Silver/quartz nanocomposite as an adsorbent for removal of mercury (II) ions from aqueous solutions

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ARTICLE INFO
Keywords:
Environmental science
Silver nanoparticles (AgNPs)
Quartz
Nanocomposite
Adsorbent
Mercury (II)

ABSTRACT
Silver nanoparticles (AgNPs) and silver/quartz nanocomposite (Ag/Q)NPs) were synthesized by sol-gel method using table sugar as chelating agent. The synthesized nanosized materials were used for mercury ions adsorption from aqueous solutions. The materials were characterized by X-ray diffraction (XRD), Transmission Electron microscope (TEM), and surface area (BET). Adsorption of Hg^{2+} (10 mg/l) is strongly dependent on time, initial metal concentration, dose of adsorbent and pH value. Silver/quartz nanocomposite ((Ag/Q)NPs)) shows better efficiency than individual silver nanoparticles (AgNPs). This composite removed mercury ions from the aqueous solution with efficiency of 96% at 60 min with 0.5g adsorbent dosage at pH 6. The adsorption process explained well by the pseudo-second-order kinetic model. In conclusion silver/quartz nanocomposite (Ag/Q)NPs)) shows higher removal efficiency for mercury ions from aqueous solutions than individual silver nanoparticles (AgNPs) or quartz (Q).

1. Introduction
Clean water is a vital demand and basic necessity for human being [1, 2]. There is a shortage in clean water resources, almost one-sixth of the world's population suffers from this crisis [3]. This crisis comes from fast increase in world population, global warming and of course rapid dwindling of water resources. So, organized usage of water resources and reuse of treated wastewater using cheap and environmental friendly technologies is an effective way of conserving the limited resources of freshwater [4, 5]. Heavy metals in water sources cause severe health problems in animals, aquatic organisms and human beings through the food chain due to their high toxicity and non-biodegradable properties [6]. These pollutants resulted from elevated release of effluents by various industries such as plating, metallurgical, leather, metal finishing, welding alloy manufacturing plants, fertilizers, chemicals etc. [7, 8]. Mercury represents one of the largest levels of toxicity which can accumulate in ecosystems as listed by the World Health Organization (WHO) [9, 10]. Inorganic divalent mercury (Hg^{2+}) is discharged into ecosystem from different industries as paper and pulp, plastic, paints, battery, pharmaceutical and oil refineries. This toxic metal can damage the kidney, brain, reproductive and respiratory system [11, 12]. The high risk of mercury pushed researchers to search for various techniques for protection of environment and human beings through different remediation processes [13]. Several techniques e.g., filtration, chemical precipitation, solvent extraction, ion exchange, electrochemical deposition, electrolysis, and membrane process have been designed. Most of these methods are either expensive or inefficient for lower concentration of the heavy metal ion [14]. The adsorption method which is one of the most suitable, simple and economically techniques used to purify water and wastewater [15, 16, 17]. Several adsorbents have been applied to remove mercury ions such as clays, silica, carbon nanotubes, polymers and activated carbons [18, 19, 20, 21, 22, 23]. The nanosized metals or metal oxides have received great attention as adsorbents in water remediation due to their high performance and lower cost than traditional old materials [24]. The nanomaterials have not only high surface area and hence high density of active sites per unit mass, but also high surface free energy, resulting in enhanced surface reactivity [25, 26, 27]. Metallic nanoparticles such as silver nanoparticles (AgNPs) have good behavior as viable adsorbents as they have good chemical and physical properties. Ag NPs have high catalytic activity, biocompatibility, high adsorption
capacity due to its high surface area and can be reused and separated easily [28, 29]. Some studies on removal of mercury have used silver nanoparticles as adsorbents [30, 31]. As the chemically synthesized AgNPs have low adsorption capacity due to its lower stability and its tendency to be aggregated, an urgent appropriate synthesis technique for the development of stable silver is required [4]. AgNPs may be stabilized by mixing with other inorganic metal oxides e.g. SiO2, TiO2, ZnO, SiO2-TiO2 forming composite nanoparticles of silver-metal oxides [32, 33, 34, 35, 36]. Quartz sand, which is the main component of natural sand stone is used widely in industrial manufacturies due to its physical and chemical characteristics such as low cost, resistant to high temperature and non-toxic [37, 38, 39]. There was no great attention to the use of quartz sand as a natural adsorbent to remove heavy metals from water. For the above reason, this study will focus on using AgNPs/quartz (Ag/Q) nanocomposite as an adsorbent to remove mercury from aqueous solution by sol-gel method, considered as a versatile and cheap technique. Table sugar was used as chelating agent to prepare AgNPs then modified by quartz to prepare AgNPs/quartz composite. The samples prepared were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and surface area (BET). The efficiency of the prepared sample for efficient removal of Hg2+ from aqueous solution was explored at different operating conditions such contact time, initial metal concentration, initial pH and adsorbent dosage. The experimental data were fitted with various kinetic and isotherm models to explain the adsorption mechanism.

