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Preparation and sorption behavior of DEAE-cellulose-thiourea-glutaraldehyde sorbent for Pt(IV) and Pd(II) from leaching solutions

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ABSTRACT

This work investigates the adsorption behavior of Diethylaminoethyl-cellulose-thiourea-glutaraldehyde (DEAE-C/TU/GA) sorbent, which was synthesized through the reaction of crosslinking of glutaraldehyde using thiourea for platinum (Pt(IV)) and palladium (Pd(II)) ions from leaching solutions. The effects of pH and adsorption parameters, such as the sorbent dosage, contact time, temperature, and adsorption isotherms, were studied. Furthermore, chemical adsorption kinetic studies for adsorptions of these metal ions were carried out. The adsorption equilibrium data were fit better using the Langmuir model than the Freundlich model. The activation energies (E_a) of Pt(IV) and Pd(II) were 77.70 and 23.03 kJ/mol, respectively. The best desorption reagent was 1.0 M HCl–1.0 M TU solution for both Pd(II) and Pt(IV), which could remove more than 85% of the Pt(IV) and Pd(II) in the fourth adsorption–desorption cycle.

Keywords: DEAE-cellulose; Adsorption; Platinum; Palladium; Leaching solutions

1. Introduction

Owing to their catalytic and chemical properties, precious metals (i.e. platinum, palladium, rhodium, and gold) are used extensively in many industrial applications such as catalytic converters, chemical industries, smart card industries, electronic parts, and plating materials [1–4]. Nowadays, the increasing demand for the precious metals in related industries, combined with the limited resources available, has led to increasing interest in the recovery of these noble elements, and thus the extraction of these metals has become particularly important [5,6].

The recent literature has included several methods for the recovery of precious metals from aqueous solutions, such as ion-exchange [4,7,8], solvent extraction [9,10], membrane filtration [11–13], cementation [14–16], and adsorption [17–19]. Of these, adsorption seems to be the most suitable method for the recovery of precious metals from low concentrations, due to its low cost and high efficiency [20]. A number of adsorbents have been developed and tested for the recovery of precious metals; these include activated carbon [21,22], membranes [13], and chelating resins [8,23,24].

In the past few years, there has been an intense interest in the preparation and application of several

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chelating resins to uptake precious metals from aqueous solutions. The selectivity for a specific metal ion depends on what kind of complexing agent is introduced into the polymeric chain. According to Pearson's theory of hard and soft acids and bases [25], metal ions will have a preference for complexing with ligands that have more or fewer electronegative donor atoms. Chelating agents containing nitrogen and sulfur groups are highly efficient for the selective adsorption of precious metals [6]. Chelating resins with amine [24], mercaptan [18], and thiourea (TU) [1,26] are widely used to functionalize the surface of supports for the effective adsorption of precious metals. Moreover, a crosslinking treatment increases the adsorption capacity and chemical stability. Glutaraldehyde (GA) is one of the crosslinks that have been used for metal ion recovery in acidic media [27,28]. For precious metal adsorption on GA-crosslinked resins, the adsorption efficiency is controlled by the composition of the solution and, especially, by the presence of competitor ions (chloride, nitrate) due to ion-exchange competition mechanisms.

The main purpose of this study is to prepare GA-crosslinked diethylaminoethyl cellulose (DEAE-C) sorbent bearing sulfur (S) and nitrogen (N) as donor atoms and investigate its adsorption properties. In this paper, a simple method for the preparation of a DEAE-C/TU/GA sorbent was reported. The application of the obtained sorbent for the adsorption of Pt(IV) and Pd(II) from waste leaching solution was investigated. Adsorption isotherms and kinetic and thermodynamic calculations for the adsorption process are also reported. Additionally, this study focuses on the study of Pt(IV) and Pd(II) desorption by various eluants.

2. Experimental

2.1. Apparatus and reagents

DEAE-C (electrically neutral, about 100 µm) was purchased from Fluka Biochemika (Lot number: 30477, Germany). TU ($SC(NH_2)_2$), GA ($CH_2(CH_2CHO)_2$, 50% in water), HCl, and NaOH were supplied by Merck (Germany). Distilled water was used for the wet chemical analyses (TKA Smart2Pure, Germany). The concentrations of elements from the combined solution were analyzed by ICP-MS (Thermo Scientific X Series II, USA).

2.2. Preparation of the DEAE-C/TU/GA sorbent

The crosslinking of TU using GA as an agent was carried out in a way similar to the procedure described by Guibal et al. [26] with DEAE-C. TU (39 mmol) and GA (2 mL of 50% v/v) were mixed in 20 mL of distilled water for per gram of DEAE-C. TU cross-linking was performed through a preliminary reaction with GA for 3 h, and then the mixture (TU–GA) was vigorously stirred with DEAE-C overnight. Finally, this sorbent was filtrated and washed several times with distilled water and dried at about 30°C overnight in a vacuum oven (10^{-1} mbar).

2.3. Generation of leaching solution

The leaching solution was obtained from nickel sulfide fire assay (NiS-FA) experiments. It is an efficient preconcentration method for platinum group elements presented in most of the materials with the small quantities [29]. The materials are fused with nickel, sulfur, $Na_2B_4O_7$, Na_2CO_3, and SiO_2 in a clay crucible at 1,000°C. The nickel sulfide (NiS) bead formed is separated from the slag, crushed, and ground to powder, then treated with HCl to remove the matrix elements. By then, a black precipitate (Me_xS_y; note that Me is a precious metal) is formed in the nickel chloride solution; the solution is cooled and vacuum filtered through cellulose acetate membrane filter disks (Sartorius, Germany) [30]. The residues that contained precious metals are dissolved with aqua regia. In our university laboratories, the solutions used for adsorption were obtained by leaching the NiS-FA bead of spent catalytic converters, ores, anode slime, polish waste, jewelry waste, etc. which contain precious metals, according to the literature [21]. Finally, the solutions were collected, combined, and then diluted to 5 L with distilled water. The concentrations of all the main elements, which are denoted as initial concentrations, are listed in Table 1.

