

Article

Evaluation of Dithiocarbamate-Modified Silica for Cisplatin Removal from Water

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Abstract: Despite the globally increasing use of platinum-based cytostatic drugs in the treatment of several types of cancer, only limited attention has been paid to developing a treatment for contaminated liquid samples originating from hospitals, laboratories and manufacturing facilities before and after their administration. In this work, we assess the efficiency of a low-cost adsorbent material, a dithiocarbamate-functionalized silica, in removing cisplatin from a solution containing it in the 0.5–150 mg L⁻¹ concentration range. The advantage of having a surface-functionalized silica is that adsorption can occur by either non-covalent interaction or surface complexation. In the latter case platinum(II) is de-complexed and the original drug is no longer present. Adsorption occurs through a first rapid step, followed by a second slower process. This is likely due to the fact that in our operating conditions (0.9% w/v NaCl), only the original compound is present, for which ligand substitution is known to proceed slowly. The interesting performance, even at low metal concentration, and facile synthesis of the material mean it could be adapted for other applications where the recycling of platinum can be realized.

Keywords: cisplatin; isotherms; adsorbent materials; water treatment; platinum recycling; calorimetry



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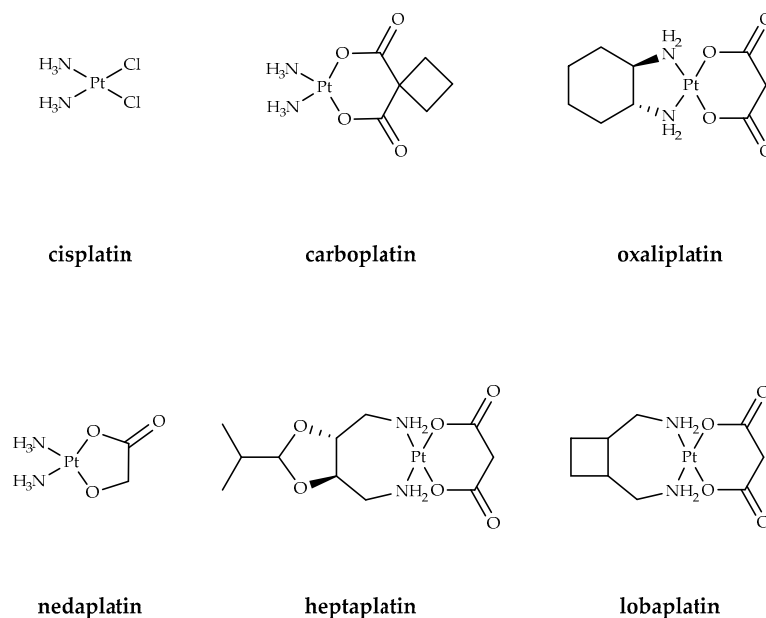
1. Introduction

Cancer is a primary and urgent global public health issue and the second cause of death worldwide [1]. The expected increment in cancer frequency, as suggested by the International Agency for Research on Cancer (IARC) [2], will lead to an increase in the use of cytostatic drugs (CDs) [3].

Among the most commonly used CDs, those based on platinum(II) compounds (Pt-CDs in Scheme 1) are currently employed in the treatment of a variety of cancers. The oldest, but still the most widely used, is cis-diaminodichloroplatinum(II), cis-[Pt(NH₃)₂Cl₂], with nearly 50% of cancer patients treated nowadays with this metal drug [4–6]. The mechanism of action of cisplatin has been widely studied throughout the last decades and it can be subdivided in a four main steps: (1) cellular uptake; (2) activation by the leaving ligands (e.g., chloride anions, in the case of cisplatin) to form aqua-derivatives; (3) DNA binding; and (4) cellular processing of DNA lesions leading to cell death [7–13].

After hospital or home treatment, these compounds are excreted from the body unchanged or as metabolites that pass into the effluents, until they arrive in the sewage system and so the wastewater treatment plant (WWTP) [3,14,15]. It has been demonstrated that Pt-CDs are expelled either as intact drugs or partially metabolized (e.g., as aqua-derivatives) and excreted intact at significant percentages [14]. Other sources of uncontrolled exposure to Pt-CD include manufacturing plants producing the active substances, as well as their

transport and storage and preparation in hospitals [16–19]. For example, several studies have provided evidence for the presence of contamination outside containers used to store and transport CDs (vials, bottles etc.) and in rinse water used for cleaning them [20]. In addition, it has been shown that conventional WWTPs are unable to completely remove Pt-CD, leading to trace levels of contamination in rivers and seas [21].



