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# Synthesis, characterization of carbon polyurethane powder and its application for separation and spectrophotometric determination of platinum in pharmaceutical and ore samples

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## ABSTRACT

A new chelating sorbent was synthesized by covalently linking carbon nano-fiber with ion exchange polyurethane foam (CNF-PUFIX). CNF-PUFIX was characterized using different tools e.g. elemental analysis, IR spectrum and SEM. The functional groups of PUF have disappeared. The phenolic, carboxylic, quaternary ammonium salt and tertiary amine groups are detected in the CNF-PUFIX. The sorption properties of platinum (IV) onto CNF-PUFIX were investigated, the maximum sorption of platinum ions ($\sim$100%) was at the pH ranges 4–5, shaking for 18 min and sample flow rate 1.3 mL min$^{-1}$. The experimental data was fitted by kinetic models, the pseudo-second order is predominant ($R^2=0.998$), the values of $h$ and $k_2$ are 4.4 mmol g$^{-1}$ min$^{-1}$ and 0.15 g mmol$^{-1}$ min$^{-1}$, respectively. The sorption capacity of CNF-PUFIX and the recovery percentage of Pt (IV) were 0.19 mmol g$^{-1}$ and 99–103%, respectively (RSD=1.72%, $n=5$). The CNF-PUFIX could be used many times without decreasing their capacities significantly. The equilibrium process is well described by the Langmuir isotherm model ($R^2=0.857$), which is attributed to the homogeneous surface structure of the CNF-PUFIX. The values of $\Delta G$ and $\Delta H$ were $-3.5$ and $-26.1$ kJ mol$^{-1}$, respectively, which indicate that the sorption of platinum onto CNF-PUFIX is spontaneous and exothermic. The lower detection limit of platinum using spectrophotometric method is 2.4 μg L$^{-1}$ (RSD$\sim$3.8%, $n=6$). The accuracy of the procedure was verified by the analysis of standard reference materials of pharmaceutical and granite samples.

## 1. Introduction

Platinum is the most important noble metal due to its applications in the chemical, electronics, aerospace and jewelry industries owing to its corrosion resistance, oxidation resistance, and excellent catalytic properties [1,2]. The materials containing platinum metal are being used extensively in the automobile industry as catalytic converters as well as in ignition control and electronic fuel injection systems [3]. Also, it is now heavily utilized in biological systems (especially DNA), hard alloy in dentistry and in the pharmaceutical industry, particularly in cancer drugs such as cisplatin, carboplatin, and oxaliplatin [4]. The most suitable analytical methods for the platinum determination, at such low concentration level, are atomic absorption spectrometry (AAS), mass spectrometry with the ICP ionization (ICP-MS) and neutron activation analysis (NAA) [5–7]. However, the direct determination of platinum is to some extent a problem because of the high concentration of interfering matrix components in most real samples. Therefore, there is a need to develop a simple, fast and accurate procedure for platinum separation and enrichment. The coupling of a separation/preconcentration procedure and elimination of interfering species prior to detection is necessary.

The method most frequently used for the separation and preconcentration of platinum are based mainly on liquid–liquid and solid phase extraction, precipitation and coprecipitation, electrochemical preconcentration, biosorption and bioaccumulation [8–12]. Among different separation techniques solid phase extraction (SPE) based on adsorption, ion-exchange or chelating properties of solid sorbents was found to be the most effective. Different sorbents such as polyTHF [13], dithizone anchored polyVP [14], polyAAAT [15], amicroporous resin [16,17], and VBC-AN-DVB copolymer [18] have been used for the separation/preconcentration of platinum.

More recently, carbon nanofibers (CNFs) have attracted scientific interest as they exhibit excellent and unique physical properties

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such as high strength, low density, good thermal and electrical conductivity and tunable morphology [19,20]. The desirable characteristics include chemical and environmental stabilities, high surface area and meso-porosity [21–23]. Surface studies are extremely important for nanomaterials because not only is the surface structurally and chemically quite different from the bulk, but its properties tend to dominate at the nanoscale due to the drastically increased surface-to-volume ratio [24,25]. Numerous methods have been developed to improve the fiber surface wettability or to increase the quantity of surface functional groups [26,27]. Chemical oxidation with $H_2O_2$, $HNO_3$, $KMnO_4$, or $H_2SO_4$ has been widely applied for the development of CNFs for removal of metal ions in aqueous solution [27,28].

The application of polyurethane foam for separation and preconcentration of various metal ions has attracted considerable attention [29,30]. The importance of PUF has been increased as a sorbent due to their efficiency, low cost, handling and storage. Many reports studied the uses of the PUF with reagent immobilization [31], incorporation of the chelating ligands onto a matrix [32], coupling of the ligand with PUF backbone [33] and chemically cross-linked ternary blends [34]. Although conventional PUFs sometimes have excellent properties for the preconcentration and separation of specific metal ions, the capacities of these PUFs are very low.

In the present work a new sorbent was prepared by a coupling of carbon nano-fiber with ion exchange polyurethane foam. This type eliminates the problem of low capacity of PUF sorbent. The interfacial bond between the carbon nano-fiber and the PUFIX matrix can be enhanced by enlarging the surface area, which provides more sites of contact/anchorage and interactions between the sorbent and the metal ions. The characterization of the CNF-PUFIX showed that it has high capacity and stability, which has been recycled many times after regeneration using $NH_4OH$ (1:1), HCl (1:1) and $H_2O$ without decreasing their capacities. Also, the CNF-PUFIX was found to be very stable toward the acids, alkalis and organic solvents. The sorption behavior of Pt (IV) on to the CNF-PUFIX has been studied to optimize the best conditions for separation and preconcentration of platinum metal ions from aqueous solution. Data have been obtained for kinetic, thermodynamic, and equilibrium situations. The proposed method had been successfully applied for extraction of Pt (IV) from different samples of ores.

## 2. Experimental

### 2.1. Apparatus

All spectrophotometric measurements were performed on a Shimadzu Model UV-1800 (Shimadzu Corporation, Japan). IR spectra were recorded on a Shimadzu FTIR-8400 Fourier transform infrared spectrophotometer. The pH measurements were carried out using a pH meter from Microprocessor pH Meter (HANNA Instruments).

### 2.2. Reagents and materials

Ion exchange polyurethane foam (PUFIX) [35] was prepared by cutting of polyurethane foam (commercial PUF) into similar cubes (~0.125 $cm^3$). 5 g PUF cubes were soaked in 3 mol $L^{-1}$ solution of HCl for 24 h. They were washed with distilled water after that placed into a 0.1 mol $L^{-1}$ HCl solution then cooled in an ice bath. 50 mL of ethyl iodide was added dropwise to PUF with strong stirring and left for 24 h in the fridge. PUFIX was air-dried and then blended in a food-processing blender.

The carbon nanofiber/ion exchange polyurethane foam composite (CNF-PUFIX) was prepared by addition of 5 g of PUFIX and 5 g of carbon nano-fibers (Nanostructured & Amorphous Materials Inc, USA, the purity of raw CNFs >95%, outside diameters are 100–200 nm and the length reach up to 30 μm) to 200 mL of ethanol and refluxed for 6 h. The black CNF-PUFIX material was washed with distilled water followed by acetone and the air-dried. CNF-PUFIX was blended in a food-processing blender. The CNF-PUFIX was sieved and the particles between 45 and 90 μm were used for adsorption studies.

Stock solution of the platinum (IV) ions was prepared by dissolving 0.0432 g of analytical reagent grade of $PtCl_4$ (Aldrich, Milwaukee, USA) in 25 mL of distilled water. A series of 25 mL for platinum (IV) standard solutions (0–72.0 μg $mL^{-1}$ Pt in 0.32 mol $mL^{-1}$ KSCN) was used for calibration curve. The absorption spectrum is shown in Fig. S7 ($\lambda_{max}=286$ nm). The linear regression equation obtained was $A=0.026C-0.034$ ($R^2=0.999$, Fig. S8).

### 2.3. Recommended procedures

All surface acid sites of CNF-PUFIX matching the carboxylic and phenolic sites were determined. A 25 ml of 0.05 mol $L^{-1}$ NaOH solution was added to 0.05 g of CNF-PUFIX then the flask was shaken for 24 h. A 10 ml of the residual solution was titrated with HCl (0.05 mol $L^{-1}$) in the presence of methyl orange as indicator. Also, the basic sites of CNF-PUFIX were back titrated with a 0.05 mol $L^{-1}$ HCl solution.