2.4. Adsorption studies

The pH effect on the adsorption of Pt(IV) and Pd (II) using 100 mg of the sorbent was determined for a range of −0.70–1.52 for 480 min at 25°C and 600 rpm in a flask containing 100 mL of solution.

The effect of varying the sorbent dosage from 100 to 800 mg (i.e. 1 to 8 mg/mL) was investigated. For this experiment, 100 mL of the solution was brought into contact with the sorbent for 480 min at 25°C and 600 rpm in a flask containing 100 mL of solution.

The effect of contact time on the sorbent adsorption of Pt(IV) and Pd(II) using 100 mg of the sorbent was investigated in a flask containing 100 mL of solution. The flasks were vigorously stirred with a magnetic stirrer at 25°C and 600 rpm. 10 mL of the solution were extracted at different time intervals for

Table 1
Specifications of the NiS fire assay solution

Element	Concentrations (mg/L)
Pt	26.63
Pd	42.59
Rh	1.17
Os	N/A
Ir	N/A
Ru	0.05
Au	0.01
Cu	0.28
Ni	0.83
Zn	0.26
Sn	1.48
Te	0.53
Fe	N/A
Pb	N/A

Note: N/A: not available.

analyzing the residual metal ion concentration in the solution. A similar procedure was utilized to test for the effect of temperature, which ranged from 25 to 45˚C.

Adsorption isotherm experiments were conducted with different initial metal ion concentrations diluted by the main solution. 100 mL of the solutions and 100 mg of the sorbent were placed in each of the four flasks for 480 min at different temperature (25–45˚C) and at 600 rpm.

The final experimental series investigated the adsorption kinetics and thermodynamics. The adsorption percentage was calculated using the following equation:

$$Adsorption\ \% = [(C_0 - C_t)/C_0] \times 100 \quad (1)$$

in which C_o and C_t (mg/L) are the metal ions concentration present in the solution before and after adsorption, respectively.

The concentrations of elements were analyzed by ICP-MS (Thermo Scientific X Series II, Germany). The analysis conditions were: forward power 1,400 W, viewing height 150 mm, argon plasma gas flow rate 18 L/min, argon nebulizer gas flow rate 0.9 L/min, and argon intermediate gas flow rate 0.7 L/min. Certified standard platinum and palladium solution (1,000 ppm; Merck, Germany) were used as stock solution for instrument calibration.

2.5. Desorption and reuse studies

Desorption experiments were carried out with varying concentrations of (0.5–2.0 M) HCl, (0.5–2.0 M) TU, 0.5 M HCl–1.0 M TU, and 1.0 M HCl–1.0 M TU. The Pt(IV) and Pd(II) ions loaded onto DEAE-C/TU/GA sorbent were washed with deionized water several times and introduced into the flasks. 25 mL of desorption solutions were added to 250 mg of the loaded sorbent, and then the flasks were vigorously stirred with a magnetic stirrer at 600 rpm at 25˚C for 180 min. The concentration of metal ions released from the DEAE-C/TU/GA sorbent into the aqueous phase was analyzed by ICP-MS. In order to determine the potential reusability of the DEAE-C/TU/GA sorbent, sequent adsorption–desorption cycles were repeated four times. The desorption percentage was calculated as follows:

$$Desorption\ \% = [(C_d \times V_d)/(C_0 - C_t) \times V] \times 100 \quad (2)$$

where C_d (mg/L) is the concentration of the solutes in the desorption solutions; V_d (in L) is the volume of the desorption solution; and C_0; C_t (mg/L) are the metal ions concentration present in the solution before and after adsorption; and V is the volume of the solution (in L).

3. Results and discussion

3.1. Characterization of the DEAE-C/TU/GA sorbent

A new DEAE-C derivative was synthesized by crosslinking with an intermediary product that resulted from the chemical reaction of TU and GA. This derivative acted as a linking spacer between DEAE-C and TU. GA and TU had been previously reacted together and then were subsequently added to DEAE-C.

The FTIR spectra of DEAE-C, TU, GA, and crosslinked DEAE-C/TU/GA sorbent are presented in Fig. 1(a)–(d), respectively.

In the DEAE-C spectrum (Fig. 1(a)), the peaks at 3,340 cm^{-1} are attributed to –OH groups, whereas other characteristic bands are due to C–N and C–O groups that are recorded at 1,365 and 1,059 cm^{-1}, respectively [31].

The FTIR spectra exhibited the stretching bands of N–H, C–N, and C=S at 3,366–3,267 cm^{-1}, 1,460–1,079 cm^{-1}, and 1,406–727 cm^{-1}, respectively [26,31], which confirmed the presence of TU (Fig. 1(b)). The FTIR spectrum of GA is shown in Fig. 1(c). The peak at 3,338 cm^{-1} is attributed to the –OH group. The stretching bands of C–H and C=O are assigned at 2,959 and 1,638 cm^{-1}, respectively [31,32].