2. Materials and methods

2.1. Materials

All the reagents used were of analytical grade and used directly as received and stock solutions were prepared using deionized water. Pure AgNO3 (Aldrich, Germany) and table sugar were used to prepare silver nanoparticles. Pure quartz samples were purchased from El-Nasr Mining Company to prepare a composite of silver/quartz nanoparticles (Ag/Q) NPs. To prepare the working mercury stock solution for the adsorption experiments, Pure Hg(NO3)2 (Aldrich, Germany) was used.

2.2. Synthesis and characterization of Ag/quartz (Ag/Q)NPs composite nanoparticles

In this study silver nanoparticles (AgNPs) and composite of (Ag/Q) NPs were prepared using sol-gel technique assisted by table sugar as chelating agent. Silver nanoparticles were prepared by dissolving 4.724g AgNO3 in bidistilled water to prepare AgNO3 solution. The solution was added drop wisely to 1.5 M solution of table sugar. The entire solution was heated at 80 °C till evaporation and formation a black gel. The collected zero-gel was dried overnight at 90 °C then calcined at 350 °C for 5 hours in an ambient atmosphere yielded powder of silver nanoparticles. The same procedure mentioned above has been used to prepare silver-quartz composite (Ag/Q)NPs. Simply calculated and intended amount of quartz was dropped in the sol-solution of Ag salt and table sugar. The entire mixture was heated until formation of a gel. The collected zero-gel was dried overnight at 90 °C then calcined at 350 °C for 5 hours in an ambient atmosphere yielded composite of silver/quartz nanoparticles.

Different techniques characterized the synthesized samples. X-ray powder diffraction patterns (XRD) were recorded using a Philips X’Pert apparatus equipped with a CuKα X-ray source (λ = 1.54056 Å) in the 2θ range 10–80°. Transmission electron microscope, JEOL (TEM, JEM-1230) Japan used for investigation the morphology of prepared samples. The specific surface area was measured by nitrogen adsorption/desorption at 77 K using BET method (Quantachrome NOVA Automated Gas Sorption). The concentrations of Hg2+ were measured using inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent 5100) according to APHA 2012. Finally, mercury ions removal from wastewater using silver-quartz composite nanoparticles was studied using multiple batch sets of experiments.

2.3. Adsorption study

All batch adsorption experiments were conducted by mixing an sufficient amount of adsorbents (silver nanoparticles (AgNPs), quartz (Q) and silver-quartz composite nanoparticles (Ag/Q)NPs)) with a known volume of Hg2+ at various initial concentrations (5, 10, 50 and 100 mg/L) with shaking (150 r/min). Then, the supernatants were separated from the mixture solution by filtration with PTEF syringe filter. The influence of contact time was assessed at different time intervals by agitation (5–150 min). In order to optimize the adsorption process, other factors such as initial pH, adsorbent dose (0.05–1 g) and temperature were also examined.

Based on the following equations, the equilibrium adsorption capacity, qe (mg/g) and the removal efficiency of metal ions were estimated:

\[ q_e = \frac{(C_0 - C_e) V}{m} \]  
\[ \text{% Removal} = \frac{C_0 - C_e}{C_0} 	imes 100 \]

Where V: sample volume (L), m: mass of the adsorbents (g), C₀: initial metal ion concentration (mg/L), and Cₑ: equilibrium concentration of metal ion in the solution (mg/L).