Scheme 1. Clinically approved platinum(II) cytostatic drugs.

Several studies have shown that in the environment the total Pt concentration deriving from Pt-CD release is quite low [14,22–26], ranging from a few tens to a few hundred $\mu\text{g L}^{-1}$ [27]. Nevertheless, it has been suggested that long-term exposure low levels of CDs is potentially harmful for living organisms [28–30].

Keeping this in mind, along with the expected increase in the use of CDs in the coming years, it is clear that efficient and economically convenient methods for removing these compounds from WW and other contaminated liquid samples are needed. In addition, it could be useful to improve prediction accuracy using more advanced models for the assessment of these pollutants' dynamic evolution in water [31].

Among the removal methods proposed to treat water specifically contaminated by platinum-based cytostatic membrane bioreactors (MBRs), advanced oxidation processes (AOP) and adsorption have been assessed [27]. Adsorption has been widely used for the removal of contaminants in water, as it is a low-cost option which can be easily integrated in existing WWTP, it can reach a high selectivity and affinity for target pollutants, and it can be coupled with other degradation methods as a pre-concentration stage [9,27,32,33].

In the case of sorption of platinum compounds, synthetic sorbents have been used such as modified chitosan nanoparticles [34], chitosan hydrogels [35], activated carbon modified with biopolymer [36], graphene oxide copolymer/polypyrrole-polythiophene with Fe₃O₄ and silica-coated [37], PEI/PVC-CF polymer [38], superparamagnetic nanoparticles functionalized with 3-mercaptopropionic acid [39], magnetic porous organic polymers [40], magnetic cellulose functionalized with quaternary amine [41] and macroporous cryogels [42].

Silica gel is a commercially available material with controlled qualities and lower cost with respect to the above adsorbents [43]. It displays excellent chemical stability in various media and in different reaction conditions, has a high surface area, and is also hydrophobic with high thermal and mechanical robustness [44]. Due to those properties, silica materials are widely applied in the removal of inorganic [45–49] and organic pollutants [50–52].

Several studies have reported the use of silica gel modified by chemical treatments in the sorption of metals including Hg(II) [53]; Pb(II), Cd(II) and Cu(II) [54]; Zn (II) [55]; and Pt(IV) [56]. Amine-functionalized silicas are currently applied as low-cost materials for heavy metal scavenging from solutions [47–49]. However, adsorbents which have only polyamines as their functional group present some disadvantages, such as low selectivity and efficiency at low pH. Ligands containing dithiocarbamate groups have shown good performance as strong chelating agents for numerous metal ions, such as Co(II) [46], platinum group metals [56,57], Hg(II) [58], and others [54].

The ability of dithiocarbamate to strongly bind to most metal ions makes them a useful candidate for removing Pt-CD from contaminated aqueous samples deriving from work environments and for treating hospital WW or contaminated rinse water.

Previously [59], cryogels prepared to specifically target cisplatin have been shown to have very good performance and reusability. However, they are relatively more complicated to prepare and also their performance was studied in a concentration range (0.25–2 mg mL⁻¹) much higher than that found in real samples.

In the present work, dithiocarbamate-modified silica gel (Si-DTC) has been prepared and characterized and then employed for the removal of cisplatin from aqueous solutions in a wide range of concentrations (0.5–300 ppm). The effects of sorbent dose, solution pH, initial volume and contact time on the sorption process of this class of sorbent were studied. The results showed that Si-DTC is suitable for the decontamination of water from cisplatin.

A specific advantage over non-specific sorbent materials (e.g., activated sludge, carbon-based materials, etc.) in this case is that adsorption can occur through several mechanisms including the surface complexation of platinum ions. The latter mechanism implies that the ligands of the platinum complex are replaced by the dithiocarbamate and therefore the drug is totally or partially degraded upon adsorption. To the best of our knowledge, this work is the first study of the direct removal of cisplatin using a low-cost selective adsorbent material which can be produced in bulk quantities.