The suggested structure of the DEAE-C/TU/GA sorbent in Fig. 2 was confirmed from FTIR spectral measurements. The spectrum of the prepared sorbent

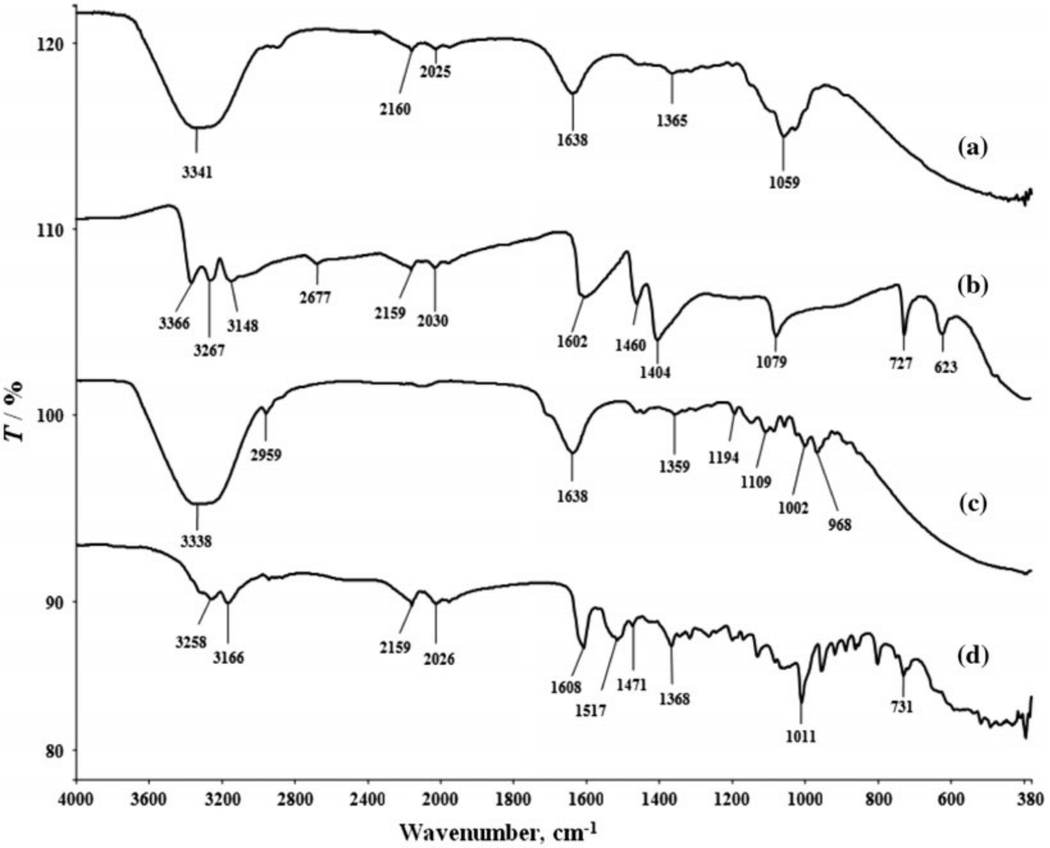

Fig. 1. FTIR spectra of (a) DEAE-C, (b) TU, (c) GA, and (d) DEAE-C/TU/GA.

is shown in Fig. 1(d). The absorption band at 1,608 cm^{-1} is assigned to the C=N bonds. Spectra of the sorbent in which the C=S group is attached to a nitrogen atom show an absorption band in the general C=S stretching region (1,010–1,300 cm^{-1}). The intense bands at 1,517 and 1,470 cm^{-1} correspond to C–N stretching. C–O bonds are identified by bands at 1,690–1,640 cm^{-1} [26,31,32]. N–H stretching in secondary amines is assigned at 3,250 cm^{-1} area. The peaks at 3,340 cm^{-1} attributed to –OH disappear from the spectrum. These bands confirmed that the condensation reaction was successfully performed between DEAE-C and TU-modified GA. It is thought that S and N donor atoms on the surfaces of the sorbent may be effective in adsorption [26].

3.2. *Effect of solution pH*

The NiS-FA solution is highly acidic (5.0 mol L^{-1} H_3O^+) and solution pH is around –0.70. Therefore, we

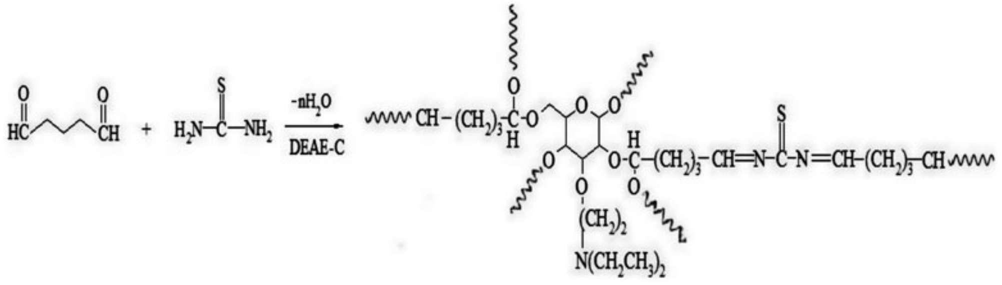

Fig. 2. Proposed structure of the prepared DEAE-C/TU/GA sorbent.

investigated the effect of acidity in the solution on the adsorption of Pt(IV) and Pd(II) using the sorbent. The pH of the solutions was adjusted by adding solid sodium hydroxide. The pH effect on Pt(IV) and Pd(II) adsorption percentage was studied in the range from −0.70 to 1.52. The results presented in Fig. 3 show that Pt(IV) and Pd(II) adsorption increased by decreasing the acidity of the solution until pH of 1.10 (0.08 mol L^{-1} H_3O^+). The Pt(IV) and Pd(II) in the solution decompose to chlorocomplexes by increasing the pH of the solution [33]. It is known that Pt(IV) and Pd(II) exist in hexachloroplatinic acid (H_2PtCl_6) and tetrachloropalladium acid (H_2PdCl_4), and the dissociation of the chlorocomplexes can be expressed by the following equations [6,34]:

$$H_2PtCl_6 + 2H_2O = PtCl_6{}^{-2} + 2H_3O^+ \tag{3}$$

$$H_2PdCl_4 + 2H_2O = PdCl_4{}^{-2} + 2H_3O^+ \tag{4}$$

At high acidity, the equilibrium tends to shift toward the left side: Therefore, Pt(IV) and Pd(II) are present in the aqueous phase in the form of the more stable H_2PtCl_6 and H_2PdCl_4 species. From Fig. 3, the adsorption percentage of Pt(IV) and Pd(II) reached about 80 and 95%, respectively, when the pH of the solution was 1.10. After this point, it was seen that the adsorption percentage decreased. Accordingly at higher pH values, the decreasing adsorption capacity may be explained by the presence of less-adsorbable Pt(IV) and Pd(II) species (i.e. hydroxide) because of the lower availability of chlorocomplexes. The results indicated that higher adsorption capacity for precious metal ions was obtained at pH 1.10 for the synthesized sorbent. So, it is clear that lower pH values are really important for the precious metal ion recovery.

