# Highly Selective Removal Mercury (II) from Aqueous Solution Using Silica Aerogel Modified with [1-(3,5-dicholorophenyl)-3(2-ethoxyphenyl)] triazene

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(Received on 16th September 2016, accepted in revised form 13th October 2017)

**Summary:** This paper reported the preparation of silica aerogel (SA) adsorbent coupling with chelating ligands of [1-(3,5-dicholorophenyl)-3(2-ethoxyphenyl)] triazene (DCPEPT) and its application for highly selective adsorption of Hg (II) ion. The functionalized nanoparticles were characterized using fourier transform infrared spectra (FTIR) and thermo gravimetric analysis (TGA) measurements, nitrogen physisorption and scanning electron microscope (SEM). The adsorption of Hg (II) on these nanomaterials was studied as a function of pH, temperature, adsorbent dosage and contact time. Langmuir and Freundlich isotherm models were applied to analyze the experimental data. Moreover, the optimum pH for the adsorption was found to be 6.0 with the corresponding adsorbent dosage level of 0.05 g at 20ºC temperature. Subsequently, the equilibrium was achieved for Hg (II) with 30 min of contact time. The best interpretation for the experimental data given by the Langmuir isotherm equation and maximum adsorption capacity of the sorbent under the optimal conditions was 198.25 $mgg^{-1}$. These facts indicate that modified silica aerogel with DCPEPT can be used as an inexpensive, efficient, and environmentally safe adsorbent for removal of Hg(II) from aqueous solutions.

Keywords: Mercury; Silica aerogel; Triazene; Selectivity; Adsorption.

## Introduction

Mercury is considered as one of the most toxic heavy metals, and its existence in water would be a potential hazard to human health [1]. According to the regulation of water quality, European Union, 1 $\mu gL^{-1}$ as the maximum mercury concentration allowed in drinking water. Therefore, a very low concentration of mercury in water is very toxic [2]. Long term effect of Hg(II)-contaminated water causes damage of central nervous system, impairment of kidney function, chest pain and genetic disorders in humans [3]. Industrial wastewaters are main sources of Hg(II) contamination in natural water. Therefore, the removal of Hg(II) from wastewaters before being disposed in the environment is required [4]. Technologies like precipitation [5], ion exchange [6], amalgamation [7], coagulation [8], membrane separation [9], and adsorption [10] are reported for Hg(II) removal from wastewater. Among them adsorption is regarded as a promising technology for its easy operation, low cost and little by-products [11]. Various synthetic materials have been reported to adsorb Hg(II) from aqueous solution[12-14]. Recently, nanomaterials have been shown to be one of the most promising adsorbents for preconcentration of the metal ions [15-16]. Aerogels are ultra-porous material made by sol–gel process and supercritical drying technology. The main properties of aerogels are very low density (between 3 $kg/m^3$ and 500 $kg/m^3$) and low thermal conductivity (<0.02 W/m K), high porosity (>90%), high specific surface area (150–1000 $m^2/g$) [17].

Silica aerogel is the most common type of aerogel, and the most extensively studied and used[18]. The major advantage of silica aerogel (SA) for use adsorption is that modifications with chelating agents. So some researchers modified aerogel with chelating agents [19], such as polyacramide [20], mercaptopropyl [21] and 4-amino-5-methyl-1,2,4-triazole-3(4H)-thion(AMTT) [22]. In this study the [1-(3,5-dicholorophenyl)-3(2-ethoxyphenyl)] triazene (DCPEPT) was used as metal chelating ligands (for structure see Fig. 1) and its application was investigated for selective adsorption of Hg (II) ion.

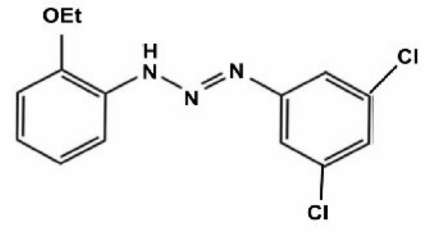

Fig. 1: Structure of [1-(3,5-dicholorophenyl)-3(2-ethoxyphenyl)] triazene (DCPEPT).

Triazene compounds, having a diazoamino group (–N=N–N–), able to form very strong complex with Hg (II) [23] ions.