2. Materials and Methods

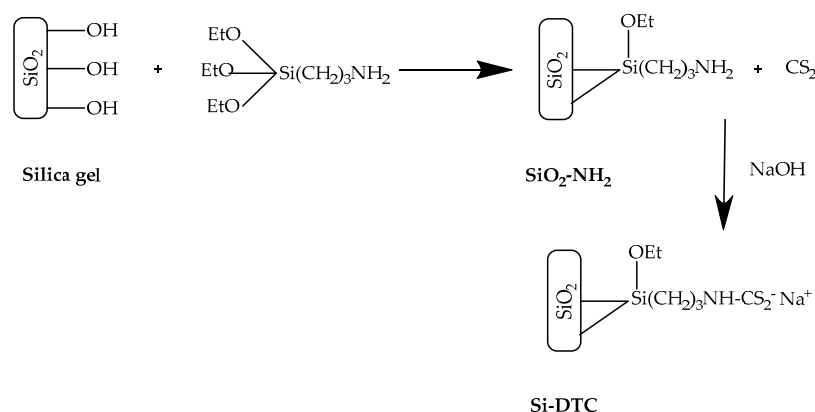
2.1. Chemicals

Silica gel 60 (ASTM Fluka, Darmstadt, Germany) was used. It was activated by drying at 120 °C in an oven for 24 h before silylation. Cisplatin (Shandong Boyuan Pharmaceutical, Jinan, China), 3-aminopropyltriethoxysilane (Sigma-Aldrich, Darmstadt, Germany), carbon disulfide (Sigma-Aldrich, Germany) and other solvents for preparation and analytical procedures were used without further purification.

All cisplatin solutions were prepared in ultrapure water with 0.9% *w/v* NaCl. In these conditions, the release of chloride ligands is suppressed and cisplatin is the sole species present in solution [60].

2.2. Material Preparation and Characterization

The modification of silica gel with dithiocarbamate was carried out following the procedure reported in literature [46]. The silica gel (20 g), toluene (108 mL) and γ -aminopropyltriethoxysilane (12.5 mL) were refluxed for 6 h. The mixture was afterwards filtered and washed with toluene, isopropanol, acetone, methanol and air-dried at room temperature in order to obtain the intermediate (3-aminopropyl)silyldiyne silica gel (SiO₂-NH₂). The obtained white-colored intermediate was then mixed with 100 mL of 0.1 M sodium hydroxide solution, 20 mL of isopropanol, and 16 mL of carbon disulfide then stirred for 4 h. The mixture was then filtered, washed with isopropanol, and air-dried at room temperature in order to give the yellowish-orange-colored final product. The reaction scheme is represented in Scheme 2.



Scheme 2. The synthesis procedure of Si-DTC.

The achievement of the surface functionalization of the material was checked by recording FT-IR spectra, which were collected in transmission mode on a Thermo Scientific, Nicolet™ iS-50 FT-IR Spectrometer from 400 to 4000 cm^{-1} . Thermogravimetric analysis (TGA) was performed by means of a TA Instruments Thermogravimetric Analyzer, TGA Q500. Typically, 15 mg of the samples was heated up to 760 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C min}^{-1}$, under a nitrogen atmosphere.

The point of zero charge (PZC) values were determined using a computer-controlled potentiometer (Amel Instruments, 338 pH Meter) connected to a combined glass electrode (Metrohm Unitrode 6.0259.100) as described in the method from the literature [61]. Suspensions of sorbent material 25 g/L were put into contact with a 0.03 M KNO_3 solution. The mixture was agitated for 24 h until the pH, which ranged from 2–10, remained constant. The pH of the remaining solution was then measured. Equilibrium pH values were plotted as a function of acid volume added to obtain the potentiometric curves. The pH of the PZC was identified as the intersection point of the potentiometric curves with the blank.

2.3. Determination of Platinum

Various analytical techniques have been reported for the determination of cisplatin, such as ICP-OES [62] and ICP-MS [63], both of which have high sensitivity; however, the use of UV-Vis spectrometry is a less expensive, simple, and easily accessible method.