2.4. Adsorption isotherms, kinetics and thermodynamic studies

The equilibrium data, commonly known as adsorption isotherms are basic parameters for the design of adsorption systems and these data provide information on the adsorbent capacity or the amount required to remove a pollutant mass under the system conditions. The equilibrium adsorption isotherm data for Hg2+ adsorption by the prepared composite (Ag/Q)NPs are fitted in different classical models. The Freundlich, Eq. (3) [40], Langmuir, Eq. (4) [41], Dubinin–Radushkevich, Eq. (5) [42] and Redlich–Peterson Eq. (6) [43] are the models used in this research to investigate the adsorption equilibrium

\[ q_e = K_F C_e^n \]  
\[ q_e = q_m K_f C_e \]  
\[ q_e = q_m e^{(-\frac{K_F C_e}{1 + K_F C_e})} \]  
\[ q_e = \frac{K_d C_e}{1 + a C_e} \]

Where, Cₑ (mg/L) is the equilibrium concentration, (Kf) and (n) are the Freundlich adsorption constants which are related to the adsorption capacity, qₑ (mg/g) and the removal efficiency of adsorption sites and qₑ (mg/g) represents the maximum theoretical monolayer adsorption capacity. Langmuir isotherm based on homogeneous and monolayer adsorption while Freundlich isotherm deals with heterogeneous and multilayer adsorption process. The favorability of adsorption of Hg2+ ions was tested using a dimensionless constant separation factor or Redlich constant (Rd) that is a characteristic parameter of Langmuir isotherm which defined based on Eq. (7):
The RL value indicates whether the isotherm is favorable (0 < RL < 1), unfavorable (RL > 1), linear (RL = 1), or irreversible (RL = 0).

The Dubinin–Radushkevich isotherm model Eq. (5) was chosen to estimate the characteristic porosity of the adsorption process where, \( \beta \) is a constant related to mean free energy (mol\(^2\)/kJ\(^2\)), and \( \varepsilon \) representing Polanyi potential, which can be calculated from Eq. (8):

\[
\varepsilon = RT \ln \left(1 + \frac{1}{C_0}\right) \tag{8}
\]

The isotherm formulated for the adsorption process following a pore filling mechanism by calculating its mean free energy, the apparent energy of adsorption \( E \) (kJ/mol), and \( \varepsilon \) representing Polanyi potential, which can be calculated from Eq. (8):

\[
E = \frac{1}{\sqrt{-2\beta}} \tag{9}
\]

Redlich-Peterson isotherm model has a linear dependence on concentration and represent adsorption equilibrium over a wide concentration range in homogeneous or heterogeneous systems. The isotherm approaches Freundlich isotherm model at high concentration (as the exponent \( \beta \) tends to zero) and is in accordance with the lower concentration limit of the ideal Langmuir condition (as the \( \beta \) values are all close to 1). \( k_g \) (L/mg) constant related to the adsorption capacity, \( k_b \) (L/mg) constant related to the affinity of the binding sites and \( g \) (g) exponent related to the adsorption intensity which lies between 0 and 1.

\[
R_i = \frac{1}{1 + bC_0} \tag{7}
\]

To investigate the adsorption mechanism its potential kinetic models have been exploited to analyze the experimental data. Adsorption kinetics were performed at different time intervals (5–120) and constant metal concentration (20 mg/l) at room temperature through adsorption experiments. Several kinetic models such as Pseudo-first-order Eq. (10) [44], pseudo-second-order Eq. (11) [45], and Intra-particle diffusion model Eq. (12) [46]:

Models are expressed in equations as follows:

\[
q_t = q_e \left(1 - e^{-k_1t}\right) \tag{10}
\]

\[
q_t = \frac{k_2q_e t}{1 + k_2q_e t} \tag{11}
\]

where, \( q_e \) is the amount of adsorbed metal at equilibrium (mg/g) at time \( t \) and \( k_1 \) (min\(^{-1}\)), \( k_2 \) (g/mg.min) are the adsorption rate constants.