The present work had two aims: first, the synthesis of silica aerogel (SA) nanoparticles

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adsorbent coupling with metal chelating ligands of DCPEPT by sol gel method. Secondly, this sorbent were evaluated for the removal of Hg (II) from aqueous solutions. The main novelty of this work is to present considerable potential of silica aerogel for the removal of Hg (II) from aqueous solution with higher adsorption capacity. The effects of the pH, temperature, adsorbent dosage and contact time were studied to determine the optimal adsorption conditions.

Regeneration and reusability of the adsorbent was also tested to evaluate the economics of the adsorbent as the Hg(II) removal. The thermodynamic functions and adsorption isotherms for Hg (II) ions onto SA-DCPEPT from aqueous solutions were also evaluated.

## Experimental

### *Materials and methods*

The chemicals used in this study for the preparation of modified silica aerogels by sol–gel synthesis were tetramethoxysilane (TMOS) and methyltrimethoxysilane (MTMS) from Aldrich. DCPEPT was prepared according to the method described by [24],. 0.1% (m/v) of DCPEPT solution was daily prepared in acetonitrile mixture. Other chemicals used in this study included methanol, $HNO_3$, KBr, KSCN, $(NH_2)_2CS$, Thiourea and NaOH were of analytical grade from E.Merck. Doubly distilled deionized water was used in all experiments.

Atomic absorption analysis of the various metal ions was performed with a flame atomic absorption spectrophotometer (Perkin-Elmer, Model 4100, made in Australia.2004), equipped with a GTA-100 graphite furnace atomizer). Morphology of samples was observed by scanning electron microscope (SEM) equipped with (EDX, XL30 and Philips Netherland).The organic and inorganic bonds forming the modified aerogel structure were studied by Fourier transform infrared spectrometer (Bruker, model vertex vo). From the thermal gravimetry (Model Mettler-851e) measurements, thermal stability of the aerogels was observed.

### *Adsorbents synthesis*

Silica gels doped with a diazoamino group (–N=N–N–), were synthesized by mixing TMOS, MPTMS, methanol and $NH_4F$ in molar ratios 1:2 (according to the procedures described in our previous work [22]). The intermediates waere homogenised by hemogeniser (20000 rpm) and during the hemogenisation stepp 0.021 g DCPEPT was added to mixture. Wet gels were aged in MeOH for five days and finally the SA-DCPEPT adsorbent was obtained. The SA-DCPEPT adsorbent were grounded into powder (size less than 0. 5 mm). The sorbent was used for tests in this form.

### *Adsorption experiments*

Batch experiments were carried out through contacting 100 mg of SA-DCPEPT with 20 mL Hg(II) solution with different initial concentrations at various pH values and temperatures of 20, 45 and 60℃. The products were placed in a shaker (Riviera, India) with 200 rpm velocity for 1h in order to accomplish adsorption process. After equilibration, suspension was filtrated and analyzed using by Atomic Absorption Spectrometry. The percentage of removed Hg(II) ions (R) was calculated using equation (1) [26]:

$$R=\frac{Co-Ct}{Co}\times 100 \qquad (1)$$

where $C_0$ is the initial concentration of Hg(II) ions in $mgL^{-1}$, $C_t$ is the concentration of Hg(II) ions at time t in $mgL^{-1}$.

Adsorption isotherms describe how adsorbates interact with adsorbents. Isotherm studies were carried out with initial concentrations of Hg(II) ranged from 10 to 300 $mgL^{-1}$. The pH of the solutions was adjusted to 6.0, which is an optimal adsorption pH, and the adsorption process was conducted with constant stirring for 1 h at 20, 45 and 60°C, respectively. Then the suspension was filtered and the concentration of Hg(II) was analyzed.

### *Desorption studies*

0.1 g of SA-DCPEPT was used for adsorbing in 20 mL of Hg(II) solution (20.0 $mgL^{-1}$) at pH 6.0. Batch desorption experiments were performed using 10mL of 1M of KBr, KSCN, $(NH_2)_2CS$, DDTC solution with constant stirring at room temperature for 3 h. The metal recovery was calculated by using equation (2)

$$\text{Recovery (\%)} = \frac{\text{amount of desorbed Hg(II)}}{\text{amount of adsorbed Hg(II)}}\times 100 \qquad (2)$$

The desorbed SA-DCPEPT was reused for adsorption test to evaluate its reusability, and the adsorption–desorption process was repeated 3 times.