The quantitative analysis of total platinum present was carried out by means of a spectrophotometric technique which modified previous methods for the determination of total Pt based on the reaction with the diethyldithiocarbamate (DDTC) anion [64,65]. Cisplatin can be quantified in solution directly by recording the absorption band at $\lambda = 300 \text{ nm}$ (calibration in Figure S1); however, the molar extinction coefficient limits the detectable concentrations [59]. On the other hand, DDTC reacts quantitatively with cisplatin, displacing the ligands to form a $\text{Pt}(\text{DDTC})_2$ complex [64,66] which is poorly soluble in water, but can be easily extracted in an organic solvent such as chloroform or dichloromethane, after which it presents a strong absorption band at $\lambda = 347 \text{ nm}$ [65]. In the present study, cisplatin solutions were prepared from a 1000 ppm stock solution in NaCl (0.9%). The samples were prepared in Falcon© tubes (total volume 50 mL) with a 1 mL of 10% (w/v) solution of DDTC prepared in 0.1 N sodium hydroxide solution for each falcon. After that, 30 mL of McIlvaine buffer and 5 mL of dichloromethane were added to each tube. The tubes were vigorously shaken for 24 h and allowed to stand at room temperature for 1 h before filtration (0.2 μm pore size). The extracted platinum ($\text{Pt}(\text{DDTC})_2$) was determined using a Varian Cary 50 spectrophotometer. Calibration curves calculated after extracting cisplatin in aqueous solutions in the 0.5–5 ppm range (Figure S2) showed total recovery in the organic phase and excellent linearity, with a limit of detection (LOD) of 0.5 ppm. All measurements were repeated in order to test their reproducibility, which was found to be around 95%.

2.4. Effect of pH

The effect of initial pH on sorption was investigated in the pH range 2–12. The pH was adjusted using concentrations of roughly 0.1 M HCl and 0.1 M NaOH. Then, 0.075 g of adsorbent samples were added to 15 mL of cisplatin solution with concentration 5 mg L⁻¹. The mixtures were mixed at constant temperature (25 °C) for 60 min.

2.5. Adsorption Kinetics

The sorption of cisplatin on the sorbent was studied as a function of shaking time, at different time intervals ranging from 3 to 120 min, at 25 °C. A sample of 15 mL of cisplatin (5 mg L⁻¹) solution at pH 6 was shaken with 75 mg of Si-DTC adsorbent.

Pseudo-first-order and pseudo-second-order kinetic models were tested in this study where the experimental data obtained for various contact times were used.

2.6. Effect of Sorbent Dose

The effect of the amount of Si-DTC on the sorption of cisplatin was studied. In order to identify the optimum adsorbent dose, 0.015, 0.03, 0.045, 0.075, 0.09, and 0.15 g of sorbent were added to six vials containing 15 mL of 5 mg L⁻¹ of cisplatin solution at pH 6. The mixtures were stirred at constant temperature (25 °C) for 60 min. The absorbance of Pt-(DDTC)₂ complex was measured by UV-visible after its extraction with dichloromethane.

2.7. Adsorption Isotherms

The adsorption isotherms was studied for comparison using functionalized (Si-DTC) and untreated material for comparison. The initial concentrations of cisplatin ranged from 5–300 mg L⁻¹ in 15 mL samples. In these experiments the sorbent mass employed was 30 mg (2 mg mL⁻¹) and the contact time 60 min at pH 6. Equilibrium data were fitted with the Langmuir and Freundlich adsorption isotherms by using MSeExcel solver and the Solverstat tool [67,68] for the statistical analysis.

2.8. Isothermal Titration Calorimetry

The calorimetric study of adsorption was carried out with a TAMIII isothermal microcalorimeter (TA Instruments) in a similar setup described in previous works [39,45,53,69]. The titration cell was filled with 3.0 mL of NaCl (0.9% w/v) solution in which 0.01 g of Si-DTC was dispersed. The suspension was stirred continuously at 50 rpm. The adsorption heat was recorded by adding in a single addition (250 µL) of cisplatin solution (5 mg L⁻¹) using a computer-controlled Hamilton syringe. The reference cell was filled with 3.12 mL of NaCl (0.9% w/v) solution. The adsorbed quantity of cisplatin was determined by analyzing the solution in the cell at the end of the experiment, using method described in Section 3.2. Then, the ΔH_{ads} (kJ mol⁻¹) was calculated by dividing the experimental heat by the adsorbed moles of cisplatin.

2.9. Desorption Experiments

After separating the material from the cisplatin solution, the elution solutions were passed through the wet material by gravity filtration. Platinum desorption experiments were performed by adding 10 mL of different solutions with a concentration of 0.1 M HCl, 0.1 M HNO₃ (Sigma-Aldrich), or NaCl (0.1 M) solution in acetic acid/sodium acetate buffer (pH of 3.5) to the material after the sorption process. All cisplatin determinations were performed using the extraction-photometric method described in literature, performing the extraction in dichloromethane and measuring the absorbance at $\lambda = 347$ nm [65].