The pseudo-second-order model could not identify the diffusion mechanism and the kinetic results were then analyzed by using the intra-particle diffusion model. In the model developed by Weber and Morris [47], the initial rate of intra-particle diffusion is calculated by linearization of Eq. (12):

\[
q_t = k_p t^{1/2} + C \tag{12}
\]

where, \( C \) is the intercept and \( k_p \) is the intra-particle diffusion rate constant (mg/g min\(^{1/2}\)).

In any adsorption process, both energy and entropy considerations
were obtained using Van’t Hoff equation. The thermodynamic parameters as Gibbs free energy (\(\Delta G^\circ\)) and entropy change (\(\Delta S^\circ\)) which are determined according equations:

\[
\Delta G^\circ = -RT\ln K_d
\]  
(13)

\[
k_d = \frac{q_t}{C_d}
\]  
(14)

\[
\Delta S^\circ = \frac{\Delta H^\circ}{T}
\]  
(15)

2.5. Leaching and regeneration studies

Leaching of Ag\(^+\) ions from the prepared composite was determined by using the batch leaching test using distilled water. The test was performed at a ratio of 0.5 g/l at different stirring times (2, 6, 12, 24, 36 and 48 h). At the end of the leaching process, the samples were filtered and the concentration of Ag\(^+\) ions were determined by means of ICP-OES (Agilent 5100). To study the regeneration ability of the adsorbent, the composite samples saturated with Hg\(^{2+}\) ions were conducted with different desorbing agents 0.1 M HNO\(_3\), and HCl for 1 h. After each cycle of sorption/desorption, the solution was washed with deionized water to reach to neutral pH and then the adsorbent was dried for reuse in the next cycle. The concentrations of Hg\(^{2+}\) and Ag\(^+\) were monitored in each cycle.

3. Results and discussion

3.1. Structural characterization

The crystal structures of silver nanoparticles (AgNPs), quartz and its composite (Ag/Q)NPs are analyzed by X-ray diffraction and displayed in Fig. 1a and their refined X-ray diffraction patterns are reported in Fig. 1b-d. XRD and refined XRD of AgNPs and quartz shown in Fig. 1a-c displayed well indexed XRD peaks for AgNPs of cubic structure with space group Fm3m (JCPDS file 03-0931). These figures confirmed also, the trigonal structure with space group P321 (JCPDS file 46-1045) for quartz. So, pure phases of AgNPs and quartz are obtained without impurity peaks. Refined XRD result of AgNPs/quartz composite (Ag/Q)NPs is shown in Fig. 1d. The composite still has the crystalline state. Strong and sharp diffraction lines originate from silver (Ag) with a cubic structure (Fm3m) and quartz with a trigonal structure (P321). From the beginning we aimed to fabricate 50:50 % of AgNPs/quartz composite. Rietveld refinement of this composite detected 46.8: 53.2% of AgNPs/quartz close to the starting ratio that we used. A slight decrease in the net area and intensity of silver and quartz diffraction lines corresponds to a decrease of silver and quartz amounts from 100% in each pure phase to 46.8 and 53.2%, respectively in the composite. In addition, quartz matrix provides incorporation of silver particles [49]. So, this quartz matrix acts as a shield and protects accommodated silver particles to be oxidized. Incorporation of AgNPs inside quartz matrix may provide not only new active centers in quartz matrix, but also a long adsorbent effect for removal of toxic heavy metals. There is no evidence in the XRD spectrum for Ag\(_2\)O or other silver oxides, as compared with reported data [50, 51].

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Fig. 2a and b, show the nitrogen adsorption–desorption isotherms and pore-size distributions (PSD) for the pure AgNPs, quartz and (Ag/Q)NPs composite, respectively. All the three samples exhibit similar shape of the isotherms that can be described as type II and H3 hysteresis loop under the IUPAC-classification [52, 53], implying the presence of porous structure [27, 54]. The analysis of the pore distribution in Fig. 2b showed that the pores distribution for all three samples is very uniform. For Ag/QNPs composite. The shift in the distribution of pores to small pores can be attributed to the presence of some silver nanoparticles within the pure quartz host matrix [55]. This phenomenon is also associated with a decrease in BET surface area. Based on the isotherms (Fig. 2a), the isotherms for the (Ag/Q)NPs composite is similar in shape to the pure AgNPs and quartz. The BET surface area, the total pore