## Results and Discussion

### *Characterization of adsorbents*

Fig. 2(a) and (b) shows the SEM micrographs of the SA and SA-DCPEPT. Silica aerogel particles range between 10-40 µm; SA-DCPEPT particles are between 30-90 µm.

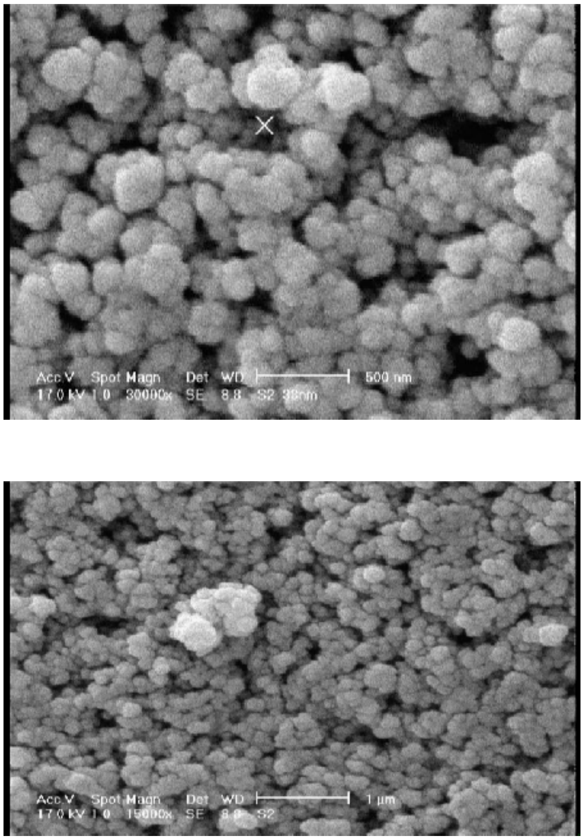


Fig. 2: The SEM image of (a) SA and (b) SA-DCPEPT.

The FTIR spectra investigation of SA-DCPEPT and SA are compared in Fig. 3. The broad absorption band in the region 3440-3435 $cm^{-1}$ and band at 1636-1642 $cm^{-1}$ respectively can be attributed to the adsorbed water and surface silanol groups [26-27]. The strong and broad peaks obtained for SA-DCPEPT samples at 1100 $cm^{-1}$ appear due to Si-OR group and at lower wavelength peaks appear due to asymmetric, symmetric and the bending modes of $SiO_2$, respectively, as in the case of unmodified silica aerogel. As expected for SA-DCPEPT samples, new but weak and sharp peaks appeared at 3120 $cm^{-1}$ due to NH groups. Also, new peaks appeared at 1315 $cm^{-1}$ due to C–N groups, 1496 $cm^{-1}$ is due to N=N stretching vibration [28-29]. This peaks is not observed for silica aerogel.

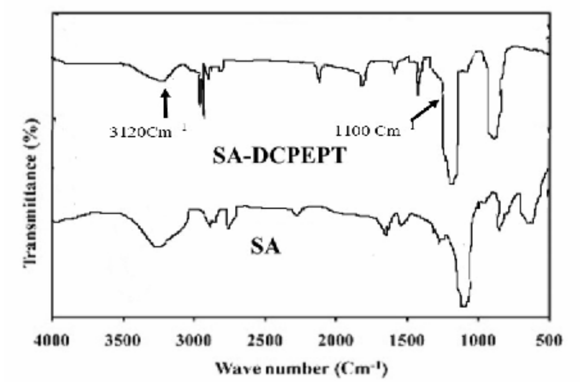


Fig. 3: FTIR absorption spectra of aerogel samples SA, SA–DCPEPT.