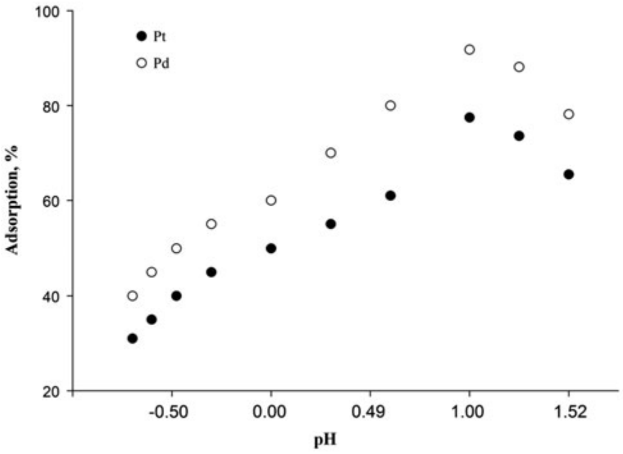

Fig. 3. Effect of pH for adsorption of Pt(IV) and Pd(II) on the DEAE-C/TU/GA sorbent (100 mg sorbent, 480 min, 25˚C, 600 rpm, 100 mL of the solution).

3.3. Adsorption mechanism

The following mechanisms are proposed for the Pt (IV) and Pd(II) adsorption from NiS-FA solution by the DEAE-C/TU/GA. When DEAE-C/TU/GA is contacted with the NiS-FA solution, Pt(IV) and Pd(II) ions are chelate bonded to the N atoms and S atoms of thiourea groups on the DEAE-C/TU/GA sorbent surface. The possible reactions are shown in Fig. 4 [35,36].

When the spectrum of Pt/Pd-adsorbed DEAE-C/TU/GA sorbent was compared with the spectrum of DEAE-C/TU/GA sorbent (see Fig. 1(d)), some peak series showed an increase. As shown in Fig. 5, the absorption band at 1,608 cm^{-1} assigned to >C=N bonds, –>C–N– stretching bands at 1,517 and 1,470 cm^{-1}, and >C=S stretching bands at 1,011–1,368 cm^{-1} were shifted to 1,617, 1,536–1,483, and 1,013–1,382 cm^{-1} regions, respectively. These band shifts indicated that the bonded S and N donor atoms play a major role in Pd(II) and Pt(IV) adsorption on DEAE-C/TU/GA sorbent.

3.4. The effect of sorbent dosage

The effect of the sorbent dosage on Pt(IV) and Pd (II) adsorption from the NiS-FA solution was investigated after a contact time of 480 min. In this experiment, a resin dosage from 1 to 3 mg/mL resulted in the adsorption of Pt(IV) and Pd(II) increasing from 77 to 98% and from 90 to 99%, respectively. It is apparent from Fig. 6 that the adsorption percentage increased with increasing sorbent dosage because the adsorption process is thermodynamically favorable when the sorbent-to-metal ratio is high. As the amount of sorbent increases, the active sites for binding metal ions increase. A similar trend was also observed for the effect of adsorbent concentration in a study by Tasdelen et al. [37]. With 3 mg/mL of the DEAE-C/TU/GA, around 99% of the Pd(II) was successfully adsorbed. The same percentage of Pt(IV) was adsorbed using 7 mg/mL of the DEAE-C/TU/GA. It is apparent that the amount of metal ions adsorbed per unit mass increases with an increasing amount of sorbent. It may be concluded that by increasing the adsorbent dose, the adsorption percentage increases but the density decreases. The decrease in adsorption density can be attributed to the fact that some of the adsorption

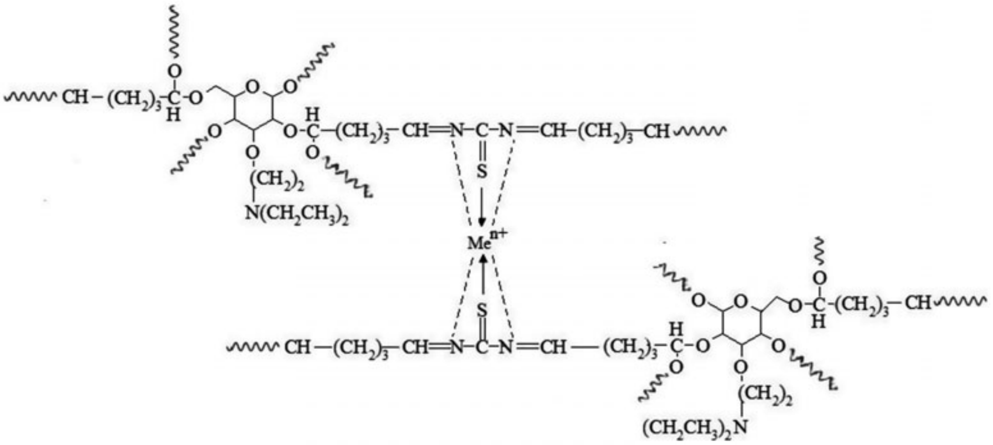

Fig. 4. Proposal structure of DEAE-C/TU/GA and metal ions interaction.