To determine the adsorption capacity (iodine number), 25 ml of 0.05 mol $L^{-1}$ iodine solution was added to 0.05 g of CNF-PUFIX. The flask was then shaken for 24 h to ensure equilibrium adsorption of iodine onto CNF-PUFIX. The iodine number (mmol $g^{-1}$) was determined from the titration of the residual solution of 10 ml with 0.05 mol $L^{-1}$ sodium thiosulfate in the presence of 1 ml of 1 wt% starch solution as an indicator.

Density of CNF-PUFIX measurement was carried out in a 10 mL density bottle. The CNF-PUFIX powder was added to the density bottle with gentle tapping to ensure that the particles settle to the bottom and all air spaces were filled. The mass of the density bottle containing the CNF-PUFIX powder was then determined.

$pH_{ZPC}$ is the pH when the charge on the CNF-PUFIX surface is zero (zero point charge), the value of the pHpzc was determined by estimating the intersection of the pH plateau with the line defined by pH final = pH initial. To determine the $pH_{ZPC}$ of the CNF-PUFIX surface, 25 mL of solutions were taken in a series of 100 mL flasks whose pH in the range 1–13 was used. The initial pH ($pH_i$) of the solutions was determined then 0.05 g of the CNF-PUFIX was added to each flasks. After completion of 24 h, the final pH ($pH_f$) of the solutions was measured. The difference between the initial and final pH values ($\Delta pH = pH_f - pH_i$) was plotted against the $pH_i$. The $pH_{ZPC}$ was noted at the pH in which the initial pH equals the final pH.

Extraction of platinum (IV) was carried out by a batch technique at 25 °C. Adsorption experiments were carried out by agitating 0.05 g of CNF-PUFIX with 25 mL of Pt (IV) solutions (2 μg $mL^{-1}$) in a shaker adjusted to the desired speed. After shaking 30 min, the platinum concentration remaining in the supernatant solution (as effluate) was determined by using UV–vis spectrophotometer at $\lambda=286$ nm. The following equations were used to calculate the uptake percentage of platinum (%E), capacity of sorbents (Q, mg/g) and distribution coefficient (K):

$$\%E = ((C_o - C)/C_o) \times 100 \tag{1}$$

$$Q = (C_o - C)V/m \tag{2}$$

$$K = ((C_o - C)/C)V/m \tag{3}$$

where $C_o$ and C are the initial and final concentrations of Pt (IV) in solution, respectively. V is the volume of solution and m is the mass of CNF-PUFIX.

In the dynamic experiments, 1.0 g portion of CNF-PUFIX was packed into a column (25-cm long and 1.5 cm in diameter). 25 mL of Pt (IV) solution (1 μg mL$^{-1}$) was passed through the CNF-PUFIX column ($L$=4 cm) at flow rate 2 mL min$^{-1}$. Effluates were collected and analyzed spectrophotometrically at $\lambda$=286 nm. The elution of the platinum from the CNF-PUFIX column was carried out using (1:1) $NH_4OH$. The eluates were collected then added 1 mL of HCl (1:1) was added and the amount of the Pt (IV) was determined spectrophotometrically at $\lambda$=286 nm.

## 3. Results and discussion

### 3.1. Characterization of CNF-PUFIX

Several analysis techniques were used to characterize the surface structure, chemical and physical properties of carbon nanofibers polyurethane sorbent (CNF-PUFIX). These techniques include infrared, ultraviolet/visible and Raman spectroscopies, elemental analysis, scanning electron microscopy, $pH_{ZPC}$, iodine number, density, acidic and basic sites.

The infrared spectra of PUF and CNF-PUFIX were run using potassium bromide. Fig. 1 shows the infrared transmission spectra for PUF and CNF-PUFIX in the region between 400 and 4000 cm$^{-1}$. The spectrum of the PUF shows several strong band stretches at 3662.1, 3264.8, 2865.7, 2242.8 and 1596.8 cm$^{-1}$ due to free $-NH_2$, –NH of urethane group, aliphatic hydrocarbon (–CH), free isocyanate (–NCO) and urethane (–NHCOO–) groups, respectively (Figs. S1). These bands had disappeared in the spectrum of CNF-PUFIX (Fig. 1), reflecting joining of these groups with the surface functional groups of carbon nano-fibers. The IR spectrum of CNF-PUFIX in Fig. S2, shows that the transmission percentage was between 89% and 98%. It shows that new absorption bands have appeared at 3425.9, 2967.9, 1639.2, 1612.3, 1573.6, 1443.5, 1385.6, 1103.2, 802.2 and 411.7 cm$^{-1}$ (Table 1). The broad band at 3425.9 cm$^{-1}$ is assigned to the O–H stretch from carboxyl group (O=C–OH) and NH of urethane group while the peaks at 1573.6 and 1443.5 cm$^{-1}$ is attributed to asymmetric and symmetric stretching vibrations of the anion carboxylate [36,37]. The bands at 1612.3, 802.2 and 411.7 cm$^{-1}$ are due to C=N and C=C groups [38]. The other absorption bands 2967.9, 1385.6 and 1261.3 cm$^{-1}$ are characteristics of aliphatic hydrocarbon, quaternary ammonium salt and tertiary amino groups [35], respectively.

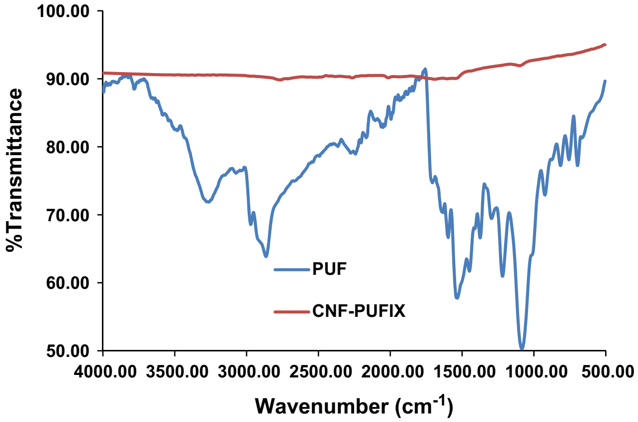

**Fig. 1.** Infrared spectra of polyurethane foam (PUF) and carbon nano-fiber/Ion exchange polyurethane foam (CNF-PUFIX).

CNF-PUFIX is insoluble in most solvents, the electronic spectra was recorded in solid state using Nujol mulls method [39]. Filter paper (3.5 × 0.8 cm$^2$) was covered with CNF-PUFIX in paraffin oil after drying; it was placed in the path of light in a cell against filter paper covered with paraffin oil without CNF-PUFIX as blank. The UV–vis spectrum of CNF-PUFIX in Figs. 2 and S3 show that many peaks between 240 and 480 nm (253, 315, 349, 377, 386, 402 and 424 nm, Table 1) have appeared due the several functional groups of CNF-PUFIX.

The elemental analysis of PUF and CNF-PUFIX was estimated. The results in Table 1 show that the carbon percentage in CNF-PUFIX (71.8%) is more than in PUF (64.0%). The percentages of hydrogen, nitrogen, sulfur and oxygen in CNF-PUFIX (6.7%, 5.0%, 0.2% and 16.3%, respectively) are less than that in PUF (9.5%, 7.2%, 0.5% and 18.8%). These results show that the carbon nano-fiber has coupled with PUFIX.

Surface morphology of CNF-PUFIX was investigated using scanning electron microscopy (SEM). Figs. 3 and S4 represent SEM images of CNF-PUFIX at magnifications of 180, 200, 400, 1600, 3000, 6000 and 12,000. The microstructure of CNF-PUFIX images showed that the surface is relatively smooth and the cells are nearly spherical and irregular in size and distribution. It contains many spaces, channels, and holes. The functional groups were irregular appeared in the surface of CNF-PUFIX.

Raman spectroscopy a powerful tool to investigate microstructures was used [39]. The Raman spectrum of CNF-PUFIX (Figs. 4 and S5) has three strong characteristic bands at 2425.0, 1553.3 and 683.6 cm$^{-1}$. The peak at 2425.0 cm$^{-1}$ is probably due to the formation of conjugated carbon–nitrogen double bonds (–C=N– group) formed by condensation between carbon nanofibers and polyurethane foam. The G band at 1500–1600 cm$^{-1}$ is attributed to the C=C stretching chain vibrations of the aromatic ring in the graphite crystallites [40] while, the band at 683.6 is due to aliphatic chain (C–C) vibrations.

