadsorbents before and after adsorption.

2.4. The adsorption studies

Hg (II) adsorption studies were carried out in a batch system to investigate the effect of different parameters such as pH, adsorbent dosage, and initial concentration of metal ion on the adsorption capacity. For each experiment, a solution of mercury with specific concentration was used by diluting the stock concentration (1000 mg/L). All the experiments were carried out with the solution volume of 20 mL at room temperature with a constant stirring speed.

Isotherm experiments were carried out at initial concentrations of mercury (40–170 mg/L), pH 6 and the adsorbent dosage 100 mg/L. Additionally, thermodynamic studies were assessed at temperatures of 278, 288, 298, and 313 K under the conditions as follows: the initial concentration of Hg (II) 125 mg/L, pH 5.25, and the adsorbent dosage 250 mg/L. These values were the center points of range for each parameter in Design Expert software. Moreover, to separate the nanoadsorbent from the media after the adsorption process, Fe₃O₄ NPs were added to the system and pH was set at 6. In this pH value, CS coagulated alongside Fe₃O₄ NPs; as a result, they could be easily separated by applying an external magnetic field (Moharramzadeh and Baghdadi, 2016). The concentration of remaining Hg (II) in the solution was determined by using an inductively coupled plasma mass spectrometry (ICP-MS, Spectro, Arco EOP, Germany). The adsorption capacity expresses the amount of adsorbed ion in a certain amount of adsorbent, which is calculated by Eq. (2) (Behjati et al., 2018):

\[
q_e = \frac{(C_0 - C_e) \times V}{M},
\]

where “C₀”, “Cₑ”, “V”, and “M” are the initial concentration of metal ion (mg/L), the equilibrium concentration of metal ion (mg/L), the volume of adsorption medium, and mass of the adsorbent (mg), respectively. Furthermore, the removal percentage of metal ion can be calculated using Eq. (3) (Behjati et al., 2018):

\[
\text{Removal (\%) } = \frac{(C_0 - C_e)}{C_0} \times 100.
\]

The overall schematic of this work from CS functionalization to prepare the NPs using capillary MF device is illustrated in Fig. 1. The adsorption of Hg (II) via the nanoadsorbents and their separation using a magnetic field are also shown.

In order to investigate the effect of TDS on the Hg (II) adsorption using the nanoadsorbent (the initial concentration of Hg (II) 200 mg/L,}
2.5. Box-Behnken design method

In this study, the adsorption capacity of Hg (II) on the thiol-functionalized CS NPs was evaluated using a response surface methodology (RSM) [Design-Expert software, Version 10, Minneapolis, United States]. The RSM is a collection of mathematical and statistical techniques, which is beneficial for analyzing the effects of several independent variables.

In this work, the Box-Behnken design (BBD) method was utilized to evaluate the relationship between the response and independent variables because this method has less number of experiments and more efficiency compared to the central composite design (CCD) and Doehlert designs (Lung et al., 2018). With this regard, the pH range of the adsorption medium was chosen less than 6 to prevent the Hg (II) precipitation. In the designed experiments, the role of time has not been considered owing to the rapid adsorption process during a few minutes. Based on Table 1, the pH value (4.5–6), the adsorbent dose (100–400 mg/L) and the initial concentration of Hg (II) (50–200 mg/L) were selected as the independent variables. Eventually, 17 runs were set to express the predicted response values. Among them, 5 central points were considered to repeat for statistical analyses. In general, a quadratic polynomial model based on Eq. (4) was used:

\[ Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=1, j \neq i}^{k} \beta_{ij} X_i X_j, \]  

(4)

In this equation, “Y” is the predicted response, “X” is an experimental variable, and “k” is the number of independent variables. The “\( \beta_0 \)” is the intercept coefficient that reveals a result when all the variables are null. The “\( \beta_i \)” is the linear coefficient, represents the main effects of the independent variables. The “\( \beta_{ii} \)” and “\( \beta_{ij} \)” coefficient indicates interactions between the two variables. The “\( \beta_{ij} \)” is the quadratic coefficient, which explains the quadratic nature of responses (Davodi et al., 2017).