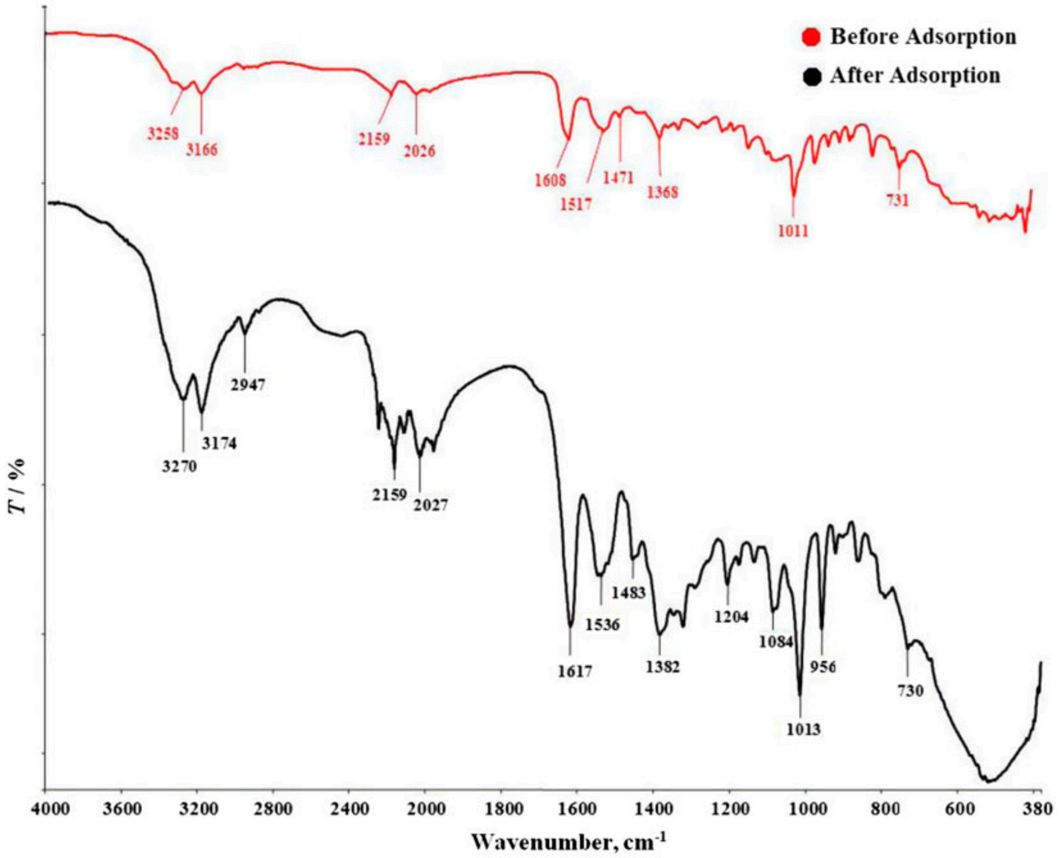

Fig. 5. FTIR spectra of Pt(IV)/Pd(II) loaded DEAE-C/TU/GA sorbent.

remains unsaturated during the adsorption process, whereas the number of available adsorption sites increases with an increase in the sorbent, thereby resulting in an increase in adsorption percentages [20,38].

3.5. The effect of contact time

Fig. 7 presents the effect of contact time on the adsorption percentage of Pt(IV) and Pd(II) by the DEAE-C/TU/GA sorbent in the range of 5–480 min.

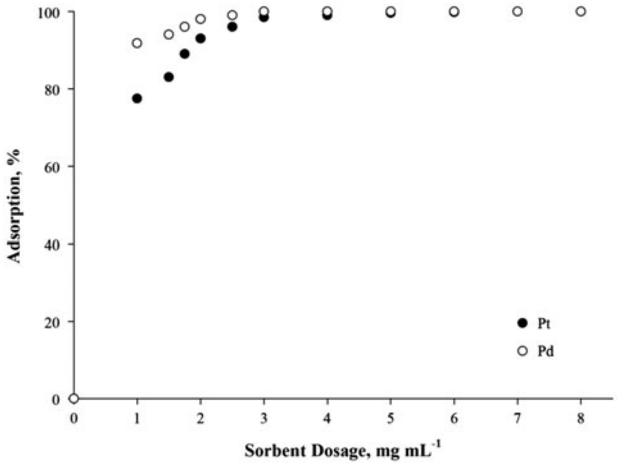

Fig. 6. The effect of the sorbent dosage on Pt(IV) and Pd (II) adsorption (480 min, 25˚C, 600 rpm, pH 1.10, 100 mL of the solution).

As seen in Fig. 5, the adsorption equilibrium time for Pt(IV) ions from the solution was 420 min, while for Pd(II) ions the maximum adsorption is attained in 180 min. The results for DEAE-C/TU/GA showed a short adsorption time for Pd(II). The higher selectivity of DEAE-C/TU/GA as a sorbent for Pd(II) is attributed to the surface-modified thiourea possessing a high affinity for Pd(II), which is in a good agreement with Pearson's HSAB theory [25]. However, it is worth pointing out that another possibility is that the Pt(IV) was adsorbed at the surface.

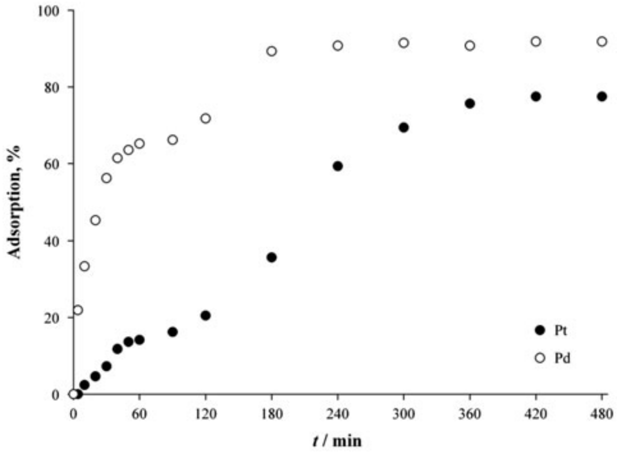

Fig. 7. The effect of contact time on Pt(IV) and Pd(II) adsorption (100 mg sorbent, 25˚C, 600 rpm, pH 1.10, 100 mL solution).