The densities of the PUF and CNF-PUFIX were measured. The values of densities of PUF and CNF-PUFIX are 13.5 and 0.1 kg/m$^3$, respectively (Table 2). This result indicates that the CNF-PUFIX is less dense than the PUF. The low density of the CNF-PUFIX than the PUF is attributed to the coupling between CNF and PUFIX.

**Table 1**
Comparison between the spectra data of PUF and CNF-PUFIX.

| Property | PUF | CNF-PUFIX |
|---|---|---|
| **IR spectra** | | |
| Main strong stretches absorption band (cm$^{-1}$) | 3662.1, 3264.8, 2865.7, 2242.8, 1596.8 | 3425.9, 2967.9, 1639.2, 1612.3, 1573.6 |
| **UV–vis spectra** | | |
| $\lambda_{max}$ (nm) | Nil | 253, 315, 349, 377, 386, 402, 424 |
| **Elemental analysis** | | |
| C, H, N, S and O % | 64.0, 9.5, 7.2, 0.5 and 18.8 | 71.8, 6.7, 5.0, 0.2 and 16.3 |
| **Raman spectra** (cm$^{-1}$) | – | 2425.0, 1553.3 and 683.6 |

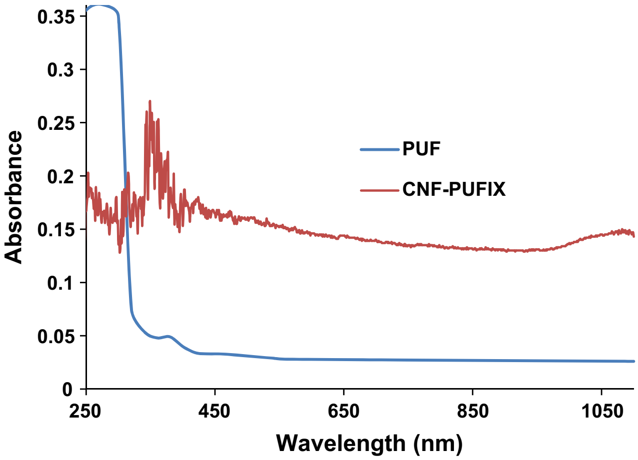

**Fig. 2.** Ultraviolet/visible spectra of polyurethane foam (PUF) and carbon nanofiber/Ion exchange polyurethane foam (CNF-PUFIX).

The $pH_{ZPC}$ value is determined to be approximately 8.9 and 8.6 for the PUF and CNF-PUFIX (Figs. 5 and S6). The $pH_{ZPC}$ value is based on terminal groups and membrane-like structure of the CNF-PUFIX. At pH lower than of $pH_{ZPC}$ ($pH < 8.6$), the surface of the CNF-PUFIX is positively charged while at pH greater than pH CNF-PUFIX, the surface of the CNF-PUFIX becomes negatively charged. The positive charge of CNF-PUFIX in acidic medium is due to the protonation on the oxygen and nitrogen atoms while for pH between 7 and 8.6 may be due to the dissociation of some functional groups. While, the negative charge of CNF-PUFIX (in $pH > 8.6$) is due to deprotonation of phenolic and carboxylic groups.

The total surface acid sites of CNF-PUFIX matching the carboxylic, phenolic and lactonic sites were determined using a 0.05 mol $L^{-1}$ $NaHCO_3$, $Na_2CO_3$ and NaOH solutions [41]. The CNF-PUFIX was shown to contain 0.4, 0.2 and 0.3 mmol $g^{-1}$ of lactonic, carboxylic and phenolic groups, respectively, and the total acidity is 0.9 mmol $g^{-1}$ (Table 2). This result indicates that the surface of CNF-PUFIX contains acidic sites (carboxylic, lactonic and phenolic groups) and is a good adsorbent for extraction of organic and inorganic species as chelating polymer. The carboxylic, lactonic and phenolic groups on the surface of CNFs may be produced during the synthesis of CNF-PUFIX. The amount of surface acidic sites of CNF-PUFIX is 0.90 mmol $g^{-1}$ while the amount of surface acidic sites of CNF-PUFIX is 0.18 [29].

The amount of surface basic sites was estimated by using HCl (0.05 mol $L^{-1}$), is 0.5 mmol $g^{-1}$ (Table 2) due to quaternary ammonium salt and tertiary amino groups. By comparing of the total acidic sites of CNF-PUFIX with basic sites, the total acidic sites are higher than the basic sites (0.9 mmol $g^{-1}$: 0.5 mmol $g^{-1} \approx 2$: 1). These results indicate that the surface of CNF-PUFIX is mainly acidic (–C═O, –OH and –COOH).

The iodine number (adsorption capacity) was determined from the adsorbed iodine per unit mass of CNF-PUFIX, which depends on the number of pores per gram of sorbent. The sorption capacity of CNF-PUFIX is 2.2 mmol $g^{-1}$ (279.2 mg I $g^{-1}$, Table 2). The result shows that the extraction process depends on the adsorption of iodine molecules onto the CNF-PUFIX. Also, this result indicates that the CNF-PUFIX exhibits better capacity value when compared with other sorbents, the capacities of miswak [42], pine cone [43], Jatropha husk [44] and coir pith carbon [45] are 0.13–0.96 mmol $g^{-1}$.

### 3.2. Optimum condition for extraction of platinum (IV) ions using CNF-PUFIX

The optimization for quantitative extraction of Pt (IV) from aqueous or thiocyanate solution using batch and dynamic techniques was performed. The experimental conditions such as pH (1–13), platinum concentration (0.01–0.36 mmol $L^{-1}$), thiocyanate concentration (0.01–0.32 mol $L^{-1}$), shaking time (1–60 min), solution temperature (25–55 °C), sample and eluent volume (25–250 mL), flow rate (0.5–4.0 mL $min^{-1}$) on the preconcentration and determination of platinum were estimated. The effects of eluting agent and interfering ions on the sorption and desorption of Pt (IV) ions was also studied.

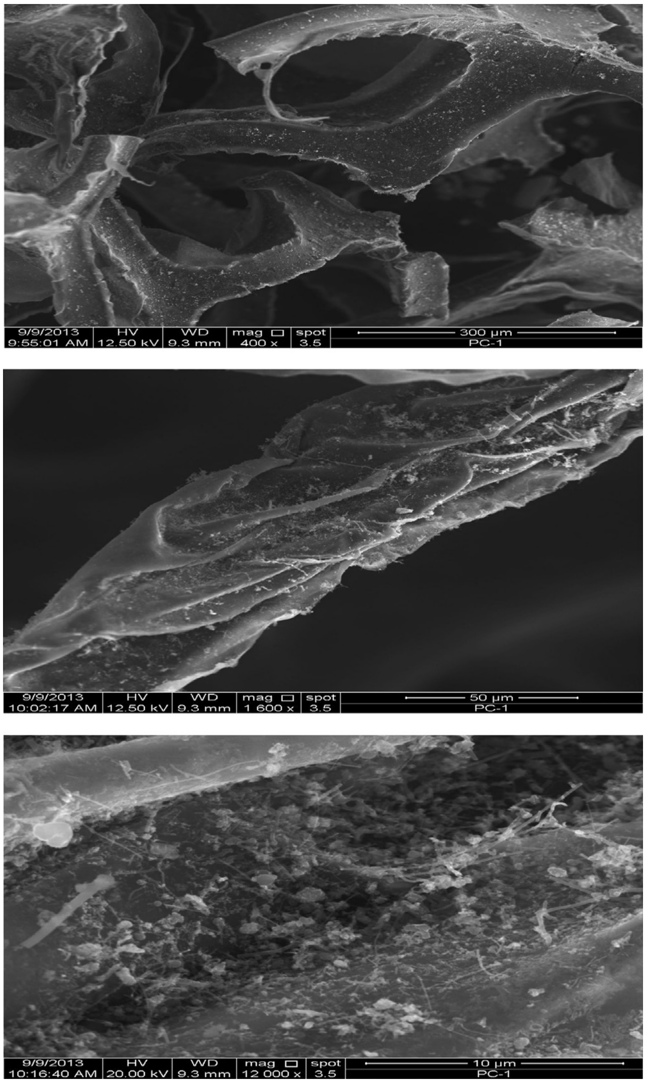

**Fig. 3.** Surface morphology of CNF-PUFIX by scanning electron microscopy at magnifications of 400, 1600 and 12,000.

The pH of the solution is an important parameter to study because the charge of CNF-PUFIX sorbent and formation of the platinum thiocyanate complex are strongly dependent on the hydronium (or hydroxide) ions concentration in the media. The effect of pH on the extraction of Pt (IV) ions from thiocyanate solution using CNF-PUFIX has been examined by batch technique, the pH of the Pt (IV) solution was adjusted before equilibration with pH using HCl and NaOH. The percentage extraction of Pt (IV) was plotted against the pH value (Fig. 5). The sorption of Pt (IV) was increased from pH 1–5, the maximum extraction of platinum (99–100% Pt) was in pH 4–5 then decreased to ~80% in pH 7. The result obtained is in good agreement with platinum extracted as thiocyanate complex with pyridine in pH 2.5–3 [46], triphenylisopropylphosphonium salt in pH 1.5 [47] and as chloride complex with ion exchange in pH 2–3 [48].