2.6. Error analyses

The consistency between the experimental and predicted data was determined using the residual root-mean-square error (RMSE) and the chi-square test \( (\chi^2) \) as follow:

\[ \text{RMSE} = \sqrt{\frac{1}{n-p} \sum_{i=1}^{n} (q_{e, \text{exp}} - q_{e, \text{cal}})^2}, \]

(5)

\[ \chi^2 = \sum_{i=1}^{p} \left( \frac{(q_{e, \text{exp}} - q_{e, \text{cal}})^2}{q_{e, \text{cal}}} \right), \]

(6)

where “\( q_{e,\text{exp}} \)” and “\( q_{e,\text{cal}} \)” are the experimental results and calculated values using the model, respectively. Also, “n” is the number of experimental data and “p” is the number of model variables. The errors calculated using Eq. (4) and (5) should be as small as possible, and the lowest value of an error function indicates the best model.

The results indicated as mean ± SD (standard deviation) and the results with p-value less than 5% were significant and reported.

3. Results and discussion

3.1. CS functionalization with thiol group

The optimization of functionalizing CS to enhance Hg (II) adsorption is essential. With this regard, the nanaoadsorbents were prepared in different molar ratios of epichlorohydrin to cysteaminium chloride mentioned earlier at pH 5, the initial Hg (II) concentration of 100 mg/L, and the adsorbent dosage of 200 mg/L. As is shown in Fig. S1, the molar ratio of 2.73 for epichlorohydrin to cysteaminium chloride had the highest percentage of Hg (II) removal. Accordingly, when the molar ratio of epichlorohydrin was increased from 0.91 to 2.73, the reaction efficiency was increased for the synthesis of the active arm, thereby increasing the reaction modification owing to providing the active arm with the suitable connection to the surface of CS (Fig. 2). On the other hand, by increasing the molar ratio to 3.64, the excess amount of epichlorohydrin, which had not participated in the reaction (1), could act as a cross-linker and involve some active groups onto the surface of CS, which led to a decline in Hg (II) removal (Ge and Hua, 2016). In addition, confirming the functionalization of CS, CHNS test was performed, and the results are reported in Table 2. As is evident, the presence of sulfur with the amount of 3.61% and also the increase in nitrogen content from 6.75 to 7.30 after the functionalization revealed that the process was carried out properly.
3.2. The optimization of CS/TPP mass ratio in MF device

As aforementioned, the synthesis of NPs is highly dependent on the ionic interactions involved between CS and TPP, in which their ratios can have a key role in the size of them. Fig. 3a displays the variations of CS/TPP mass ratios as a function of NPs size obtained from DLS. As is seen, by decreasing the mass ratio or in other words, increasing the TPP flow rate, the size was decreased and then increased. Instantly, at CS flow rate of 24 mL/min, the NPs size was reduced to 49 nm corresponding to the mass ratio of 5 and then increased. This behavior could be attributed to the positive charge density of CS, which provides many active sites for the cross-linking process. When the mass ratio of CS/TPP was high, the reaction solution was clear that explained the amount of TPP was not sufficient to form the cross-linked NPs. By increasing the TPP content (mass ratio reduction), a decrease in the NPs size could be occurred due to an increase in the cross-linking density between CS and TPP. In continuous, while the TPP flow rate was gradually increased, the size of NPs was raised. The reason for this observation attributed to the excess TPP, leading to more molecules of CS involved in the formation of the NPs. A similar trend has been reported by Zhang et al. (2004), who obtained the optimized CS to TPP mass ratio of 5 to 1. Based on Fig. 3a, the same behavior could be considered in the other different CS flow rates. Overall, the NPs size was decreased by increasing the CS flow rate from 18 mL/min to 24 mL/min. The reaction solution was clear at the flow rate of CS higher than 24 mL/min, which meant that TPP was not sufficient to form NPs, and hence the optimum CS flow rate was selected 24 mL/min for further evaluations. Also, in order to verify the surface charge of the NPs produced in the optimum CS flow rate, zeta potential analysis was performed, and the data are reported in Fig. 3b. As is evident, the amount of surface charge of the NPs was reduced by decreasing the CS/TPP mass ratio due to neutralization of protonated amino groups by TPP anions (Fan et al., 2012).