3.6. The effect of temperature

In this series of experiments, the effect of temperature on Pt(IV) and Pd(II) adsorption was studied in the range of 25 to 45˚C. The percentage adsorption of Pt(IV) and Pd(II) as a function of temperature is presented in Fig. 8.

Increasing the contact time from 120 to 480 min increased the Pt(IV) adsorption percentage by a factor of four when the reaction was run at room temperature. However, when we increased the adsorption temperature from 25 to 45˚C, the same adsorption percentage (i.e. at 25˚C and for 480 min) was reached for 120 min when reaction was run at 45˚C.

For the Pd(II) adsorption on the sorbent, when we increased the temperature from 25 to 45˚C, for 480 min, the adsorption percentage increased by around 10%. Temperature clearly plays an important role for Pt(IV) and a moderate role for Pd(II) adsorption from the solution. The easier adsorption of Pd(II) at a lower temperature than Pt(IV) is because the surface modified thiourea possesses a high affinity for Pd (II). Adsorption of Pt(IV) should not be carried out at room temperature. Therefore, an increase in the temperature during the adsorption process is important if a greater adsorption percentage is desired.

3.7. Adsorption isotherms

In order to describe the adsorption system of the DEAE-C/TU/GA sorbent, adsorption isotherms were investigated. The equilibrium data were fit to the Langmuir and Freundlich isotherm models, and their equations are shown below [38–40]:

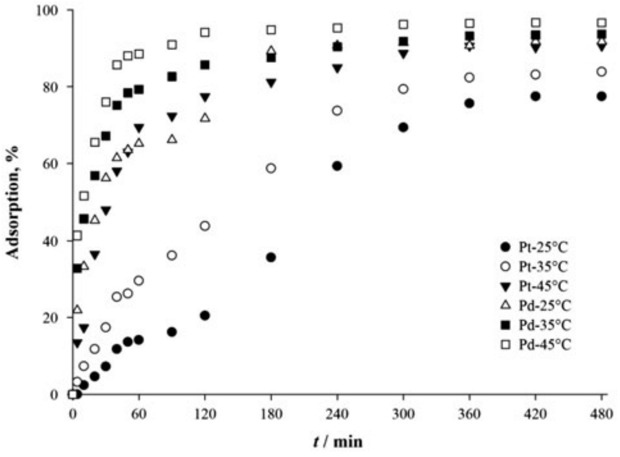

Fig. 8. The effect of temperature on Pt(IV) and Pd(II) adsorption (100 mg sorbent, 600 rpm, pH 1.10, 100 mL solution).

$$C_e/q_e = 1/(Q_{max}K_L) + (1/Q_{max})C_e \quad (5)$$

$$\log q_e = \log K_f + 1/n \log C_e \quad (6)$$

where q_e is the amount of metal ions adsorbed at equilibrium per unit weight of sorbent (mg/g), Q_{max} is the monolayer capacity of the adsorbent (mg/g), C_e is the equilibrium ion concentration present in the solution after adsorption, K_L (L/mg) and K_F (mg/g) are the constants in the Langmuir and Freundlich isotherm models that are related to adsorption capacity, respectively, K_L (L/mg) is the constant in the Langmuir isotherm model related to the energy or net enthalpy of adsorption, and n is the constant in the Freundlich isotherm model that measures the adsorption intensity.

The plots of log q_e vs. log C_e for Pt(IV) and Pd(II) ions adsorption onto the DEAE-C/TU/GA yield straight lines with positive slopes, given by $1/n$, and the intercepts are at log K_f (not shown here).

Fig. 9 shows the Langmuir adsorption isotherm plot of C_e/q_e vs. C_e. A comparison of the coefficient of determination for the two isotherms was made and these values are listed in Table 2.

The values of each model and the correlation coefficient, R^2, were calculated from these plots. The correlation coefficients showed that the Langmuir isotherms ($R^2 \geq 0.99$) were better fitted than the Freundlich isotherms ($R^2 < 0.99$) for the adsorption of Pt(IV) and Pd(II) on the DEAE-C/TU/GA sorbent at various temperatures. These results indicate that the adsorption of Pt(IV) and Pd(II) onto the surfaces of the sorbent is a monolayer adsorption process.

3.8. Adsorption kinetics

It is known that the kinetic model can be calculated with several methods (e.g. Differential rate, integrated rate, Half-life, Method of initial rates, and isolation method). Either the differential rate law or integrated rate law can be use to determine the reaction order from experimental data. To investigate the controlling mechanism of the adsorption process, (e.g. zero, pseudo-first, first, pseudo-second, second, third, one-dimensional diffusion order rate etc.) were studied for Pt(IV) and Pd(II) ions by DEAE-C/TU/GA. In these experiments, several mathematical models were studied for temperatures in the range of 25 to 45°C, and the data are presented in Fig. 8. In order to ascertain the appropriate kinetic equation, these results were checked against a plot of the final concentration vs. time. The experimental data is superimposed on the theoretical curves in order to determine which theory best fits the experimental data (plots not shown here). Kinetic studies show that a good fit was provided by the first-order ln (C_0/C_t) and the one-dimensional diffusion $((C_0–C_t)/C_0))^2$ models, which are shown here as Eqs. (7) and (8), respectively [21,41], and are functions of time.

$$kt = \ln (C_0/C_t) \textit{ for Pt(IV) adsorption} \quad (7)$$

$$kt = ((C_0 - C_t)/C_0))^2 \textit{ for Pd(II) adsorption} \quad (8)$$

where k is the rate constant, t is the time (min), C_0 is the initial concentration, and c_t is the final concentration.