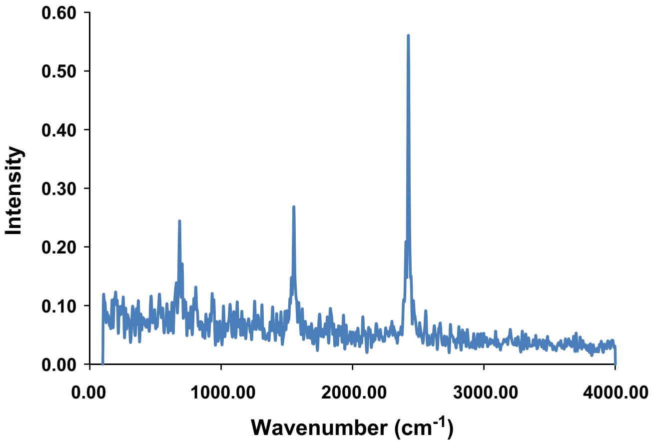

**Fig. 4.** Raman spectrum of CNF-PUFIX.

**Table 2**
Chemical and physical properties of CNF-PUFIX.

| Property | CNF-PUFIX |
|---|---|
| **Color** | Black |
| **Density** (Kg m$^{-3}$) | 0.11 |
| **$pH_{ZPC}$** | 8.6 |
| **Total acidity** (mmol g$^{-1}$) | 0.9 |
| **Phenolic** (mmol g$^{-1}$) | 0.3 |
| **Carboxylic acid** (mmol g$^{-1}$) | 0.2 |
| **Lactones** (mmol g$^{-1}$) | 0.4 |
| **Iodine number** (mmol g$^{-1}$) | 2.2 |
| **Total basisty** (mmol g$^{-1}$) | 0.5 |

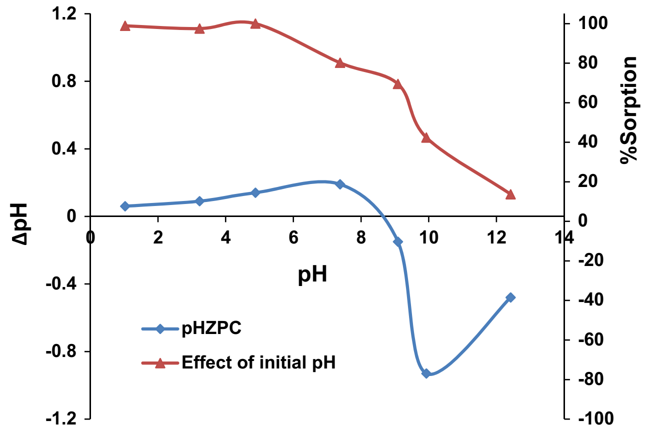

**Fig. 5.** $pH_{ZPC}$ of CNF-PUFIX and effect of initial pH on the sorption of platinum (IV) thiocyanate complex onto CNF-PUFIX

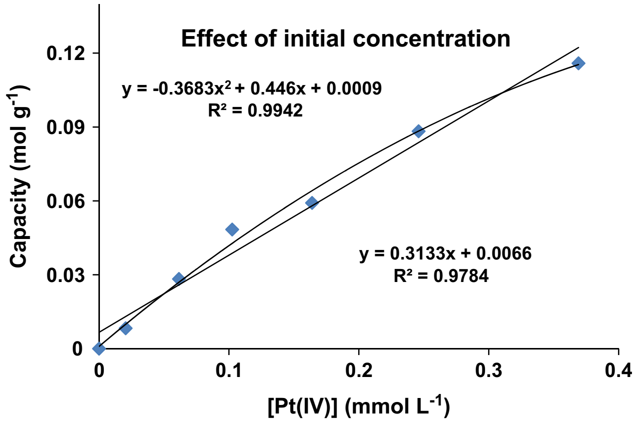

**Fig. 6.** Effect of initial platinum concentration on the extraction of platinum (IV) thiocyanate complex onto CNF-PUFIX.

The effect of initial platinum concentration on the sorption capacity of CNF-PUFIX was studied. Fig S9 shows that relation between the amount of sorbed platinum per unit mass of CNF-PUFIX (capacity, $Q_c$) and the initial Pt (IV) concentration. A perfect linear curve with zero intercept ($6.6\times10^{-3}$) and good correlation ($R^2$=0.978) has been obtained. It is clear that the capacity was increased with increasing the initial concentration and reached a plateau (maximum uptake capacity values) were obtained (Fig. 6). The sorption capacities of CNF-PUFIX for platinum from thiocyanate and aqueous solutions were estimated to be 0.19 and 0.12 mmol g$^{-1}$ (38.0 and 24.1 mg g$^{-1}$), respectively. It is evident from the achieved results that the developed sorbent exhibits greater capacity towards Pt (IV) in thiocyanate solution than platinum in aqueous solution. The sorption capacity of CNF-PUFIX is compared with other sorbents [49–53]; the CNF-PUFIX exhibits better capacity values in comparison to dithizone diaion resin (31.2 mg g$^{-1}$), polyamine functionalized polystyrene nanofibers (7.4 mg g$^{-1}$), aluminum hydroxide gel (23.9 mg g$^{-1}$), $Fe_3O_4$ nanoparticles (13.3 mg g$^{-1}$) and tannin from Indian almond leaf biomass (22.5 mg g$^{-1}$).

The limit of detection (LOD=3$\sigma$, where $\sigma$ is the standard deviation of blank determination) and limit of quantitation (LOQ=10$\sigma$) for platinum ions were established by analyzing six blank solutions. The value of LOD and LOQ of Pt (IV) were 2.4 ng mL$^{-1}$ and 8.2 ng mL$^{-1}$, respectively. The LOD and LOQ values for the platinum ions would be enabling the use of CNF-PUFIX in determination of platinum at a trace concentration with high accuracy. Also, the lower detection limit of Pt (VI) by using the spectrophotomeric determination method indicates that the CNF-PUFIX sorption method (0.0024 μg mL$^{-1}$) is more sensitive than the PUF method (0.1 μg mL$^{-1}$) [54].

The accuracy and precision for the different fortification levels of the platinum samples were estimated. The recoveries percentage values ranged from 99% to 100% with the low relative standard deviation values (RSD=1.72%, $n$=5) for the analysis of five samples replicates of Pt (IV) indicate a good precision and accuracy of the proposed method.

The effect of thiocyanate concentration on the extraction of Pt (IV) was examined (Fig. S10). A 0.2 mol L$^{-1}$ is the minimum concentration of KSCN necessary for the maximum extraction (99–100%) of Pt (IV). Also, the extraction of platinum ions from thiocyanate solution is larger than those from aqueous solution. This confirms that the CNF-PUFIX is more efficient for extraction of platinum ions in thiocyanate solution than that from aqueous solution due to the ion-pairs formation between CNF-PUFIX with anion platinum (IV) thiocyanate complex.

The rate of extraction of platinum ions onto CNF-PUFIX was measured using batch extraction mode. The result obtained shows that the time required for complete extraction of Pt (IV) onto CNF-PUFIX is 20 min (Fig. S11). The initial extraction rate of platinum is very fast (~80% of platinum sorbed in the first 5 min) and then becomes progressively slower with increasing time (20% sorption of platinum since 15 min). The result indicates that the rate of sorption of the platinum ions onto CNF-PUFIX was rapid. This rapid sorption rate of platinum is due to the strong bond formation with the CNF-PUFIX.