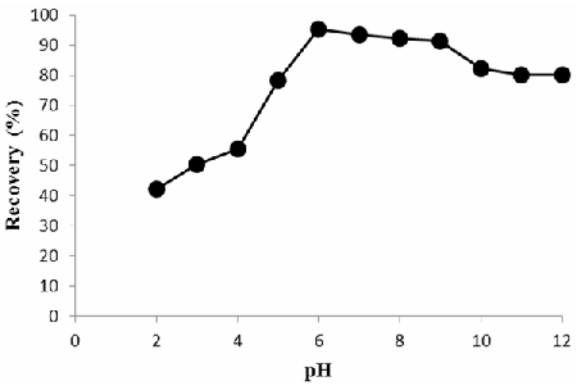
The result of TGA, demonstrated that there is a very little weight loss up to a temperature of 300ºC. A further increase of temperature causes weight loss along with exothermic peaks corresponding to the oxidation of surface organic ($CH_3$) groups. This is the reason why samples became hydrophilic after heating above a temperature of around 300 ºC.

*Adsorption studies*

*Effect of pH on adsorption*

Solution pH is an important parameter that influences adsorption of metal ions on adsorbents, as it not only affects metal species in solution, but also influences the surface properties of the adsorbents .To evaluate the effect of pH on the Hg (II) adsorption, experiments were carried out with solutions of initial concentration at several pH values in the range of 2-11. Diluted $HNO_3$ and NaOH solutions were used for adjusting the initial pH of solutions. The experimental results are presented in Fig. 4. As shown in Fig. 4, the solution pH had a significant effect on percent removal, and percent removal of Hg(II) were seen to increase with increased solution pH. The optimum pH value appeared to be about 6.0. At lower pH (<6), Hg(II) was in the free ionic form of Hg(II) [30].When pH increases in the range of 2–6, metal is present predominantly as metal ions in the solution and also a concentration of $H^+$ ions will decrease proportionally which affects the competition between $H^+$ and $Hg^{++}$ ions for active adsorption sites on surface of modified aerogel.

At lower pH (>6) the surface of SA-DCPEPT was negatively charged, which decreased negatively surfactant coating through electrostatic force of repulsion. Therefore, percent removal decreases at pH values higher than 6.



($[Hg^{2+}]_0$ = 20 mg $L^{-1}$ ; contact time = 1h ; mass of adsorbent = 100 mg ; solution volume = 20 mL )

Fig. 4: Effect of pH on adsorption of mercury(II) ions.

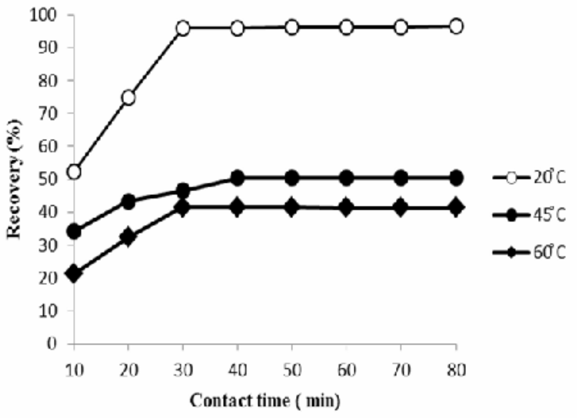
Therefore higher percent removal of Hg(II) ions at higher pH values appears due to precipitation of non soluble metal hydroxyl complexes. As we want to adsorb Hg(II) ions on the adsorbent and not to precipitate, pH 6.0 was selected for the further experiments.

*Effect of contact time and temperature*

Adsorption of Hg(II) ion using SA-DCPEPT adsorbent as a function of contact time was investigated in three different temperatures at 20, 45 and 60ºC for Hg(II)ions solutions at initial concentration 20 mgL$^{-1}$ and adsorbent dose 100 mg. The sorption of Hg (II) by SA-DCPEPT at various contact times ranging from 10 min to 80min was tested. The obtained results were demonstrated in Fig. 5. It can be noticed that the contact time significantly affects the Hg(II) uptake; the metal sorption increases sharply in the first 30min and tapers off there after, as equilibrium is approached. This shaking time was selected for further experiments. As shown in Fig. 5, amount of adsorbate per unit mass of adsorbent at time t (mg/g), removal percent was decreased for Hg(II) ions from 20 to 60ºC indicating exothermic nature of adsorption process.