For further investigation, the morphology and size distribution of NPs produced using MF technique and BM method at the optimized condition (CS/TPP mass ratio of 5) were exhibited in Fig. 4a1, a2 and Fig. 4b1, b2, respectively. As is seen in Fig. 4a1, a2, the MF-based samples have an average diameter of 48 nm with a polydispersity index (PDI) of 0.19. It showed that the fabricated NPs have a uniform spherical shape. Conversely, the BM-assisted samples showed an average diameter of 125 nm with a PDI of 0.35. Based on this method, the

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functionalized CS</td>
<td>30.94</td>
<td>5.84</td>
<td>7.30</td>
<td>3.61</td>
</tr>
<tr>
<td>Neat CS</td>
<td>38.27</td>
<td>6.91</td>
<td>6.75</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 2. The overall schematic of thiol-functionalized CS preparation in detail.

Fig. 3. The variations of CS/TPP mass ratio as a function of NPs size along with CS flow rates alterations (Q) (a), and the changes of CS/TPP (mass ratio) versus zeta potential (b).
produced NPs have a non-uniform shape alongside a bimodal distribution peak. Moreover, Fig. 4c1–d2 depicts the morphologies and size distribution of those NPs fabricated using the MF technique at different conditions such as CS/TPP mass ratios of approximately 8.5 and 7.5. As is evident, these samples have uniform shapes relatively with average diameters of approximately 369 nm and 304 nm in the order mentioned above. It could be concluded that the MF technique has a high ability to control the NPs size in a wide range.

3.3. Characterization of the nanoadsorbent

Fig. 5 demonstrates the TEM image of MF-fabricated NPs based on thiol-functionalized CS at the optimum condition. As can be seen, they have uniform shape with an average diameter size of 18 ± 3 nm. The difference between this value and DLS results was due to the disparity in the samples preparation (Manikandan and Sathiyabama, 2016).

The FTIR spectra of the samples including neat CS, thiol-functionalized CS, and MF-fabricated sample based on thiol-functionalized CS NPs are shown in Fig. 6. In the neat CS, the peaks at 3359 cm⁻¹, 3475 cm⁻¹, and 3409 cm⁻¹ were attributed to the stretching vibrations of primary amine (―NH₂), and hydroxyl (―OH) groups. These peaks converted to the new single peak at the wavenumber of 3443 cm⁻¹ assigning to the stretching vibrations of −OH and secondary amine (―NH) for the thiol-functionalized CS. Regarding this sample, the peak intensity at 1382 cm⁻¹ was also increased due to an increase in amine groups content through functionalization process (Galhoum et al., 2015). Additionally, the intensity of the peak at 1094 cm⁻¹ associated with stretching acetyl (C–O) groups was increased by functionalizing the CS. Moreover, the weak peak at 2579 cm⁻¹ for thiol-functionalized CS referred to thiol (―SH) groups, which showed the proper deposition of the synthesized active arm onto the surface of CS (Madrakian et al., 2016). Regarding the MF-fabricated thiol-functionalized CS NPs, the peak at 1222 cm⁻¹ was appeared owing to the presence of P=O groups in TPP cross-linker. The cross-linking process between the amine groups in the CS structure and TPP could be confirmed by shifting the characteristic peak from 1608 cm⁻¹ to 1596 cm⁻¹.

The XRD patterns of neat CS, MF fabrication of thiol-functionalized CS NPs, Fe₃O₄ NPs, and MF fabrication of thiol-functionalized CS plus Fe₃O₄ NPs are shown in Fig. S2. As is seen, the pattern related to neat CS has two characteristic peaks, appearing in 20.2° (110) and 10.41° (020). By nanoparticulating the CS using MF combined with ionic gelation methods, the two characteristic peaks appeared in 2-theta angles of 22.75°, and 9.3°, which the first peak was broader and its intensity was lower compared to neat CS. It could be referred to the formation of amorphous structure in the CS after the MF process because of reducing compactness within the CS chains by ionic interaction between CS and TPP, thereby reducing crystallinity (Qi and Xu, 2004). In fact, the crystallinity acts as an obstacle to the adsorption process, which means that CS with a lower crystallinity degree has a higher adsorption
capacity. Therefore, by changing the CS structure from microscale to nanoscale, the adsorption capacity of the polymer can be increased due to the formation of more amorphous phase as an open structure (Piron and Domard, 1998). For the synthesized Fe₃O₄ NPs, the characteristic peaks were observed in 2-theta angles of 62.6°, 57.15°, 53.6°, 43.2°, 35.6°, and 30.16° attributing to the crystal plates at locations of (440), (511), (422), (400), (311), and (220), respectively. The obtained results were in reasonable agreement with the standard XRD pattern of cubic Fe₃O₄ (magnetite, JCPDS card no. 75-1610). Eventually, for the mixture of Fe₃O₄ and MF fabrication of thiol-functionalized CS NPs, all the characteristic peaks related to CS and Fe₃O₄ could be observed.

