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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 (~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 ΔG and ΔH 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~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 ($\sim$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 (λ_{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 (ΔpH=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 λ=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):

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

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

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