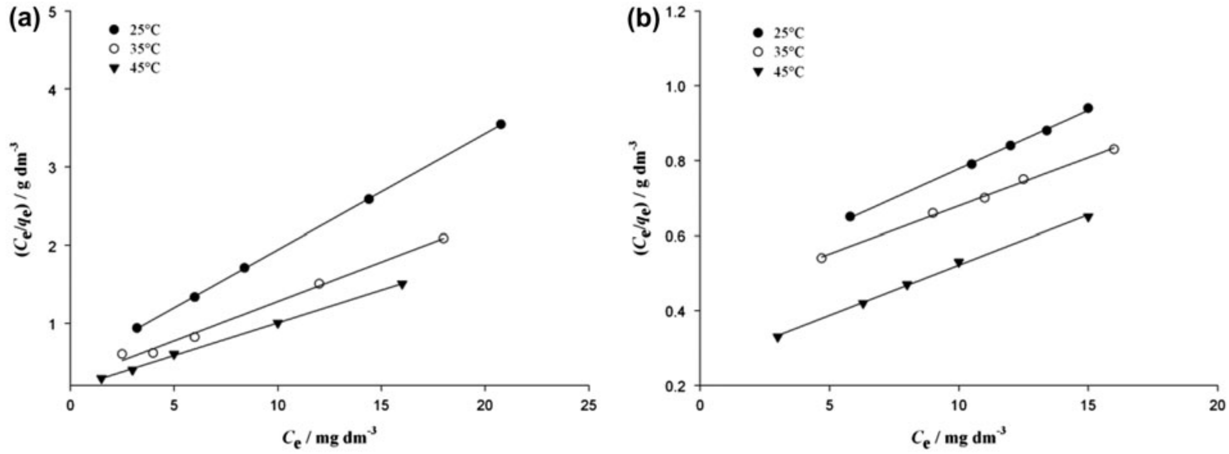

Fig. 9. (a) Langmuir isotherm for Pt(IV) and (b) Pd(II) onto the sorbent at different temperatures (100 mg sorbent, 600 rpm, 100 mL solution).

Table 2
Freundlich and Langmuir isotherm constants for the adsorption of Pt(IV) and Pd(II)

Pt(IV) adsorption				Pd(II) adsorption		
$T/(℃)$	$1/n$	$K_F/(mg/g)$	R^2	$1/n$	$K_F/(mg/g)$	R^2
Freundlich isotherm constants						
25	0.28	2.50	0.97	1.64	0.28	0.98
35	0.34	3.29	0.88	1.25	0.85	0.98
45	0.30	4.83	0.97	0.90	3.00	0.98
$T/(℃)$	$Q_{max}/(mg/g)$	$K_L/(L/mg)$	R^2	$Q_{max}/(mg/g)$	$K_L/(L/mg)$	R^2
Langmuir isotherm constants						
25	6.72	0.33	1.00	16.64	0.04	0.99
35	9.91	0.41	0.99	58.44	0.03	0.99
45	11.90	0.51	0.99	112.30	0.03	1.00

The activation energy (E_a) was calculated by the Arrhenius equation, according to the following formula [40]:

$$\ln k = \ln A - E_a/RT \tag{9}$$

where k is the rate constant, E_a is the activation energy, R is the gas constant, and T is the temperature (K).

Fig. 10 shows the Arrhenius plot of $\ln k$ vs. $1{,}000/T$ for Pt and Pd(II) adsorption. The rate constants k and $\ln k$ as functions of temperature are given in Table 3.

The activation energies of the diffusion-controlled processes are low and vary around 4–13 kJ/mol; values of the activation energy of a chemically controlled process are usually larger than 42 kJ/mol. The reactions controlled by a mixed mechanism (intermediate-controlled process) have activation energies in the range of 20–35 kJ/mol [40]. The activation energies for Pt(IV) and Pd(II) adsorption by DEAE-C/TU/GA sorbent were calculated to be 77.70 and 23.03 kJ/mol, respectively. Furthermore, the adsorption of Pt(IV) is a chemically controlled process, while the adsorption of Pd(II) is intermediate-controlled process.

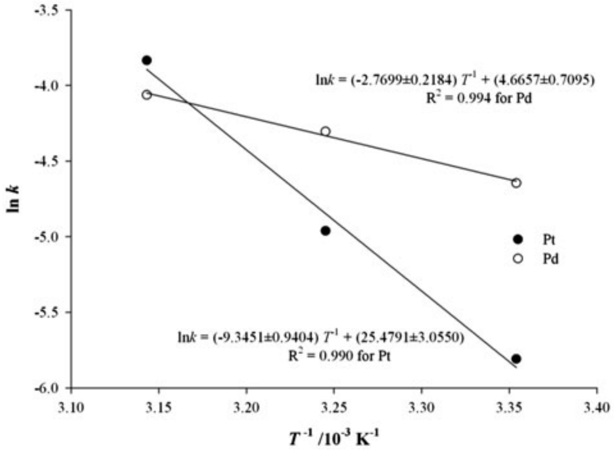

Fig. 10. The Arrhenius plots of ln k vs. $T^{-1}/10^{-3}$ for Pt(IV) and Pd(II) onto the DEAE-C/TU/GA sorbent.