Fig. S3 shows the magnetic property and the morphology of Fe₃O₄ NPs and MF fabrication of thiol-functionalized CS plus Fe₃O₄ NPs. The saturation magnetization of the synthesized Fe₃O₄ NPs was 52 emu, which decreased to 26 emu by incorporating with CS NPs. This decline was due to the volume distribution of non-magnetic CS NPs. Nevertheless, these NPs have still enough saturation magnetization to be sensitive by an external magnetic field. Also, the morphologies of synthesized Fe₃O₄ NPs (right-hand side) and the mixture of Fe₃O₄ besides CS NPs (left-hand side) could be observed.

The EDAX analysis of the synthesized nanoadsorbent before and after the adsorption process is shown in Fig. 7a and b. As is shown in Fig. 7a for the sample based on thiol-functionalized CS plus Fe₃O₄ NPs before adsorption, the elements of Na, C, N, O, Fe, S, P, and N were present. Also, the presence of sulfur element (S) confirmed the proper functionalization of CS. On the other hand, the presence of elements such as phosphorus (P) and sodium (Na) was due to the cross-linking reaction of CS with TPP. After the adsorption process, the presence of mercury element (Hg) in the structure was visible, which indicated the effective adsorption on the nanoadsorbent [Fig. 7b].

### 3.4. The optimization of Hg (II) adsorption using BBD method

Table 3 exhibits the results based on BBD method to study three independent variables such as pH (A), the initial concentration of Hg (II) (B), and the adsorbent dosage (C) on the adsorption process. The generalized model (Eq. (7)) based on experiments is as follows:

\[
q_\text{e} = 412.71 + 163.99A + 188.39B - 134.71C + 100.41AB - 71.33AC - 88.09A^2 + 29.91C^2 .
\]  

(7)

In this equation, the coefficients with positive and negative signs meant that those have desirable and undesirable effects on the Hg (II) adsorption process. Accordingly, the highest value was related to the parameter "B" attributing to the initial concentration of Hg (II), which was the most significant factor, affecting the adsorption process.

In order to verify the validity of the model and the significance of the variables, analysis of variance (ANOVA) was used, and the results are shown in Table S1. As is shown, the variables with p-value < 0.05 were considered significant statistically. In this line, some variables were eliminated in this equation because their p-value was more than 0.05, showing their insignificant effects on the adsorption process. Moreover, the p-value associated with the lack of fit attributed to the error was not significant, which indicated that the model was well-covered by experimental data. In addition, the high F-value for the model (145.19) showed that the most variations in response could be explained using the regression equation. The high regression coefficient (R² = 0.9922) also confirmed the validity of the proposed model. Moreover, reasonable agreement between the predicted "R²adj" and the adjusted "R²adj" proved the accuracy of the model. At last, the close values between the experimental data and the predicted values by the model for the Hg (II) removal (Table 3) showed that this equation was appropriate to use for further evaluation in this work.

### 3.5. Effect of variables and their interactions

Fig. 8a–c depicts the various effects of variables on the amount of adsorption capacity of the nanoadsorbent. As shown in Fig. 8a, by increasing pH the amount of adsorption capacity was increased due to the fact that at low pH, the concentration of H⁺ was high, leading to a competition between the H⁺ and Hg (II) ions for the adsorption onto the surface of CS. In addition, the high concentration of H⁺ resulted in the protonation of the active sites on the CS structure, indicating an inhibitory effect on the adsorption. In other words, the protonation of the functional groups on the CS structure led to electrostatic repulsion between the adsorbent and Hg (II). Besides the pH value, the initial concentration of Hg (II) showed an effective role on the adsorption process because it acted as a driving force to overcome the mass transfer resistance of ions between the solution and solid phases (Manzoor et al., 2013). Finally, by increasing the amount of the