The dependence of extraction of platinum onto CNF-PUFIX with temperature has been studied. The result shows that the maximum extraction of platinum ions (99–100%) occurs at low temperature and the sorption of Pt (IV) decreases with the increasing temperature. Thermodynamic parameters for the sorption of Pt (IV) were estimated using the equations: $\ln K=-\Delta H/RT+\Delta S/R$, $K=((C_o-C)/C)$ and

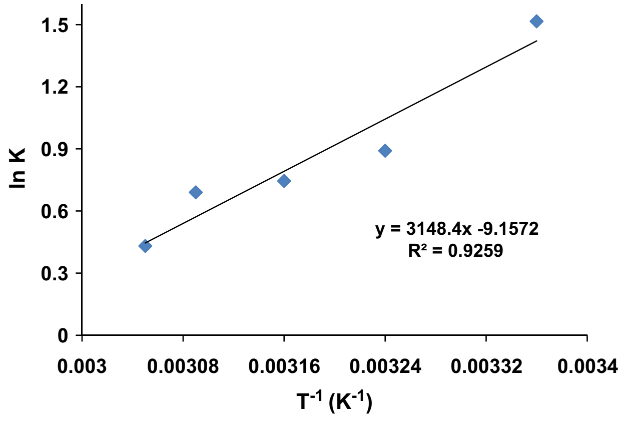

**Fig. 7.** Effect of temperature on the sorption of platinum (IV) thiocyanate complex onto CNF-PUFIX.

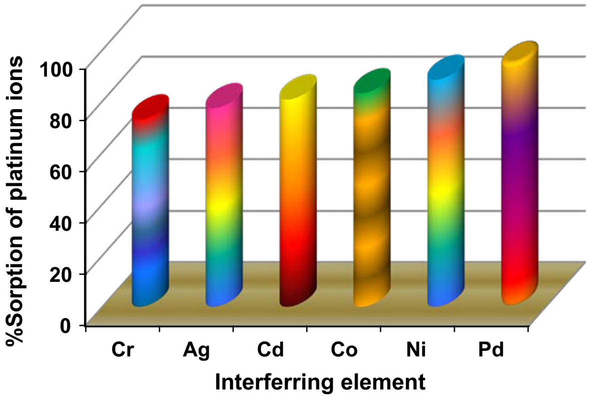

**Fig. 8.** Effect of interfering metal ions on the sorption of platinum (IV) thiocyanate complex onto CNF-PUFIX.

$\Delta G = \Delta H - T\Delta S$ where K is the distribution coefficient for sorption. The plot of $\ln K$ vs. $1/T$ gives $\Delta H$ and $\Delta S$ values from slope and intercept ($R^2 = 0.926$, Fig. 7). The negative value of $\Delta H$ ($-26.1$ kJ mol$^{-1}$) interpret that the sorption process of platinum is exothermic chemisorptions. The value of entropy (76.0 J K$^{-1}$ mol$^{-1}$) is an indication of the faster sorption of platinum onto CNF-PUFIX. $\Delta G$ have been evaluated using the equation: $\Delta G = \Delta H - T\Delta S$. The negative values of $\Delta G$ ($-3.5$ kJ mol$^{-1}$) indicate that the feasibility of the process and its spontaneous nature without induction period.

The effect of batch factor (sample volume to the 0.05 g of CNF-PUFIX, V/m) on the uptake of Pt (IV) has been studied (Fig. S12). The result indicated the maximum extraction of platinum ions in batch factor (V/m) 500–1000. Also, the uptake of Pt (IV) decreases with the increasing of the batch factor, recovery percentage becomes 60 in V/m value 1500.

The effects of foreign ions which may interfere with extraction of the platinum ions were studied in order to identify the method selectivity. For this purpose, 25 mL solution containing 5 µg of Pt (IV) was mixed with the interfering ions (200 µg) and adjusted to optimum pH and shacked for 15 min. The obtained data show that $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Al^{3+}$, and $Mo^{6+}$ are not affected on the extraction of platinum ions. $Pd^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Cd^{2+}$, $Ag^+$, $Fe^{2+}$ and $Cr^{3+}$ reduce the extraction of platinum ions from 5.4% to 27.1% (Fig. 8). While $Cu^{2+}$, $Fe^{3+}$ and $Bi^{3+}$ are the strongest interference. Adding masking agent such as phosphate and citrate ions with adjusting the pH medium minimizes their interfering effect. Generally, the majority of the examined foreign ions were not found to interfere, that is to confirm the adequate selectivity of the CNF-PUFIX method and feasibility for determination of platinum in natural samples with relevant accuracy.

The effect of sample flow rate (1–3.5 mL min$^{-1}$) through the CNF-PUFIX column on the uptake of platinum ions was studied. The retention percentage of the platinum ion into the column was determined (Fig. S13). The maximum recovery observed in the range 0.5–1.0 mL min$^{-1}$. Faster flow rates than 1.0 mL min$^{-1}$ led to decrease the recovery percentage from 100% to 93.9%. This confirms the relation between the retention sensitivity and the contact time of Pt (IV) with CNF-PUFIX.

The effect of different eluent (HCl, $NH_4OH$ and $H_2NCSNH_2$) on the stripping of platinum from CNF-PUFIX column was studied. From the results obtained the platinum was completely eluted from CNF-PUFIX column with $NH_4OH$ and $H_2NCSNH_2$. The elution of platinum e from CNF-PUFIX column was examined at concentration range from 0.5 to 4.0 mol L$^{-1}$ $NH_4OH$. A 0.5 mol L$^{-1}$ is the minimum concentration of $NH_4OH$ necessary for completely elution of Pt (IV). The recovery of Pt (IV) was decreased with decreasing of the ammonium hydroxide concentration. This result is indicates that the ammonium salts can be used in the stripping of platinum from the CNF-PUFIX column (to form $[Pt\ (NH_3)_4]^{4+}$).

### 3.3. *Sorption mechanism*

The IR spectra of CNF-PUFIX and Pt(IV)–CNF-PUFIX complex (Figs. 9 and S14) show that the transmission percentage of the Pt (IV)–CNF-PUFIX complex increased. The presence of platinum ions modifies the infrared transmission bands, mainly in the region between 400 and 1800 cm$^{-1}$; this is related to the vibration absorptions of Pt–O and Pt–N stretching. This observation further confirms that CNF-PUFIX joined by coordination with Pt(IV). Also, they show that the absorption bands at 3425.9, 1639.2, 1573.6, 1443.5, 1385.6, 1103.2 and 1056.8 cm$^{-1}$ are shifted to 3447.1, 1630.5, 1552.4, 1459.2, 1371.1, 1093.3 and 1034.6 cm$^{-1}$. Also, new absorption bands have appeared at 714.5, 482.1 and 430.1 cm$^{-1}$. While the bands at 1612.3 and 411.7 cm$^{-1}$ have disappeared. The results obtained in the Pt(IV) SCN:CNF-PUFIX complex spectrum show that there are shifts in the absorption bands of CNF-PUFIX groups to 3434.6, 1632.4, 1542.5, 1430.9, 1366.3, 1098.3 and 1025.9 cm$^{-1}$. On the other hand, additional band at 2366.5 cm$^{-1}$ characteristic of the thiocyanate group has appeared. Also two new bands appeared at 718.4, 465.7 and 428.1 cm$^{-1}$ reflecting that the CNF-PUFIX is joined by coordination of platinum (IV) thiocyanate complex.

The electronic spectra of platinum (IV) CNF-PUFIX and platinum (IV) thiocyanate: CNF-PUFIX complexes were recorded in the

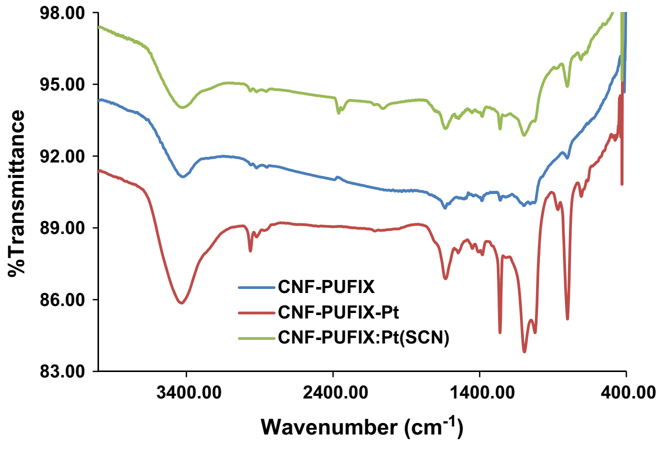

**Fig. 9.** Infrared spectra of (a) CNF-PUFIX, (b) CNF-PUFIX after sorbed platinum ions and (c) CNF-PUFIX after sorbed Pt (IV) thiocyanate complex.