3. Results and Discussion

3.1. Characterization of the Material

The synthesis of DDTC-functionalized silica was performed by means of a two-step synthesis (Scheme 2). In Figure 1 the FTIR spectra of the starting silica gel, the intermediate product (3-aminopropyl)silyldiyne silica (SiO₂-NH₂), and the final Si-DTC are shown.

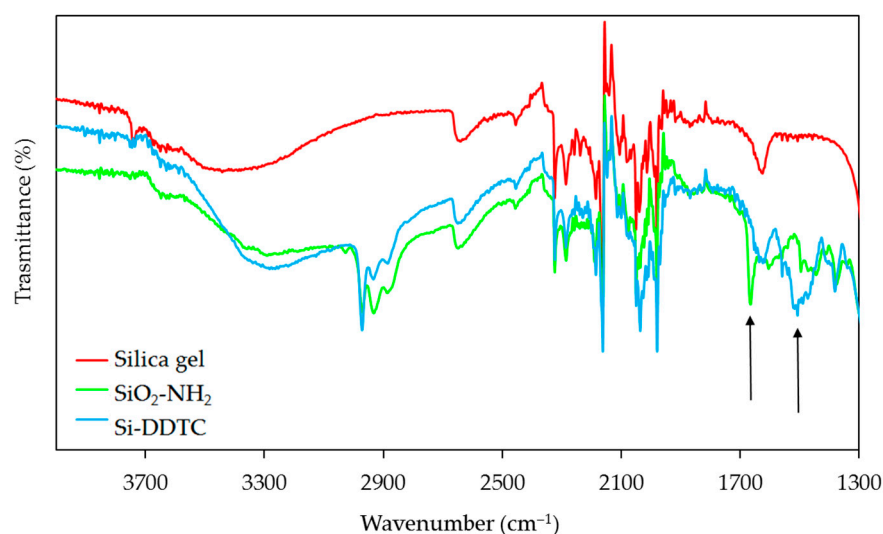


Figure 1. FT-IR spectra of: (red) silica gel, (green) $\text{SiO}_2\text{-NH}_2$, and (blue) Si-DTC. The arrows at 1663 cm^{-1} and 1507 cm^{-1} indicate the NH_2 and N-CS_2 vibration of the $\text{SiO}_2\text{-NH}_2$ and Si-DTC, respectively.

As shown in Figure 1, the appearance of a new band in the region of $3290\text{--}3000\text{ cm}^{-1}$, characteristic of the stretching vibration of the NH_2 group, confirms the aminopropylation of the silica support. The same band is present in Si-DTC, indicating that it is also supported by the stretching and bending vibration modes of aliphatic -CH_2 groups appearing at 2970 , 2931 , 2884 , 1454 , and 1378 cm^{-1} , respectively. The -NH_2 bending vibration of $\text{SiO}_2\text{-NH}_2$ emerges at 1663 cm^{-1} . In the FTIR spectrum of Si-DTC (Figure 1), the stretching and bending vibrations of the -NH_2 group disappear because of dithiocarbamate group formation by the reaction of carbon disulfide with $\text{SiO}_2\text{-NH}_2$. The adsorption peak at 1507 cm^{-1} is attributed to N-CS_2 vibration [54]. Other peaks around 1165 and 653 cm^{-1} were obscured by the strong absorption peaks of the silica gel matrix at 1100 , 790 , and 450 cm^{-1} .

The thermogravimetric analysis (Figure 2) of the intermediate product, $\text{SiO}_2\text{-NH}_2$ shows a final mass loss of 13% that could be assigned to the decomposition of the surface groups. For the intermediate product, a mass loss is occurring from 300 to $500\text{ }^\circ\text{C}$, which could be associated with the decomposition of the NH_2 and CH_2 groups [70]. The final product, Si-DTC, showed an overall loss of mass of 15% which confirms the successful functionalization of the material.