Table 1

| Sample     | BET surface Area (m²·g⁻¹) | Total pore volume (cm³·g⁻¹) | Average pore size (nm) |
|------------|---------------------------|----------------------------|------------------------|
| AgNPs      | 138                       | 0.0051                     | 14.76                  |
| quartz     | 189                       | 0.0070                     | 14.78                  |
| (Ag/Q)     | 172                       | 0.0031                     | 5.78                   |

---

Fig. 2. (a) N₂ adsorption-desorption isotherms and (b) the pore size distribution (PSD) curves of (AgNPs), quartz and AgNPs/quartz composite.
volume and the porosity of the (Ag/Q)NPs composite are smaller than that obtained for the pure AgNPs and quartz (Table 1). This can be due to the dispersion of Ag nanoparticles inside the mesoporous quartz and decrease the degree of porosity of quartz, but increase the active adsorbent sites of composite as we will notice in adsorption activity of composite for removal of Hg.

Transmission electron microscopy (TEM) has been employed to characterize the size, shape and morphology of silver nanoparticles (AgNPs), quartz and (Ag/Q)NPs composite as shown in Fig. 3a–c. Fig. 3a shows that AgNPs are spherical in shape having smooth surface and are well dispersed. TEM image also show that the AgNPs having different size distributions between 12-60nm. The minimum and maximum size of AgNPs are about 12 and 60 nm respectively, the large particles size may be due to aggregation or clustering of the Ag nanoparticle. The average diameter of AgNPs is found to be approximately 25nm. TEM images of pure quartz (Fig. 3b) show irregular, big and non-homogeneous particles. TEM of (Ag/Q)NPs composite is shown in Fig. 3c, the nanocomposite consists of AgNPs not only located on the surface but also embedded within the matrix of quartz.

3.2. Adsorption studies

Contact time and concentration dependence sorption of Hg\(^{2+}\) was studied within a wide range of initial concentrations using the examined adsorbents. Fig. 4 shows the removal efficiency of Hg\(^{2+}\) ions with time by AgNPs, quartz and (Ag/Q)NPs composite at initial metal concentration of 10 mg/L. The removal of Hg\(^{2+}\) in the first 30 min attained 82%, 86.5% using AgNPs and Q respectively while (Ag/Q)NPs composite removed 92.1% of Hg\(^{2+}\) ion at the same time (30 min). The adsorption attained an apparent equilibrium at 60 min with a removal percentage of 96 % using (Ag/Q)NPs composite, while, the adsorbed Hg\(^{2+}\) remained constant. Further increase of contact time does not significantly affect the Hg\(^{2+}\) adsorption capacity due to the saturation of the active binding sites. By increasing the initial concentration of Hg\(^{2+}\) ions, the adsorption decreases as shown in Fig. 5. At low concentration, for few numbers of mercury ions to be adsorbed, more effective adsorption sites are available, but at higher concentration, the number of mercury ions is much higher than the available adsorption sites. The rivalry of mercury ions for response with the adsorbent surface is growing by raising the original concentration of mercury ions. As a consequence, more active adsorbent sites are saturated. Furthermore, the amount of collisions between mercury ions and adsorbents is increasing and adsorption is increasing [56]. The adsorption efficiency reached 97, 96, 88 and 83 % using 5, 10, 50, 100 mg/L.
100 mg/L respectively. The equilibrium time of adsorption is independent of initial concentrations. Slight differences in removal percentage obtained between initial concentrations of 5 and 10 mg/L.