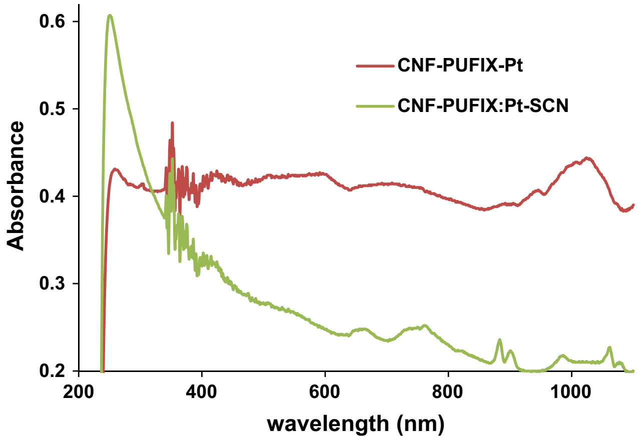

**Fig. 10.** Ultraviolet/visible spectra (a) CNF-PUFIX after sorbed platinum ions and (b) CNF-PUFIX after sorbed Pt (IV) thiocyanate complex.

solid state using Nujol mulls method using CNF-PUFIX as blank. In the platinum (IV) CNF-PUFIX complex spectrum (Figs. 10 and S15), the absorption bands appeared at 258, 591, 692, 889, 945 and 1024 nm. These values are higher than the corresponding absorption bands for the CNF-PUFIX itself which are observed at 253, 315, 349, 377, 386, 402 and 424 nm. The same trend can be observed for the platinum (IV) thiocyanate: CNF-PUFIX complex, the peak values are in the range 249, 664, 757, 883, 899, 992, 1061 and 1083 nm which are higher than the absorption bands for the CNF-PUFIX. This may be due to the coordination of the CNF-PUFIX functional groups to the platinum ions.

The sorption of platinum metal ions and platinum (IV) thiocyanate complex on the surface of CNF-PUFIX was assessed by the SEM at different magnifications (180, 400, 1600 and 3000, Figs. 11 and S16–S18). Detailed analysis of the CNF-PUFIX material surface shows a deposited layer of platinum (IV) thiocyanate complex and homogeneously distributed over the CNF-PUFIX structures while the platinum (IV) ions are deposited inside the spaces and holes of CNF-PUFIX. These results proved the formation of ion association between platinum (IV) thiocyanate complex and CNF-PUFIX and a coordination of the CNF-PUFIX functional groups with platinum ions.

The CNF-PUFIX surface was positively charged at pH lower than 8.6 and becomes negative charge at $\text{pH} > 8.6$. Accordingly, an electrostatic attraction between the anion platinum thiocyanate complex and CNF-PUFIX took place in $\text{pH} < 8.6$. The extraction process mainly depends on the ion exchange and/or ion association complex formed between the CNF-PUFIX cation in the medium has $\text{pH} < 8.6$ and the anion complex of the platinum (IV) thiocyanate (CNF-PUFIX $^{+}$: $[\text{Pt(SCN)}_4]^-$). The sorption of Pt (IV) was decreased from 100% to 72.6% with increasing of pH 5 to pH 8.6 due to the formation of platinum (IV) thiocyanate complex. Although, the positive charge density of the CNF-PUFIX surface at pH 1–3 is more than it in pH 4–5 due to protonation of oxygen and nitrogen atoms the platinum sorption was increased. This result indicates that the reaction between Pt (IV) ions and the function group of CNF-PUFIX has been occurred and the sorption mechanism of Pt (IV) onto CNF-PUFIX is also ion chelation process. These results indicate that the ion chelation and ion association might be the most probable mechanism of platinum sorption onto CNF-PUFIX.

Fig. S19 shows that relation between the sorption capacity of CNF-PUFIX and the remaining Pt (IV) concentration in solution (isotherm curve). The values of intercept and correlation coefficient for the linear plot are 0.27 and 0.873, respectively. The data of the platinum sorption isotherm was fitted using Freundlich ($\log Q_c = \log K_F + \frac{1}{n} \log C_e$) and Langmuir $[C_e/Q_c = (1/K_L b) + (C_e/K_L)]$ models (Fig. 12). Where $C_e$ is the amount of platinum sorbed at equilibrium. $K_F$, $n$, $K_L$ and $b$ are constants. The correlation values ($R^2$) for the plot of Freundlich and Langmuir models are 0.704 and 0.875, respectively (Figs. S20 and S21). The $R^2$ value for Langmuir model is higher than $R^2$ value for Freundlich. The result obtained shows that the Langmuir sorption

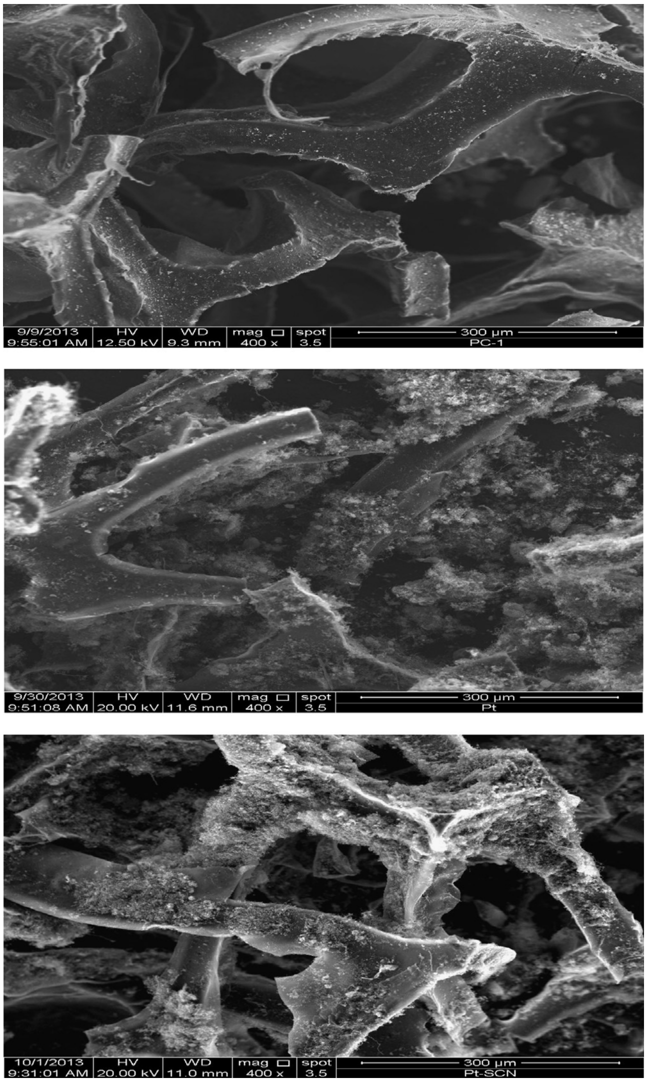

**Fig. 11.** SEM images of (a) CNF-PUFIX, (b) CNF-PUFIX after sorbed platinum ions and (c) CNF-PUFIX after sorbed Pt (IV) thiocyanate complex.

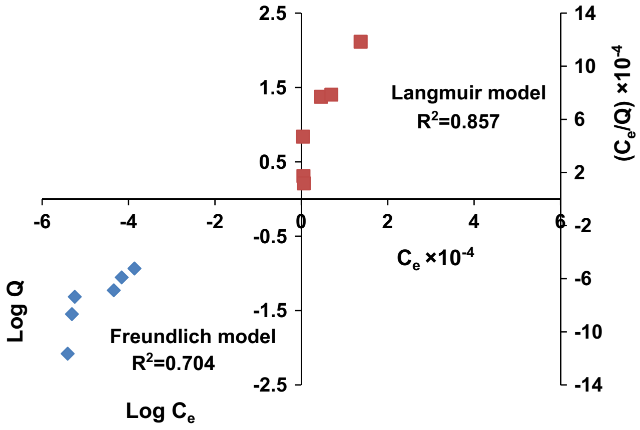

**Fig. 12.** Freundlich and Langmuir models for the sorption Pt (IV) thiocyanate complex onto CNF-PUFIX.

mechanism is predominant. This model suggested that the sorption of platinum from thiocyanate solution to the CNF-PUFIX is monolayer coverage.