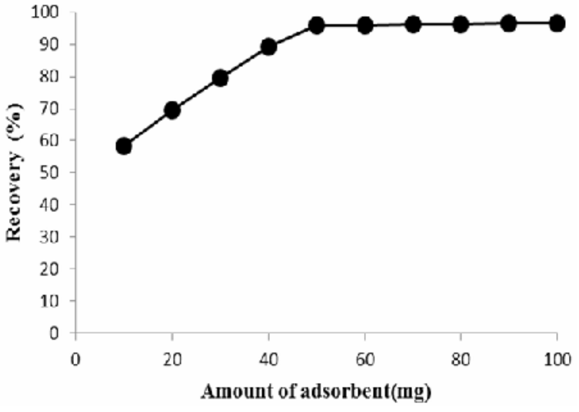
*Effect of adsorbent dose*

The dependence of Hg(II) sorption on adsorbent dosage was studied by varying the amount of SA-DCPEPT from 10 to 100 mg, while keeping other parameters (pH and contact time) constant. The effect of adsorbent dose on Hg(II) removal percentage is shown in Fig. 6. Experiments showed that increase of percent removal with adsorbent dose, but this rising from 50 g to 100 g either couldn't change the value of removed ions or had a little effect on it. Increase in adsorption with increase in adsorbent dosage attributed to greater number of available exchangeable sites. Therefore, 50mg of SA-DCPEPT is demonstrated as optimum adsorbent quantity to Hg (II) removal in this study.



($[Hg^{2+}]_0$ = 20 mg $L^{-1}$; mass of adsorbent = 100 mg ; solution volume = 20 mL ; pH= 6)

Fig. 5: Effect of adsorption contact time of mercury(II) ion at different temperatures 20, 45 and 60℃.



($[Hg^{2+}]_0$ = 20 mgL$^{-1}$ ; contact time = 1 h ; solution volume = 20 mL ; pH= 6 ; 20 $^0$C )

Fig. 6: Influence of adsorbent dose on mercury(II) adsorption.

*Adsorption isotherms*

In the present investigation the equilibrium data were analyzed using the Langmuir and

Freundlich isotherm models. Langmuir model [31,32] is often used for monolayer adsorption occurred on a homogeneous surface with identical adsorption sites, which can be expressed by the following equation

$$C_{e/}q_e = 1/q_{max}.b + 1/q_{max}.C_e \quad (3)$$

where $q_{max}$ is the monolayer capacity of the adsorbent ($mgg^{-1}$) and b is the Langmuir equilibrium constant ($Lmg^{-1}$). By using the linear form of this isotherm, the plot of $C_e/q_e$ versus $C_e$ gives a line with a slope of $1/q_{max}$ and b were determined respectively from the slop and intercept of the plots. For Langmuir type sorption process, to determine if the sorption is favorable or not, a dimensionless separation factor is defined as [33]

$$R_L = 1/1+bC_0 \quad (4)$$

where b is the Langmuir constant and $C_0$ is the initial concentration of metal ions. If $R_L > 1$, the isotherm is unfavorable; $R_L = 1$, the isotherm is linear; $0 < R_L < 1$, the isotherm is favorable; $R_L = 0$, the isotherm is irreversible. In the present work, the $R_L$-values of the Hg (II) ions adsorption by SA-DCPEPT are in the ranges of 0.007–0.020. This result shows that the adsorption process is favorable.

The empirical equation used to describe the Freundlich isotherm[34] is given by

$$\log q_e = \log K_F + 1/n \log C_e \quad (5)$$

where n is the empirical constant for intensity of adsorption related to adsorbent hetero- geneity. and $K_F$ is the adsorption capacity of the adsorbent ($Lg^{-1}$), both commonly temperature dependent. n is typically greater than 1 and the larger is its value, the adsorption isotherm becomes more non-linear and the system becomes more heterogeneous [35]. The model constants of both Langmuir and Freundlich along with correlation coefficients ($R^2$) are listed in Table-1. As presented, the Langmuir model fits the data better than Freundlich model.