### Table 3

<table>
<thead>
<tr>
<th>Run</th>
<th>Factor</th>
<th>Adsorbent dosage (mg/L)</th>
<th>pH</th>
<th>Hg (II) (mg/L)</th>
<th>Adsorption capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>4.5</td>
<td>125</td>
<td>400</td>
<td>142.14</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>4.5</td>
<td>125</td>
<td>100</td>
<td>249.98</td>
</tr>
<tr>
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<td>125</td>
<td>250</td>
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<td>6</td>
<td>4.5</td>
<td>50</td>
<td>250</td>
<td>57.20</td>
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<tr>
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<td>250</td>
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<td>120.44</td>
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<td>17</td>
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<td>250</td>
<td>375.10</td>
</tr>
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</table>

**Fig. 7.** The EDAX spectra of thiol-functionalized CS plus Fe₃O₄ NPs: before Hg (II) adsorption (a), and after Hg (II) adsorption.
adsorbent, the level of adsorption capacity was reduced, which could be explained in this way that in a more adsorbent dose, the adsorption sites remained unsaturated during the process (Özacar and Şengil, 2005).

In Fig. 6b, at pH 4.5, by increasing the initial concentration of Hg (II), a slight increase was occurred in the adsorption capacity of the nanoadsorbent, whereas at pH 6, by increasing the initial concentration of the ion, a significant increase was happened in the adsorbent capacity. This behavior could be due to the fact that there were a few active sites in the acidic environment, thereby saturating the active sites occurred rapidly at high concentration of Hg (II). In contrast, at pH 6, the almost active sites on CS structure were available, leading to an increase in Hg (II) adsorption capacity. Furthermore, the pH of zero point of charge (pH_{ZPC}) for the adsorbent used in this work was obtained 5.1, which was using the method mentioned in the literature (Wang et al., 2017a). The negative charge of the adsorbent at the pH levels higher than the ZPC was due to the anionic functional groups of TPP. On the other hand, CS component in the adsorbent was responsible for the positive charge density at the pH levels lower than ZPC. At higher pH levels, Hg (II) could be adsorbed through electrostatic interactions with anionic polyphosphate and complexation with the functional groups on the structure of modified CS. Similarly, the effect of pH values higher than ZPC has been also reported in the literature (Zhang et al., 2017). However, at lower pH levels, the charge density of TPP was low and that of CS was high, resulting the net positive charge density onto the surface of adsorbent. As a consequence, the adsorption could be only due to the complexation reaction. Therefore, the increase in adsorption capacity by increasing the pH was due to an increase in negative surface charge density and decrease in H^+ concentration, which could compete with Hg (II) for adsorption using functional groups through complexation reaction. Also, Fig. 8c shows the relationship between the pH and the nanoadsorbent dose as a function of Hg (II) removal percentage. Hereby, at pH 4.5, by increasing the adsorbent dosage, no significant change in the adsorption capacity was observed, while the pH was increased to 6, the almost adsorbent sites were active, and some of them remained unsaturated owing to an increase in adsorbent dose. Therefore, more decrease in the adsorption capacity could be observed.

3.6. The adsorption process optimization

One of the objectives of the RSM method is to find the optimal process conditions for maximizing the adsorption capacity by choosing the correct range of the effective parameters. In this study, based on Eq. (7), the optimum conditions for the maximum Hg (II) removal were set as follows: the initial concentration of Hg (II) 195.6 mg/L, the adsorbent dose 133 mg/L, and pH 5.8. To confirm the predicted model, the experiments were carried out two times under above-mentioned conditions. The amount of experimental adsorption capacity for each repeat were 897 and 900 mg/g, which were close to 904.14 mg/g obtained from the model. Consequently, the proposed model was in good agreement with the experimental data.

3.7. Effect of total dissolved solids (TDS)

Fig. S4 shows the results of the Hg (II) adsorption capacity at different concentration of TDS solution. The condition for carrying out this test were set based on run 10 from Table 3. As can be seen, the TDS has a little impact on the adsorption capacity because the cations such as Ca^{2+} and Mg^{2+} were the hard elements which did not tend to interact with functional groups on the CS such as sulfur and nitrogen. However, these cations due to the electrostatic interaction with negative TPP groups could partially reduce the adsorption capacity of the nanoadsorbent. Moreover, in contrast to cations, the anions have not the unoccupied orbitals, in consequence, they did not tend to attract by means of nitrogen and sulfur groups.