Also, the sorption isotherm data was analyzed using Dubinin Radushkevich $(\ln Q_c = \ln k_{dr} - \beta\varepsilon^2$ and $\varepsilon = RT \ln[1+(1/Q_c)])$ equations where $K_{DR}$ is the maximum amount of Pt (IV) retained onto the CNF-PUFIX; $\beta$ is a constant related to the energy of transfer of the solute from the bulk aqueous solution onto the solid sorbent and $\varepsilon$ is Polanyi potential. The value of $\beta$ for sorption of Pt (IV) onto CNF-PUFIX is $-0.0039$ (Fig. S22, $R^2=0.712$). The value of sorption energy, (activation energy, $\Delta E$), was correlated to $\beta$ $(E = 1/\sqrt{-2\beta})$. The value of $(E)$ evaluated is 11.3 kJ mol$^{-1}$. Thus, a dual sorption mechanism involving "ion association" and/or an "anion exchange" is most probable model for platinum uptake by CNF-PUFIX.

In order to study the particle diffusion mechanism of the sorption of Pt (IV) onto CNF-PUFIX, the Morris–Weber $(q_{tt} = k_M\sqrt{t})$ equation was applied (Figs. S23 and S24). Where $q_t$ is the amount of platinum ions sorbed at time $t$ and $k_M$ is the rate constant of interparticle transport. The obtained data (Fig S23) shows that the plot of $q_t$ vs. $\sqrt{t}$ is linear ($R^2=0.889$) and this line do not pass through the origin ($k_M=5.2$ μmol g$^{-1}$ min$^{-1/2}$). The obtained data in Fig. S24 shows that the plot consists of three lines (three stages) as predicted. The diffusion rate is high in the initial stage and then decreased with the passage of time. The values of $k_M$ of these stages are 13.7, 5.0 and 1.6 μmol g$^{-1}$ min$^{-1/2}$ with correlation values ($R^2$) 0.994, 0.994 and 0.946, respectively. The decrease of $k_M$ in the second and third steps is due to the retardation and blocking of the active centers which mean the saturation of the surface by sorbed molecules [55].

The pseudo-first order $[\log(Q_e - Q_t) = (\log Q_e) - (k_1 t/2.303)]$ and pseudo-second order $[t/Q_t = (1/k_2 Q_e^2) + t/Q_e)]$ kinetic models are tested to fit the experimental data for the sorption of platinum ions onto CNF-PUFIX (Figs. S25 and S26). The $R^2$ value for pseudo-second order sorption model (0.998) is higher than the value of $R^2$ (0.982) for pseudo-first order model. This suggests that the pseudo-second order sorption mechanism is predominant. The initial rate constant $(h = k_2 Q_e^2)$ and second order rate constant are calculated, the $h$ and $k_2$ values are 4.4 mmol g$^{-1}$ min$^{-1}$ and 0.15 g mmol$^{-1}$ min$^{-1}$, respectively.

### 3.4. Analytical applications

The tests of addition/recovery of different amounts of platinum were performed for the underground water of Makkah city (water composition: Na: 19 mg L$^{-1}$; K: 1.8 mg L$^{-1}$; Ca: 19 mg L$^{-1}$; Mg: 3 mg L$^{-1}$; Fe: 0.0 mg L$^{-1}$; TDS: 127 mg L$^{-1}$; $HCO_3$: 29 mg L$^{-1}$; Cl: 33 mg L$^{-1}$; $SO_4$: 27 mg L$^{-1}$, $NO_3$: 2.8 mg L$^{-1}$, F: 1.0 mg L$^{-1}$, Pt: 0.0 and pH: 7.6) in order to estimate the accuracy of the presented procedure. A 0.05 g portion of the CNF-PUFIX was mixed with 25 mL of water sample which spiked with 10–40 μg of Pt (IV) and the batch procedure applied. The results are given in Table 3. The recovery percentage of platinum ions from the water samples onto CNF-PUFIX were 90.3–98.8%. Good agreement between the added and recovery platinum content using the batch procedure have been obtained. The standard deviation value for the spiked samples was 3.75%.

**Table 3**
Extraction of platinum from Makkah underground water using CNF-PUFIX.

| Concentration (μg/L) | Recovery | | |
|---|---|---|---|
| | μg | % | RSD% |
| 10 | 9.88 | 98.8 | 3.75 |
| 20 | 19.06 | 100.9 | |
| 30 | 28.05 | 93.5 | |
| 40 | 36.12 | 90.3 | |

**Table 4**
Determination of platinum in certified samples using batch technique.

| Sample | Conc. (μg mL$^{-1}$) | Found (μg mL$^{-1}$) | Recovery (%) | RSD (%) |
|---|---|---|---|---|
| Pharmaceutical, Carboplatin Actavis | 40 | 40 | 100 | 0.00 |
| Electrode platinum wire, OGUSSA | 20 | 19.985 | 99.93 | 1.66 |

**Table 5**
Determination of platinum in real samples using dynamic technique.

| Sample | Conc. (μg) | Found (μg) | Recovery (%) | RSD (%) |
|---|---|---|---|---|
| Pharmaceutical | 60 | 59.85 | 99.75 | 0.73 |
| Sea water | 25 | 25.38 | 101.52 | 1.40 |

CNF-PUFIX sorbent was used for determining platinum in carboplatin (Actavis, Nerviano, Milano, and Italy) using batch (Table 4) and dynamic (Table 5) techniques. A 0.1 mL of carboplatin Actavis (1 × 15 mL Vail, 10 mg mL$^{-1}$) which containing 1.0 mg of Pt was mixed in a 25 mL flask with 1.0 mL of concentrated $HNO_3$ and diluted with distilled water. The pH of solution is adjusted to 5.0 and adds 2.0 mL of 4 mol L$^{-1}$ KSCN then the recommended procedures applied. The recoveries percentage of Pt (IV) are 100% (RSD 0.0%, $n=4$, Table 4) using the batch method and 99.8% (RSD 0.73%, $n=4$, Table 5) by dynamic technique. These results showed the suitability of the CNF-PUFIX for determination of platinum in carboplatin samples.

The assaying of platinum in electrode platinum wire (OGUSSA, Austria, 99.99% Pt) was studied using batch technique. A 0.1 g portion of platinum wire was dissolved in 10 mL of aqua regia and evaporates the solution nearly to dryness. 5 mL of conc. HCl and 0.1 g NaCl were added and the solution was evaporated to dryness. The residue was dissolved in 20 mL HCl (1:1) and diluted with deionized water to 100 mL in a measuring flask [56]. The average platinum concentration was found to be 99.93% using the proposed method (RSD = 1.66%, $n=4$, Table 4).

The applicability of the CNF-PUFIX was evaluated by analysis of the geological samples. The Granite reference sample (G2, US Geological Survey Certificate of Analysis, USGS) was analyzed. The obtained result shows that recovery values were obtained to be in the range 80.7–81.5% with the value of RSD 2.79%.

Determination of Pt (IV) in sea water of Arabian Gulf in Dammam city using dynamic technique (water composition: Na: 3511 mg L$^{-1}$; K: 177 mg L$^{-1}$; Ca: 160 mg L$^{-1}$; Mg: 468 mg L$^{-1}$; TDS: 12721 mg L$^{-1}$ Pt: 0.0 and pH: 7.5) has been investigated. Using 25 μg of Pt (IV) in 25 mL of sea water samples (adjusted pH at 5) has been allowed to pass through the CNF-PUFIX column at flow rate of 1.0 mL min$^{-1}$. The elution of the platinum from the CNF-PUFIX column was carried out by 10 mL of $NH_4OH$ (1:1) solution and the amount of Pt (IV) in the eluate was determined by the recommended method. The result shows that the average recovery percentages of 101.5% (RSD = 1.4%, $n=4$; Table 5). This results show that the platinum can be determined effectively in sea water using CNF-PUFIX column.

The obtained data conferred susceptible accuracy of the developed method based on the satisfactory values of RSD in addition to the reasonably high sensitivity and validity of the proposed method for determination in real samples.