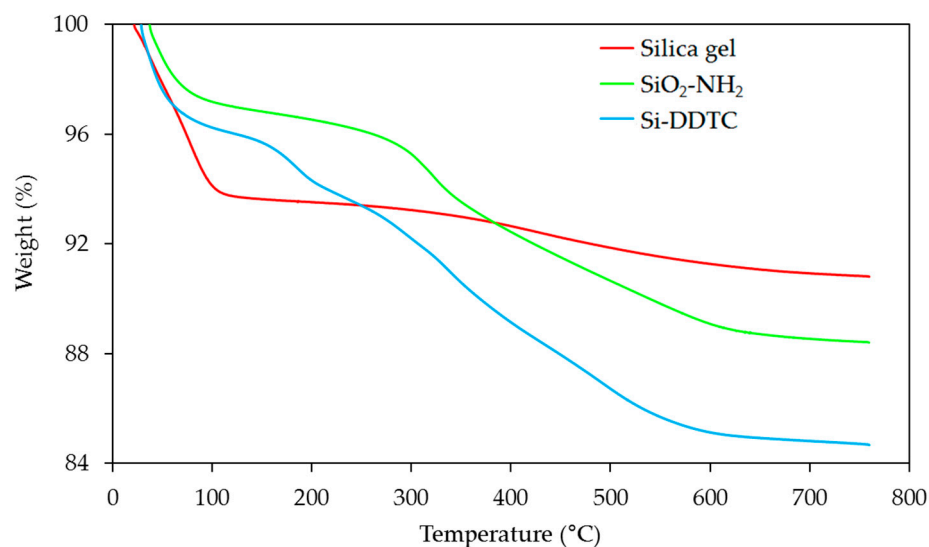


Figure 2. TGA curves of: (red) silica gel, (green) $\text{SiO}_2\text{-NH}_2$, and (blue) Si-DTC.

The PZC for silica gel was 6.0; for the Si-DTC a pH = 8.6 was obtained (Figure 3).

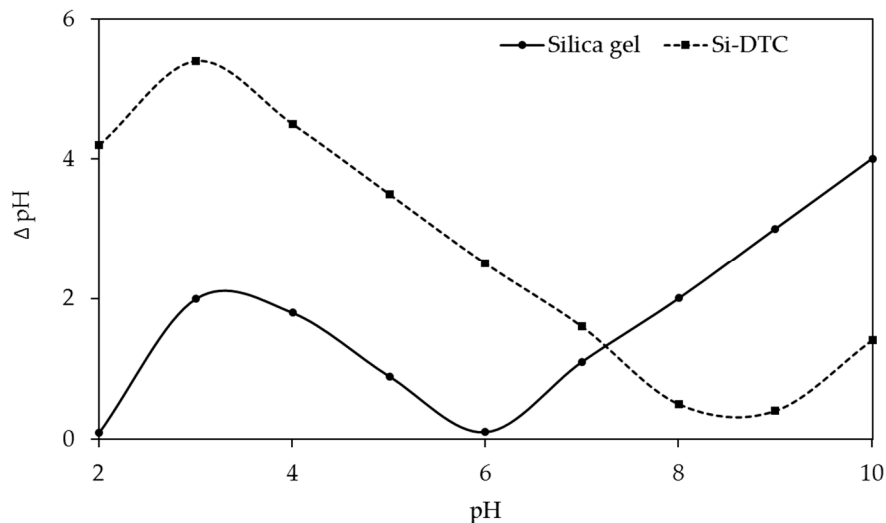


Figure 3. Determination of pH PZC.

3.2. Cisplatin Adsorption

The amount of cisplatin sorbed on Si-DTC (q) and the percentage removal ($R\%$) were calculated using Equations (1) and (2), respectively:

$$q = \frac{(C_0 - C_e) \cdot V}{M} \quad (1)$$

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (2)$$

where, q is adsorption capacity (mg g^{-1}) and C_0 and C_e are the initial and equilibrium concentrations (mg L^{-1}) of cisplatin in solution. V is the volume of the aqueous solution (L) and M is the mass of sorbent used (g).

To optimize adsorption conditions, the liquid samples were put in contact with the sorbent material for durations ranging from 10 to 120 min (Figure 4).