The effect of pH is a significant factor in the process of metals adsorption from aqueous solution. The influence of pH on mercury ions removal by the (Ag/Q)NPs composite in the pH range of 2–6 is given in Fig. 6 at the optimum time 60 min. The increase in removal percentage was observed till reached the maximum removal at pH 6. In addition, mercury ions are free of Hg²⁺ at pH less than 6 and positively charged hydrogen ions compete with Hg²⁺ for binding with adsorbent active sites on the surface of (Ag/Q)NPs composite. If the composite adsorbent surface (Ag/Q)NPs is protonated by hydrogen ions, the electrostatic interaction will reduce and the effectiveness of Hg²⁺ adsorption by the composite (Ag/Q)NPs will reduce. At pH up to 6, metal removal improved owing to the reduction in rivalry for the same functional groups between proton and metal cation. Hg²⁺ particles start depositing as hydroxides Hg(OH)₂ or soluble Hg(OH)⁺ at pH more than 6 [57,55]. The studies were therefore not carried out at pH more than 6 because the precipitates in the solution will be created. As consequence, this research regarded that the optimum pH was equivalent to 6.

The effect of (Ag/Q)NPs composite dose on Hg²⁺ removal was investigated at 60 min and pH 6 for dose (0.05–1 g). Increasing the amount of adsorbing sites available results in enhanced adsorbent effectiveness in removing ions from mercury to a certain limit. After this limit and at elevated adsorbent dose, the level of mercury in solution reaches a minimum quantity, and then the effectiveness of removing Hg²⁺ starts to decrease. This conduct is shown clearly in Fig. 7. Hg²⁺ ions removal percentage increased from 81% to 96% using 0.05 g and 0.5 g, respectively. The efficiency of removal using dose greater than 0.5 g showed no significant increase in removal of Hg²⁺, so the optimum adsorbent dose was considered to be 0.5 g.

Using isothermic models (Langmuir Eq. (3), Freundlich Eq. 4, Dubinin–Radushkevich (D-R) Eq. (5) and Redlich–Peterson (R-P) eq.6) were evaluated to optimize the adsorption method. The experimental information were better fitted with the Langmuir model with correlation factor (R²) 0.98 as shown in Table 2 and Fig. 8. In this study the qₘₐₓ value for Hg²⁺ ions adsorption on the nanocomposite was 376.2 mg g⁻¹. The values of Rₑ are ranged between 0.12 and 0.92 revealing that the adsorption is favorable. The value of (1/n) is 0.35 which less than unity indicating a favorable adsorption process of Hg²⁺ ions onto (Ag/Q)NPs composite and chemisorption reaction. The values of the apparent energy E, obtained from D-R model is 11.7 kJ/mol that is between 8 and 16 kJ/mol revealing chemical ion exchange mechanism. The Redlich-Peterson isotherm showed the less fitting of the equilibrium data. The values of the applied isotherm parameters are listed in Table 2. The value of g in Redlich–Peterson is equal 1, indicating a favorable adsorption and the R–P equation can be reduced to the Langmuir equation. So, Langmuir is the most appropriate model describing the experimental data for Hg²⁺ adsorption.

Different kinetic adsorption models (Pseudo-first order, Pseudo-second order, and intra-particle diffusion) were used for Hg²⁺ ions adsorption on (Ag/Q)NPs composite in order to recognize the kinds of
adsorption mechanism. Fig. 9 shows the nonlinear fitting of kinetic models of Hg$^{2+}$ ions adsorption. Table 3 shows the estimated values for (qe) and the constants of the models. It can be seen that the value of the correlation coefficients (R2) acquired for the pseudo-first-order kinetic model Eq. (10) was small, which shows a poor linearization, and the estimated values (qe) collected from the plots were not compatible with the experimental values showing the adsorption by the pseudo-first-order kinetic model. The equation parameters of the pseudo-second-order kinetic model Eq. (11) are shown in Table 3 and, as noted, the correlation coefficient (R2) was close to 1 and the calculated (qe) value was well agreed upon by the experimental value indicating that the response is well matched by pseudo-second-order and that adsorption may happen through chemisorption response.