3.8. Equilibrium studies

The isotherm of adsorption expresses how adsorbent and adsorbate interact with each other. Determining the equilibrium curves and a model that the data follow is important for designing an adsorption process for heavy metals removal from wastewaters. Hereby, it has been considered different isotherm models including two and three parameters.

In the Langmuir isotherm model (Langmuir, 1916), it is assumed that mono-layer adsorption acts homogeneously. Also, the adsorption occurs only in a limited number of specific sites without any subsequent interactions between the adsorbed molecules. In this model, each molecule has an enthalpy and constant adsorption energy. A dimensionless constant namely “Ri” is known as the separation factor used for determining the favorability of the model (Maneerung et al., 2016).

The Freundlich isotherm model can be studied for multi-layer adsorption with non-uniform distribution of adsorption heat at a non-homogeneous surface. Therefore, in this model, the interactions between the adsorbed molecules should be considered (Yang, 1998).

In the Temkin model assumption (Temkin, 1940), the heat of adsorption of all molecules in the layer would decrease linearly with coverage, and the adsorption is characterized by a uniform distribution of binding energies.

Dubinin-Radushkevich isotherm (Dubinin, 1960) assumes that a heterogeneous surface on which the adsorption process occurs is produced due to the steric hindrance between adsorbed and incoming adsorbates.

The above four isotherms are two-parameter models which are explained in brief. At this section, three-parameter models are introduced concisely.
The Redlich-Peterson model (Redlich and Peterson, 1959) approaches the Langmuir model at low concentrations and the Freundlich model at high concentrations and can be employed either in heterogeneous or homogeneous systems. The equations are solved by maximizing the correlation coefficient between the experimental data points and theoretical model predictions or minimizing the error functions with the solver add-in function of the Microsoft Excel (Wong et al., 2004).

The Radke–Prausnitz isotherm (Radke and Prausnitz, 1972) has been developed on the basis of ideal thermodynamic solutions, which is mostly used for adsorbing systems with low adsorbent concentrations.

UT (University of Tehran) isotherm model (Baghdadi, 2017) is a dose-independent model capable of estimating the maximum adsorption capacity. The adsorption capacity achieved using the UT model is related to the multi-layer adsorption, while the adsorption capacity obtained from the Langmuir model corresponds to the monolayer adsorption on the surface of the adsorbent.

In order to estimate the accuracy of the isotherm models, the parameters of $R^2$, RMSE, and $\chi^2$ were calculated for each model, and the results are reported in Table 4. As is seen, amid the two-parameter isotherms, the Freundlich model with $r^2$ of 0.9984, RMSE of 9.506, and $\chi^2$ of 0.864 was the best correspondence to the experimental data, indicating that multi-layer adsorption has occurred on the heterogeneous surface. This could be due to the presence of various functional groups on the nanoadsorbent surface. On the other hand, among the 3-parameter isotherms, all three isotherms have the same performance. In general, 3-parameter isotherm models provided better simulation with $R^2$, RMSE, and $\chi^2$ with the amounts of 0.9995, 5.023, and 0.3, respectively. A similar trend was also reported by Behjati and coworkers (Behjati et al., 2018). The parameters of various isotherms are

\begin{table}[h]
\begin{tabular}{|c|c|c|c|}
\hline
Model & $R^2$ & RMSE & $\chi^2$ \\
\hline
Langmuir & 0.9877 & 28.32 & 9.689 \\
Freundlich & 0.9984 & 9.506 & 0.864 \\
UT isotherm & 0.9995 & 5.023 & 0.300 \\
Redlich-Peterson & 0.9995 & 5.023 & 0.300 \\
Radke-Prausnitz & 0.9989 & 5.023 & 0.300 \\
Temkin & 0.9839 & 24.319 & 8.639 \\
Dubinin-Radushkevich & 0.8028 & 102.17 & 104.97 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\begin{tabular}{|c|c|c|}
\hline
Model & Equation & Parameter Value \\
\hline
\begin{align*}
\text{Freundlich} & : \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \\
\text{Langmuir} & : \frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \\
\text{Radke-Prausnitz} & : \frac{C_e}{q_e} = \frac{1}{K_{RP} q_m} + \frac{C_e}{q_m} \\
\text{UT isotherm} & : \ln \left( \frac{C_e}{q_e} \right) = -b \ln C_e + b \ln C_r \\
\text{Redlich-Peterson} & : \ln \left( K_R \left( \frac{C_e}{q_e} - 1 \right) \right) = g \ln C_e + \ln a_R \\
\text{Temkin} & : q_e = R T \ln \left( 1 + \frac{1}{\beta} \right) \\
\text{Dubinin-Radushkevich} & : \ln q_e = \ln q_{oc} - \beta e^2 \\
\end{align*}
\end{tabular}
\end{table}