## 4. Conclusion

The present work is concerned with the preparation of new sorbent (CNF-PUFIX). The CNF-PUFIX was used for extraction and determination of Pt (IV) traces. The kinetic and thermodynamic of the platinum ions sorption onto CNF-PUFIX was studied. The negative values of $\Delta G$ and $\Delta H$ indicated that the spontaneous and exothermic nature of the sorption of Pt (IV). The sorption mechanism of platinum ions onto CNF-PUFIX may proceed via the chelation and ion association. This study could conclude that CNF-PUFIX has the ability to separate and determine platinum in water, granite and carboplatin. Finally, CNF-PUFIX was used as an excellent sorbent, which processes good stability in different solvents and high sorption capacity for platinum ions. CNF-PUFIX has an interesting property of relatively fast separation and preconcentration of platinum ions compared to other solid sorbents.

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## Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.12.050.

## References

[1] K. Pyrzynska, Talanta 47 (1998) 841–848.
[2] Q. Hu, X. Yang, Z. Huang, J. Chenc, G. Yang, J. Chromatogr. A 1094 (2005) 77–82.
[3] W.H. Hsu, S.J. Jiang, A.C. Sahayam, Anal. Chim. Acta 794 (2013) 15–19.
[4] Y. Li, Y.F. Huang, Y. Jiang, B. Tian, F. Han, X.P. Yan, Anal. Chim. Acta 692 (2011) 42–49.
[5] M. Balcerzak, E. Swiecicka, E. Balukiewicz, Talanta 48 (1999) 39–47.
[6] J. Chwastowska, W. Skwara, E. Sterlinska, L. Pszonicki, Talanta 64 (2004) 224–229.
[7] Xinhua Zhang, Huifen Li, Yufang Yang, Talanta 42 (1995) 1959–1963.
[8] E. Mladenova, I. Dakova, I. Karadjova, M. Karadjov, Microchem. J. 101 (2012) 59–64.
[9] B. Godlewska-Zytkiewicz, Microchim. Acta 147 (2004) 189–210.
[10] G.V. Myasoedova, O.B. Mokhodoeva, I.V. Kubrakova, Anal. Sci. 23 (2007) 1031–1039.
[11] M.L.A. Castillo, A.G. de Torres, E.V. Alonso, T.S. Cordero, J.M.C. Pavón, Talanta 99 (2012) 853–858.
[12] M. Hidalgo, A. Uheida, V. Salvado, C. Fontas, Solvent Extr. Ion Exch. 24 (2006) 931–942.
[13] R.D. Oleschuk, A. Chow, Talanta 45 (1998) 1235–1245.
[14] R. Shah, S. Devi, Anal. Chim. Acta 341 (1997) 217–224.
[15] B.L. Gong, Y. Wang, Anal. Bioanal. Chem. 372 (2002) 597–600.
[16] Z. Su, Q. Pu, X. Luo, X. Chang, G. Zhan, F. Ren, Talanta 42 (1995) 1127–1133.
[17] A. Parodi, T. Vincent, M. Pilsniak, A.W. Trochimczuk, E. Guibal, Hydrometallurgy 92 (2008) 1–10.
[18] D. Jermakowicz-Bartkowiak, B.N. Kolarz, React. Funct. Polym. 65 (2005) 135–142.
[19] D. Rosenthal, M. Ruta, R. Schlogl, L. Kiwi-Minsker, Carbon 48 (2010) 1835–1843.
[20] K.P. de Jong, J.W. Geus, Catal. Rev. Sci. Eng. 42 (2000) 481–510.
[21] P. Serp, M. Corrias, P. Kalck, Appl. Catal. A 253 (2003) 337–358.
[22] J.H. Zhou, Z.J. Sui, P. Li, D. Chen, Y.C. Dal, W.K. Yuan, Carbon 44 (2006) 3255–3262.
[23] P. Tribolet, L. Kiwi-Minsker, Catal. Today 102 (2005) 15–22.
[24] P. Tribolet, L. Kiwi-Minsker, Catal. Today 105 (2005) 337–343.
[25] K.L. Klein, A.V. Melechko, T.E. McKnight, S.T. Retterer, P.D. Rack, J.D. Fowlkes, D. C. Joy, M.L. Simpson, J. Appl. Phys. 103 (2008) (061301-1-26).
[26] D.K. Seo, J.P. Jeun, H.B. Kim, P.H. Kang, Adv. Mater. Sci. 28 (2011) 31–34.
[27] F.M. Fernandes, R. Araujo, M.F. Proença, C.J.R. Silva, M.C. Paiva, J. Nanosci. Nanotechnol. 7 (2007) 3514–3518.
[28] Y.-H. Li, S. Wang, Z. Luan, J. Ding, C. Xu, D. Wu, Carbon 41 (2003) 1057–1062.
[29] E.A. Moawed, M.F. El-Shahat, Anal. Chim. Acta 788 (2013) 200–207.
[30] E.A. Moawed, N. Burham, M.F. El-Shahat, J. Assoc. Arab Univ. Basic Appl. Sci. 14 (2013) 60–66.
[31] L.C. Zhou, Y.F. Li, X. Bai, G.H. Zhao, J. Hazardous Mater. 167 (2009) 1106–1113.
[32] E.A. Moawed, A.B. Farag, M.F. El-Shahat, J. Saudi Chem. Soc. 17 (2013) 47–52.
[33] S.M. Abdel-Azeem, N.R. Bader, H.M. Kuss, M.F. El-Shahat, Food Chem. 138 (2013) 1641–1647.
[34] S. Jayakumar, P.N. Sudha, Spectrochim. Acta A 105 (2013) 20–23.
[35] E.A. Moawed, Anal. Chim. Acta 580 (2006) 263–270.
[36] M.A. Atieh, Int. J. Environ. Sci. Dev. 2 (2011) 1–4.
[37] H. Sone, B. Fugetsu, S. Tanaka, J. Hazardous Mater. 162 (2009) 423–429.
[38] F. Pashaloo, S. Bazgir, M. Tamizifar, M. Faghihisani, S. Zakerifar, Text. Sci. Tech. J. 3 (2008) 1–10.
[39] A.A.A. Emara, M.A. Tawab, M.A. El-ghamry, M.Z. Elsabee, Carbohydr. Polym. 83 (2011) 192–202.
[40] S. Meškinis, A. Vasiliauskas, K. Slapikas, G. Niaura, R. Juškėnas, M. Andrulevičius, S. Tamulevičius, Diamond Relat. Mater. 40 (2013) 32–37.
[41] E.A. Moawed, A.B. Abulkibash, J. Saudi Chem. Soc. (2012) 1–8, http://dx.doi.org/10.1016/j.jscs.2012.10.011.
[42] E.A. Moawed, J. Taibah Univ. Sci. 7 (2013) 26–34.
[43] C. Namasivayam, D. Sangeetha, R. Gunasekaran, Trans IChemE, Part B: Process Saf. and Environ. Prot. 85 (B2) (2007) 181–184.
[44] A.E. Ofomaja, E.B. Naidoo, Carbohydr. Polym. 82 (2010) 1031–1042.
[45] D. Kavitha, C. Namasivayam, Bioresour. Technol. 98 (2007) 14–21.
[46] J.H.W. Forsythe, R.J. Magee, C.L. Wilson, Talanta 3 (1960) 330–334.
[47] P. Senise, L.M. Pitombo, Talanta 11 (1964) 1185–1191.
[48] O.N. Kononova, A.M. Melnikov, T.V. Borisova, A.S. Krylov, Hydrometallurgy 105 (2011) 341–349.
[49] J. Chwastowska, W. Skwara, E. Sterli´nska, L. Pszonicki, Talanta 64 (2004) 224–229.
[50] O.E. Fayemi, A.S. Ogunlaja, P.F.M. Kempgens, E. Antunes, N. Torto, T. Nyokong, Z.R. Tshentu, Miner. Eng. 53 (2013) 256–265.
[51] F. Ogata, N. Kawasaki, J. Environ. Chem. Eng. 1 (2013) 1013–1019.
[52] A. Uheida, M. Lglesias, C. Fontas, M. Hidalgo, V. Salvado, Y. Zhang, M. Muhammed, J. Colloid Interface Sci. 301 (2006) 402–408.
[53] P. Ramaku, Y. Yanachawakul, N. Leepipatpiboon, N. Sunsandee, Chem. Eng. J. 193–194 (2012) 102–111.
[54] D. Kundu, S.K. Roy, Talanta 39 (1992) 415–418.
[55] E.A. Moawed, Anal. Chem. Indian J. 10 (2011) 93–100.
[56] Z. Marczenko, Spectrophotometric Determination of Elements, 3rd ed., Ellis Horwood, Chichester, 1986.