The kinetic data were analyzed by the intra-particle diffusion kinetic using Weber’s equation Eq. (12) to explain the mechanism of chemical adsorption. The adsorption process may be controlled by film and pore diffusion (intra-particle diffusion), surface diffusion and adsorption on the pore surface [58]. The model is applied by plotting of qt vs. t$^{1/2}$ as shown in Fig. 10 and the parameters of the model are listed in Table 3. The plot should be linear if the adsorption follows a diffusion mechanism. The acquired plot shown in Fig. 10 did not pass through the origin and stated multi-step adsorption mechanism which shows that not only intra-particle diffusion influenced adsorption by more than one method. The plot’s original part stated external surface adsorption, while the solid-solution interface and a elevated mercury ion affinity to form mercury amalgam. This hypothesis of the formation of silver amalgam was endorsed by Z. Tuanov et al. He used zeolite nanocomposite impregnated with carbon fly ash/silver NPs to remove Hg$^{2+}$ from aqueous solution [59]. The mechanism of adsorption on the prepared nanocomposite may result from redox reaction of Ag$/\text{Ag}^+$ (+0.80 V) and Hg$^{2+}$/Hg$^+$ (+0.85 V), which occurs due to close redox potentials of two metals. The mechanism also suppose the formation of an amalgam between two metals Ag$_x$Hg$_y$ or precipitation of Hg$^+$ on the composite surface. So the mechanism of Hg$^{2+}$ removal might physical adsorption and/or precipitation of mercury as Hg$^+$. Henglein and Brancewicz [60] and Henglein [61] observed the Hg$^{2+}$ reduction and amalgamation according to the following reactions

$$\text{Hg}^2+ + \text{mAg} \rightarrow \text{mAg}^+ + \text{m/2 Hg} \quad (16)$$

$$\text{Ag}_x\text{Hg}_y + \text{Hg}^+ \rightarrow \text{Ag}_x\text{Hg}_y + 2\text{Ag}^+ \quad (17)$$

Additional studies are required to comprehend the Hg$^{2+}$ removal mechanism and to assess the expenses and advantages of using quartz/Ag NPs nanocomposite materials.

### 3.3. Thermodynamic studies

Temperature-dependent adsorption isotherms (Eqs. (13), (14), and (15)) can be used to estimate the thermodynamic parameters ($\Delta H$, $\Delta S$ and $\Delta G$) for Hg$^{2+}$ ions adsorption on (Ag/Q)NPs composite nanoparticles. The values ($\Delta H$) and ($\Delta S$) can be predicted from the lnKd plot versus 1/T (Fig. 11). The positive ($\Delta H$) value indicates the process's endothermic nature. The free energy ($\Delta G$) of Hg$^{2+}$ ions adsorption (Ag/Q)NPs is more negative at greater temperatures, which shows that the spontaneous nature of the adsorption method is more negative. The beneficial value of entropy change is due to the increased randomness of the solid-solution interface and a elevated mercury ion affinity (see Table 4).

### 3.4. Leaching and regeneration studies

Silver ions were leached slightly after 2hours using distilled water as the eluent. The leaching decreased with time and the release began to equilibrate at 12 hours with silver concentration of 0.01 mg/l (Fig. 12). Using HCl seems to be the highest eluent with an efficiency equal to 97% suggesting that (Ag/Q)NPs composite has a decent desorption capacity for Hg$^+$. After four cycles of adsorption – desorption as shown in Fig. 13, the desorption capacity of the prepared composite slightly decreased. The release of Ag$^+$ ions using HCl acid by desorption of Hg$^{2+}$ was very low and can be ignored, which can help the adsorption of Hg$^{2+}$ on the composite surface. The desorption of Hg$^{2+}$ ions efficiency equal to 80 % using HNO$_3$ acid. The composite's reusability for Hg$^{2+}$ adsorption was

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### Table 3

| Kinetic models            | Parameters   | First order model | Second order model | Intraparticle diffusion model |
|---------------------------|--------------|-------------------|--------------------|-------------------------------|
|                           | qe (mg/g)    | k$_1$ (min$^{-1}$) | k$_2$ (mg/g/min)   | K$_p$ (mg/g min$^{1/2}$)     |
|                           | 18.3 ± 0.31  | 0.34 ± 0.06       | 19.2 ± 0.23        | 0.66                          |
|                           | 0.38         |                   | 0.006 ± 0.005      | 14.3                          |
|                           |              |                   | R$^2$              |                               |
|                           |              |                   | 0.977              |                               |
|                           |              |                   |                   |                               |

### Table 4

| Temperature (K) | $\Delta G$ (kJ/mol) | $\Delta H$ (kJ/mol) | $\Delta S$ (J/mol K) | R$^2$ |
|-----------------|----------------------|---------------------|----------------------|-------|
| 313             | -10.3                | 8.3                 | 59.8                 | 0.978 |
| 333             | -11.5                |                     |                      |       |
| 348             | -12.6                |                     |                      |       |
reported at 95%, which before adsorption is almost the same. The (Ag/Q)NPs composite was therefore an effective and stable Hg²⁺ removal adsorbent. Due to adsorbent structural instability, the adsorption capacity may be decreased after regeneration.