$q_{oc}$: maximum adsorption capacity (mg/g), $K_d$: desorption constant, $b$: UT exponent, FCF: dimensionless factor of UT isotherm related to adsorption affinity, $K_R$: (L/g) Redlich-Peterson constants and $g$: Redlich-Peterson exponent, $K_{RP}$: Radke-Prausnitz constant (L/mg), $R$: 8.314 gas universal constant (kJ/mol K), $T$: absolute temperature (K), $K_F$: isotherm constant indicates the capacity parameter (mg/g) (L/mg)$^{1/n}$, $K_L$: Langmuir constant or adsorption equilibrium constant (L/mg), $b$: (J mol$^{-1}$) Temkin constant $q_{oc}$ adsorption capacity (mg g$^{-1}$), $\beta$: constant of Dubinin-Radushkevich (mol$^2$ J$^{-2}$), $E$: related to free energy (kJ mol$^{-1}$).
calculated and reported in Table 5. Also, different chart diagrams and laboratory data are shown in Fig. 9.

The maximum adsorption capacity was calculated using the UT isotherm with the amount of 1126 mg/g, which was in good agreement with the experimental data. Langmuir isotherm also predicted a maximum adsorption capacity of 1192 mg/g. Although Radke-Prausnitz isotherm covered the experimental data appropriately, it could not calculate the maximum adsorption capacity. The predicted value of this model for the adsorption capacity was 196 mg/g, which was significantly different from the real value. Moreover, the value of “1/n” in the Freundlich isotherm was calculated around 0.46, which was close to zero, thereby confirming the heterogeneity of the nanoadsorbent surface. In addition, “R” parameter in the Langmuir isotherm was calculated in the range of 0.14–0.40, indicating that the adsorption process was favorable. Finally, the low value of the dimensionless parameter called free capacity fraction (FCF) in the UT isotherm showed that the Freundlich isotherm was more accurate than the Langmuir isotherm, which was in accordance with the parameters χ² and RMSE.

### 3.9. Thermodynamics studies

The thermodynamic parameters can provide useful information for detecting the nature of the adsorption process. In this study, the effect of temperature on the Hg (II) adsorption using thiol-functionalized CS NPs was investigated, and the results are represented in Fig. S5. As can be seen, increasing the temperature was favorable for the adsorption process. The thermodynamic parameters obtained from Eqs. (15)–(17) (Sahan et al., 2018) as follows were calculated and the results listed in Table 6.

\[
K_e = \frac{q_e^D}{c_e},
\]

\[
\Delta G^o = -RT \ln(K_e),
\]

\[
\ln(K_e) = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R},
\]

where “T” is the absolute temperature (K), “R” is the universal gas constant (8.314 J/(mol K)), “D” is adsorbent dosage, and “Ke” is the thermodynamic equilibrium constant of the adsorption. By plotting “ln (K_e)” as a function of “1/T”, “ΔH” can be calculated from the line slope, and “ΔS” can be obtained from the intercept according to Fig. S5. The positive value of “ΔH” demonstrated that the adsorption was endothermic. The positive value of “ΔS” was due to an increase in randomness at the solution/solid interface during adsorption (Qin et al., 2009). Furthermore, the negative value of “ΔG” showed the spontaneous nature of the adsorption process. This trend was due to the more increase in mobility of Hg (II) ions around the active sites of the adsorbent by increasing the temperature.