Table-1: Langmuir and Freundlich model's regression constants for Hg(II) adsorption on SA–DCPEPT at different temperatures.

| **Temperature ($^0$C)** | **Langmuir constants** | | | **Freundlich constants** | | |
|---|---|---|---|---|---|---|
| | **$q_{max}$ ($mgg^{-1}$)** | **b ($Lmg^{-1}$)** | **$R^2$** | **n** | **$K_F$ ($Lg^{-1}$)** | **$R^2$** |
| **$20^0$C** | **198.25** | **$1.58\times10^{-2}$** | **0.990** | **1.480** | **7.753** | **0.902** |
| **$45^0$C** | **125.23** | **$1.25\times10^{-2}$** | **0.985** | **1.151** | **5.598** | **0.912** |
| **$60^0$C** | **110.48** | **$1.98\times10^{-2}$** | **0.947** | **1.492** | **0.123** | **0.989** |

In Table-2 Hg(II) adsorption capacities of SA-DCPEPT and SA were compared with other modified silica aerogel that published in previous literature. It can be seen from Table-2 that the adsorption capacities of SA-DCPEPT for Hg(II) ions are much higher than many other previously reported adsorbents, indicating that the SA-DCPEPT has great potential for application in Hg(II) removal from water.

*Adsorption thermodynamics*

The thermodynamic equilibrium constant ($K^{\circ}_C$) was studied by using equation (7):

$$K'_C = C_0/C_e \quad (7)$$

where $C_0$ is the initial concentration of Hg(II) ions in $mgL^{-1}$, $C_e$ is the concentration of Hg(II) ions at equilibrium in $mgL^{-1}$.

Adsorption thermodynamics analysis is applied to understand the nature and mechanism of adsorption process. $\Delta G^{\circ}$, $\Delta H^{\circ}$ and $\Delta S^{\circ}$ values are calculated from equations 8 and 9 to describe thermodynamic behavior of adsorbate:

$$\ln K_C = -\Delta H^{\circ}/RT + \Delta S^{\circ}/R \quad (8)$$

and

$$\Delta G^{\circ} = -RT \ln K_C \quad (9)$$

where, $\Delta H^{\circ}$ (J/mol) and $\Delta S^{\circ}$ (J/mol.K) are predicted from slope and intercept of data plotting of ln (Kc) versus 1/T. The thermodynamic parameters are reported in Table-3. The negative $\Delta G^{\circ}$ values confirm the spontaneous nature of Hg(II) adsorption. The $\Delta G^{\circ}$ values are in the range -20 to 0 kJ/mol which indicates Hg(II) adsorption is a physisorption process [38]. Moreover, negative values of $\Delta H^{\circ}$ showed that the sorption process of Hg(II)ions by SA-DCPEPT was exothermic process. The positive value of $\Delta S^{\circ}$ indicates the reversible adsorption of Hg(II) ion with SA-DCPEPT nanoparticles.

*Desorption study*

To study the possibility of regeneration of SA-DCPEPT adsorbent, we have investigated desorption experiments. The desorption of the sorbed Hg(II) ions from SA-DCPEPT was studied in a batch system same procedures as in section 2.3. Hg(II) ions sorbed onto SA-DCPEPT was eluted with Thiourea, and KSCN, HCl, KBr and $HNO_3$ solution. The results are shown in Fig. 7. The highest desorption is demonstrated for the KBr solution as the effluent (97.85%).

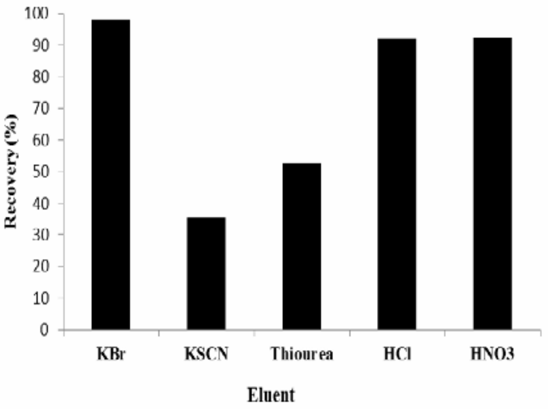
Table-2: Adsorption capacities of SA-DCPEPT and with other modified silica aerogel that published in previous literature.