3.5. Comparison with other studies

Many variables play a crucial role in the efficiency of adsorption capacity such as the origin of the adsorbent, the type of modification, metal ion solution experimental conditions (pH, ionic medium, ionic strength, metal ion concentration, temperature). This makes it hard to compare the adsorption capacity of the distinct adsorbents as it depends on the variables listed above. Table 5 shows the ranges of maximum adsorption capacity values (qm) of some adsorbents towards Hg²⁺ removal. As we observe in this work, composite (Ag/Q)NPs removed 376.3 mg/g Hg²⁺ ions at pH 6 from the aqueous solution. This good result is ascribed to wealthy active adsorbent sites in (Ag/Q)NPs composite, besides being non-toxic and having antibacterial activity [62]. The (Ag/Q)NPs composite could therefore be one of the best candidates to remove mercury ions from water solution for drinking water preparation.

![Image](43x217 to 284x344)

Fig. 12. Leaching test of Ag from (Ag/Q)NPs composite using distilled water.

![Image](43x217 to 284x344)

Fig. 13. Regeneration of Hg²⁺ ions from (Ag/Q)NPs composite.

### Table 5

Ranges of maximum adsorption capacity values (qm) of some adsorbents towards Hg²⁺ removal.

| Adsorbent                             | Maximum adsorption capacity (qm) | Ref. |
|---------------------------------------|----------------------------------|------|
| Ag supported on nano mesoporous silica. | 42.26 mg/g                        | [55] |
| buckwheat hulls                       | 243.90 mg/g                      | [63] |
| LCF wastes of coconut                 | 144.4 mg/g                       | [64] |
| Apatite                               | 38 mg/g                          | [65] |
| Hybrid nanosilica                     | 134 mg/g                         | [66] |
| modified sodium montmorillonite       | 140.84 mg/g                      | [67] |
| Ag/quartz nanocomposite               | 376.3 mg/g                       | This work |

4. Conclusion

In this study, natural quartz, silver nanoparticles AgNPs and Ag/quartz nanocomposite (Ag/Q)NPs were used as adsorbents to remove mercury ions from aqueous solution. AgNPs and (Ag/Q)NPs composite were synthesized by sol-gel method using table sugar as chelating agent. The prepared samples were characterized using XRD results emphasized the formation of (Ag/Q)NPs composite where AgNPs are embedded inside the quartz matrix. The BET surface area, the total pore volume and the porosity of the (Ag/Q)NPs composite are smaller than that obtained for the pure AgNPs and quartz. TEM of (Ag/Q)NPs composite confirmed that AgNPs not only located on the surface but also embedded within the matrix of quartz. Adsorption is strongly dependent on time, initial metal concentration, dose of adsorbent and initial pH. (Ag/Q)NPs composite yielded the maximum removal of mercury ions from the aqueous solution 96% at 60 min with 0.5g adsorbent dose at pH 6. The equilibrium adsorption isotherms are well fitted by Langmuir equations. The adsorption process followed the pseudo-second order model. Positive ΔH and ΔS values indicated that the adsorption of Hg²⁺ ions onto (Ag/Q)NPs composite was endothermic, spontaneous and feasible process.

Declarations

Author contribution statement

R. S. El-Tawil: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

S. T. El-Wakee, A. E. Abdel-Ghany: Contributed reagents, materials, analysis tools or data.

H. M. Abueid: Conceived and designed the experiments; Performed the experiments.

K. A. Selim: Contributed reagents, materials, analysis tools or data.

A. M. Hashem: Analyzed and interpreted the data; Wrote the paper.

Funding statement

This work was partially funded by National Research Center, Cairo, Egypt through house project with ID (11050104).

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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