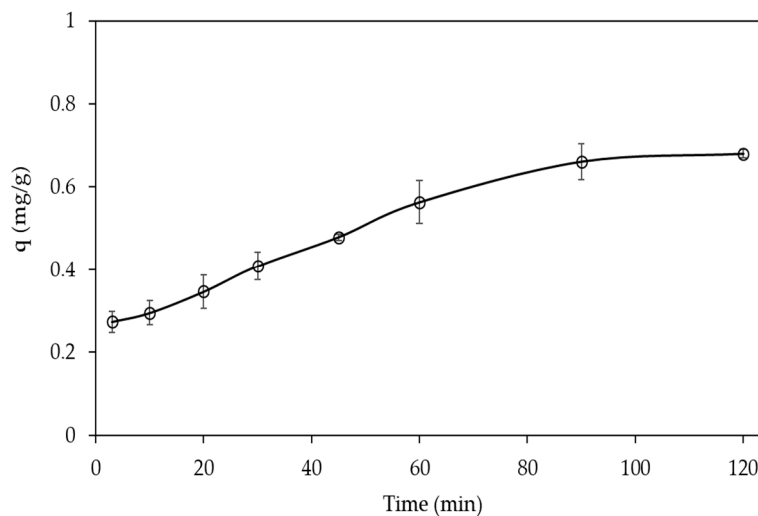


Figure 4. Mass of adsorbed cisplatin (mg)/mass of adsorbent (g) vs. contact time.

Cisplatin removal increases with contact time up to the limit value of 0.68 mg g^{-1} (q_e) at equilibrium. After a rapid initial uptake in the first 10 min, adsorption proceeds slowly reaching almost a constant value [71]. As the replacement of cisplatin ligands is a quite

slow reaction [60,72] this behavior could be assigned to a first rapid adsorption equilibrium governed by non-covalent interactions with the material surface, followed by a slower step associated with the formation of the surface complex through covalent bonding. In previous studies, Si-DTC has been shown to be much faster in adsorbing several metal ions, reaching equilibrium at ~10 min [54], probably because in that case the aqua-ions are the reactive species and the ligand replacement in surface complexation is much faster.

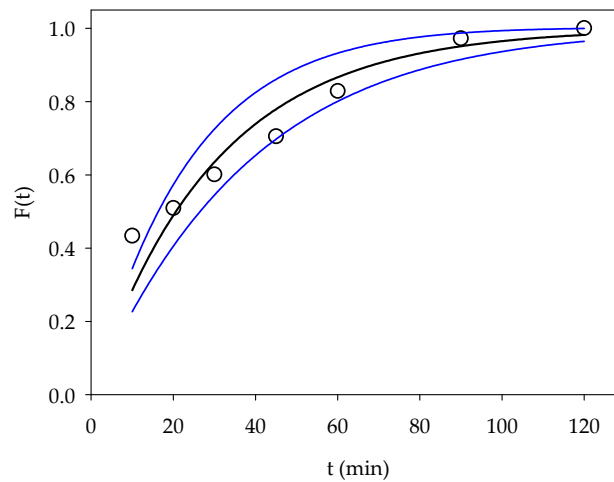
Experimental data were fitted using the pseudo-first-order [73] and pseudo-second-order [74,75] kinetic models, as defined by Equations (3) and (4), respectively:

$$F(t) = 1 - \exp(-K_1 t) \quad (3)$$

$$F(t) = \frac{q_e K_2 t}{1 + q_e K_2 t} \quad (4)$$

where the fraction uptake $F(t) = q_t/q_e$ is fitted, as the two models should be assessed for their ability to describe the same quantity to provide a more reliable analysis, as discussed in previous works [76–78]. The q_e value employed in the data analysis (0.68 mg/g) was obtained when equilibrium was reached. In Figure 5 the experimental and calculated kinetic data are shown and the fitted parameters reported in Table 1. The results show that the pseudo first order kinetic model fits slightly better the experimental data (Table 1).

(a)



(b)

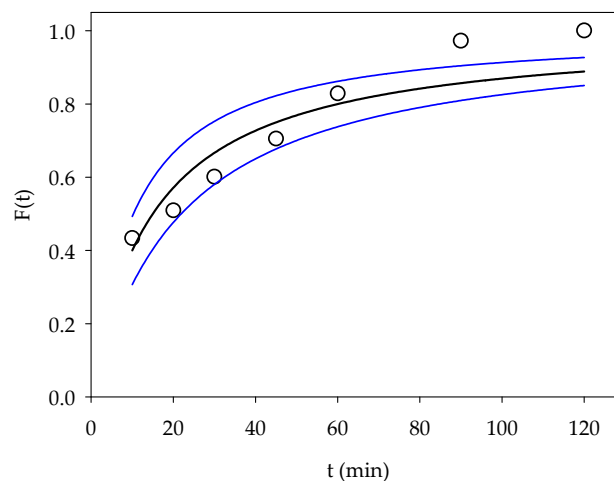


Figure 5. (a) Pseudo-first-order and (b) pseudo-second-order fitting of the fractional adsorption $F(t) = q_t/q_e$ (empty circles) data. Lines: calculated data (black), 95% confidence interval (blue).