| Adsorbent | Adsorption capacity(mgg$^{-1}$) | Reference |
|---|---|---|
| **Hybrid silica–polyacrylamide aerogels** | **17.63** | **[20]** |
| **Silica aerogels modified with mercapto functional groups** | **181.81** | **[21]** |
| **Silica aerogels** | **17.24** | **[22]** |
| **Silica aerogels modified with AMTT** | **142.85** | **[22]** |
| **Silica aerogels modified with DCPEPT** | **198.25** | **This work** |

Table-3: Thermodynamic parameters for Hg(II) adsorption on SA–AMTT at different temperatures.

| ΔH°(kJmol$^{-1}$) | ΔS° (kJmol $^{-1}$K$^{-1}$) | ΔG°(kJ mol$^{-1}$) | | |
|---|---|---|---|---|
| | | **293 K** | **318 K** | **333 K** |
| **-20.250** | **0.021** | **-12.895** | **-10.112** | **-10.031** |

The adsorption–desorption process was repeated three times showed that SA-DCPEPT remain active after three runs. The quantities of Hg(II) sorbed and desorbed were determined at the termination of each cycle for three repeated cycles (Table-4). It can be seen from Table-4, no statistically significant difference in the sorption and desorption of Hg(II).



([eluant] = 1M ; eluant volume = 10 mL; t = 3 h ; 20 $^0$C)

Fig. 7: Percentage of mercury(II) recovered by using different eluant.

Table-4: Performance of fresh and recycled.

| Cycle $^{a,b}$ | Recovery (%) | $q_e$ (mgg$^{-1}$) |
|---|---|---|
| **Fresh** | **98.9 ± 0.12** | **198.25 ± 0.21** |
| **(1st run)** | **97.79 ± 0.14** | **189.61 ± 0.35** |
| **(2nd run)** | **95.83 ± 0.21** | **185.19 ± 0.24** |
| **(3rd run)** | **95.25 ± 0.23** | **183.28 ± 0.38** |

[a] Adsorption: ([$Hg^{2+}$]$_0$ = 20 mgL$^{-1}$ , contact time = 1 h ; solution volume = 20 mL ; pH= 6 ; 20 $^0$C )

[b] Desorption: ([eluant] = 1M ; eluant volume = 10 mL; t = 3 h ; 20 $^0$C)

### *Application of SA-DCPEPT for Real Samples*

Different amounts of Hg(II) were spiked to these samples in order to estimate the accuracy and applicability of the proposed method. Table-5 shows the obtained results. The recoveries for the spiked samples were in the acceptable range of 93–99%. These results showed that the proposed procedure could be satisfactory used for the analysis of water samples.

Table-5: Determination of mercury(II) in water samples.

| Ion | Samples | Added (µgL$^{-1}$) | Found (µgL$^{-1}$)$^a$ | Recovery (%) |
|---|---|---|---|---|
| **$Hg^{2+}$** | **Tap wate** | **-** | **0.022±0.01** | **-** |
| | | **10** | **9.343±0.03** | **93.21** |
| | | **20** | **20.008±0.05** | **99.93** |
| | **lake water** | **-** | **0.250±0.03** | **-** |
| | | **10** | **10.124±0.05** | **98.74** |
| | | **20** | **20.139±0.08** | **99.44** |

[a] Mean of three experiments ± standard deviation.

## Conclusions

In this study, Modified silica aerogel with DCPEPT had been synthesized and applied to adsorb Hg(II) from aqueous solution in batch technique. Adsorption was found to dependent on pH, temperature, adsorbent dosage and contact time of the system, and the optimum pH was found to be in the range of 6–7. Maximum uptake was obtained at adsorbent dose of 0.05 g, which may be considered as optimum adsorbent dosage level at the specified conditions. The equilibrium of adsorption of Hg(II) on to SA-DCPEPT was suitably described by the Langmuir models with a monolayer adsorption capacity of 198.25 mgg$^{-1}$. SA-DCPEPT is easily desorbed using 1M KBr after the adsorption process, and it can be recycled at least 3 times without the loss of adsorption capacity to Hg(II). The thermodynamic studies showed that the sorption process of Hg(II)ions by SA-DCPEPT was more spontaneity and exothermic. Therefore, the obtained adsorbent exhibited extremely high performance for Hg(II) adsorption from aqueous solution.

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