### 3.10. The mechanism of Hg (II) adsorption

Fig. 10 depicted the FTIR spectra of MF-fabricated thiol-functionalyzed CS NPs before and after adsorption of Hg (II). As is seen, two characteristic peaks before adsorption were observed at 1596 cm⁻¹ and 1403 cm⁻¹, which shifted to 1627 cm⁻¹ and 1397 cm⁻¹ after adsorption. It was due to the formation of Hg (II) chelate with nitrogen atoms of amino groups. Moreover, the strong peak related to −OH groups at 3420 cm⁻¹ changed to 3452 cm⁻¹, clearly indicating that they could positively influence the adsorption process (Azari et al., 2017). Apart from that, the intensity at the wavenumber of 1088 cm⁻¹ was reduced and shifted to 1111 cm⁻¹, suggesting that the oxygen atom in the hydroxyl groups was also involved in the adsorption of Hg (II). This conclusion was consistent with other studies for other metal ions. For instance, Ngah and Fatinathan (2010) suggested that the adsorption of Cu (II) ions on CS-TPP beads was probably by the chelation mechanism involving the nitrogen (from −NH₂ groups), and oxygen (from hydroxyl groups) atoms. Another reduced peak was at the wavenumber of 2585 cm⁻¹ which showed that sulfur groups were also responsible for
metal ion binding through chelation mechanisms. Sulfur sites were reactive groups for metal ions adsorption due to the fact that Hg (II) is a soft acid which has a high affinity towards soft bases such as sulfur atoms (Zhou et al., 2009). In addition, the amount of P=O groups at wavenumber of 1226 cm⁻¹ was negligible after Hg (II) adsorption, resulting in the contribution of phosphate groups for Hg (II) removal (Sureshkumar et al., 2010).

3.11. Desorption studies

One of the adsorbent requirements is the capability for reuse and recovery in view of commercial applications. For this purpose, the adsorption and desorption experiments were carried out to investigate the recyclability of the nanoadsorbent. In this study, HCl (0.1 M) as eluent was used for washing the nanoadsorbent during 15 min per cycle, and the results are shown in Fig. 11. As can be seen, the nanoadsorbent capacity is reduced slightly after 4 cycles of the adsorption/desorption process. This decrease could be due to inefficient desorption of Hg (II); as a result, some superficial sites have been deactivated (Vegahen et al., 2013). However, despite this decline, the adsorption capacity and the removal percentage were still over 65% and 80%, respectively. Considering the high adsorption capacity after 4 cycles of the adsorption/desorption process and also the possibility of easy separation of the nanoadsorbent by the magnetic field in order to recover, it could be concluded that the synthesized nanoadsorbent was a promising candidate for the mercury ion removal.

Finally, to do a comparison between the synthesized nanoadsorbent in this work and other adsorbents based on CS reported recently, Table 7 listed some literature. As can be seen, the adsorption capacity of the prepared adsorbent was higher than that of other reported adsorbents.

4. Conclusions

The synthesis of thiol-functionalized CS followed by the NPs fabrication using the MF technique was successfully carried out. The goal of this work was to compare the NPs fabricated by MF and BM methods as well as using them for adsorption of Hg (II) from aqueous solutions. In this line, the adsorbent with the epichlorohydrin to cysteamine molar ratio of 2.73 showed the highest capability to adsorb of Hg (II) ion. Furthermore, by comparing the morphology, zeta potential, and DLS data of the samples, it has been found that the MF technique could be considered as an efficient tool for the production of NPs with desirable size and uniform shape. The correctly functionalized thiol groups in the CS structure was confirmed by FTIR and CHNS analyses. Moreover, the XRD results revealed that the MF technique and the addition of Fe₃O₄ did not affect the CS structure. On the other hand, due to easy of separation of the NPs after Hg (II) adsorption from the aquatic environment, magnetite NPs brought the suitable magnetization characteristic for the samples, which was proved by VSM analysis. By utilizing the MBD method, the adsorption parameters such as the adsorbent dose, the initial concentration of Hg (II), and pH value were optimized to have the highest Hg (II) removal. Furthermore, different isotherms namely Arshadi, M., Mousavinia, F., Khosravi, N., Firouzabadi, H., Abbaspourrad, A., 2017. Adsorption of mercury ions from wastewater by a hyperbranched and multi-functionalized dendrimer modified mixed-oxides nanoparticles. J. Colloid Interface Sci. 505, 293–306. https://doi.org/10.1016/j.jcis.2017.05.052.


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