3.9. Desorption and reuse studies

Desorption of the adsorbed Pt(IV) and Pd(II) ions from the sorbent could be done with high desorption ratios to use the same sorbents additional times in the adsorption–desorption cycles at low cost. This experiment series was carried out with varying concentrations of (0.5–2.0 M) HCl, (0.5–2.0 M) TU, 0.5 M HCl–1.0 M TU, and 1.0 M HCl–1.0 M TU (unsuitable reagents plot not shown here). The results indicated that the 1.0 M HCl–1.0 M TU were the best eluents and obtained the highest desorption ratios. The first desorption ratios were 94.86% for Pd(II) and 93.26% for Pt(IV) (see Fig. 11).

After four adsorption–desorption cycles of Pt(IV) and Pd(II), the desorption ratios were above 85%. This result shows that the DEAE-C/TU/GA sorbent performs well for repeated use of up to four cycles.

3.10. Comparison with other adsorbents

The comparison of the adsorption capacity of the DEAE-C/TU/GA sorbent with some previously used adsorbent is provided in Table 4. The results showed that DEAE-C/TU/GA sorbent was very effective for the removal of Pt(IV) and Pd(II) from waste solutions, and the maximum adsorption capacity (Q_{max}) of DEAE-C/TU/GA sorbent was comparable to those of other adsorbents presented in scientific literature

Table 3
Rate constant value for the adsorption of Pt(IV) and Pd(II) with respect to temperature

	Pt(IV) adsorption			Pd(II) adsorption		
T/K	k/(min^{-1})	ln k	E_a/(kJ/mol)	k/(min^{-1})	ln k	E_a/(kJ/mol)
298	0.003	−5.81	77.70	0.010	−4.65	23.03
308	0.007	−4.96		0.013	−4.31	
318	0.022	−3.84		0.017	−4.06	

Table 4
Comparative data for adsorption of Pt(IV) and Pd(II) by various adsorbents reported in the literature

Adsorbents	Studied metal	pH	Qmax (mg/g)		Reference
			Pt	Pd	
Carbonized rise husk	Pt(IV)		42.0		[20]
Melamine–formaldehyde–thiourea (MFT) resin	Pd(II)	4		15.3	[23]
L-lysine modified crosslinked chitosan resin	Pt(IV), Pd(II), Au(III)	1–2	129.2	109.4	[31]
Lewatit TP 214	Pt(IV)		33.2		[38]
Carbonized pistachio nut shells	Pt(IV)		38.3		[38]
Commercial 717 anion-exchange resin	Ag(I), Au(III), Pd(II), Pt(IV)	3	Not reported		[42]
1,5,9,13-tetrathiacyclohexadecane-3,11-diol anchored poly (p-CMS-DVB) microbeads	Au(III), Ag(I), Pt(IV), Pd(II)	0.5	595	230	[43]
Polystyrene-based nanofibers	Pt(IV), Pd(II)		7.4	4.3	[44]
Thiourea modified magnetic magnetite nanoparticle (MNP-Tu)	Pt(IV), Pd(II), Au(III)	2	43.3	111.6	[45]
DEAE-C/TU/GA sorbent	Pt(IV), Pd(II)	1.1	11.90	112.30	This study

[20,23,33,38,43–45]. Maximum adsorption capacity was obtained at lower pH values, and this becomes an advantage, due to the fact that sorbents have no or low affinity for metals, particularly in strong acidic solutions. According to these results, DEAE-C/TU/GA sorbent could be employed as low-cost adsorbents and could be considered as an alternative sorbent for the adsorption of Pt(IV) and Pd(II) from industrial effluents.

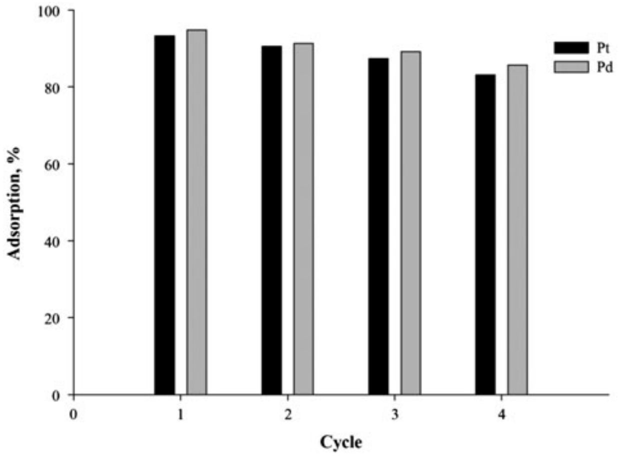

Fig. 11. Desorption and reusability test for DEAE-C/TU/GA (250 mg loaded sorbent, 25˚C, 600 rpm, 60 min, 25 mL striping solution).

4. Conclusions

In this study, an adsorption process was developed to recover Pt(IV) and Pd(II) from NiS-FA solutions. The newly synthesized DEAE-C-based sorbent can be effective for the adsorption of Pt(IV) and Pd(II) ions from aqueous solutions. The pH of the solution played an important role in the adsorption of Pt(IV) and Pd (II) on DEAE-C/TU/GA. When the pH of the original solution was increased by adding sodium hydroxide, the adsorption of Pt(IV) and Pd(II) increased and reached 80 and 95%, respectively, for a feed pH of 1.10. The activation energies of Pt(IV) and Pd(II) were founded to be 77.70 kJ/mol and 23.03 kJ/mol, respectively. By comparing the coefficient of determination using the linear method, we found that the Langmuir isotherms had higher coefficients of determination than that of the Freundlich isotherm. The maximum adsorption capacity (Q_{max}) calculated from the Langmuir isotherm model of sorbent for Pt(IV) and Pd(II) was 11.90 and 112.30 mg/g at 45°C, respectively. The kinetic of the adsorption for Pt(IV) and Pd(II) were found to follow the first-order and the one-dimensional diffusion rate equation, respectively. The elution of Pt(IV) and Pd(II) from the loaded sorbent was found to be effective using a mixture of TU and hydrochloric acid.

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