Table 1. Pseudo-first-order and pseudo-second-order kinetic parameters K_1 (min^{-1}) and K_2 ($\text{g mg}^{-1} \text{min}^{-1}$) for cisplatin sorption on Si-DTC at 25 °C.

Pseudo-First Order		Pseudo-Second Order	
K1	R2	K2	R2
0.0336 ± 0.0034	0.894	0.098 ± 0.018	0.871

The pH of the aqueous solution is an important parameter in the whole sorption process, because it affects the surface charge of the sorbent and the degree of dissociation of functional groups carried by the sorbent [79]. As can be seen in Figure 6, there was higher removal above pH = 3, as obtained previously for the adsorption of metal ions [54]. Lower values are found at the lowest and highest pH: this could be related to the instability of dithiocarbamate compounds at acidic pHs [54] and to the formation of less reactive hydroxy-derivatives of cisplatin in basic conditions [80].

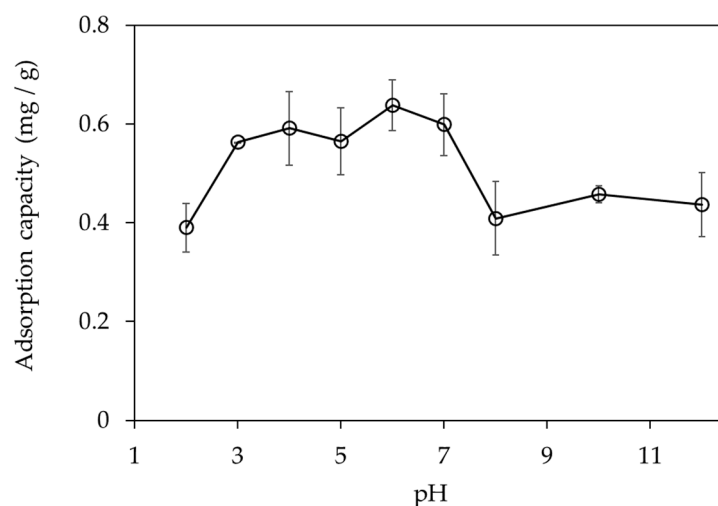


Figure 6. Effect of pH on removal of cisplatin by Si-DTC.

To evaluate the effect of sorbent dose (mass/volume ratio) on the sorption of cisplatin, equilibrium experiments were carried out by dispersing 15–150 mg of Si-DTC in 15 mL of NaCl (0.9%) ($1\text{--}10 \text{ mg mL}^{-1}$). The removal of cisplatin reached 85% at 10 mg mL^{-1} (Figure 7); however, it should be noted that even at 2 mg mL^{-1} a removal level of 68% was achieved.

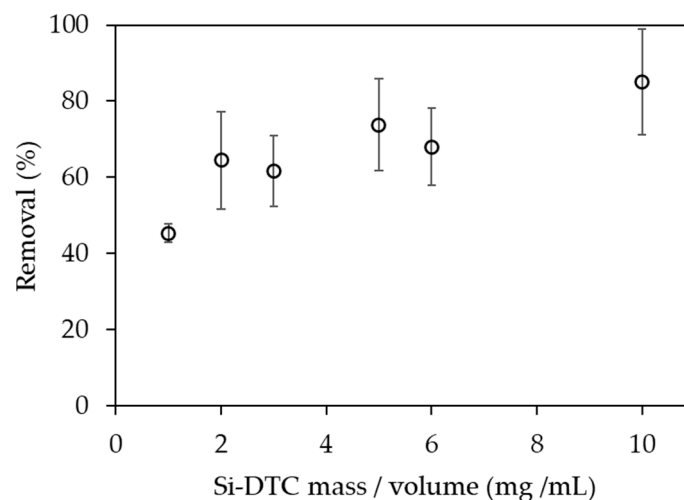


Figure 7. Effect of Si-DTC mass presented as % of removal.

The mass/volume ratio was changed by increasing the initial volume. Figure S3 shows that the removal of cisplatin dropped from 70% to 10% below 2 mg/mL.

3.3. Adsorption Isotherms

Equilibrium adsorption studies in conditions optimized for adsorption isotherms of cisplatin on silica were performed before and after DDTC functionalization. The graph of sorption capacity vs. initial concentration is shown in Figure 8a.

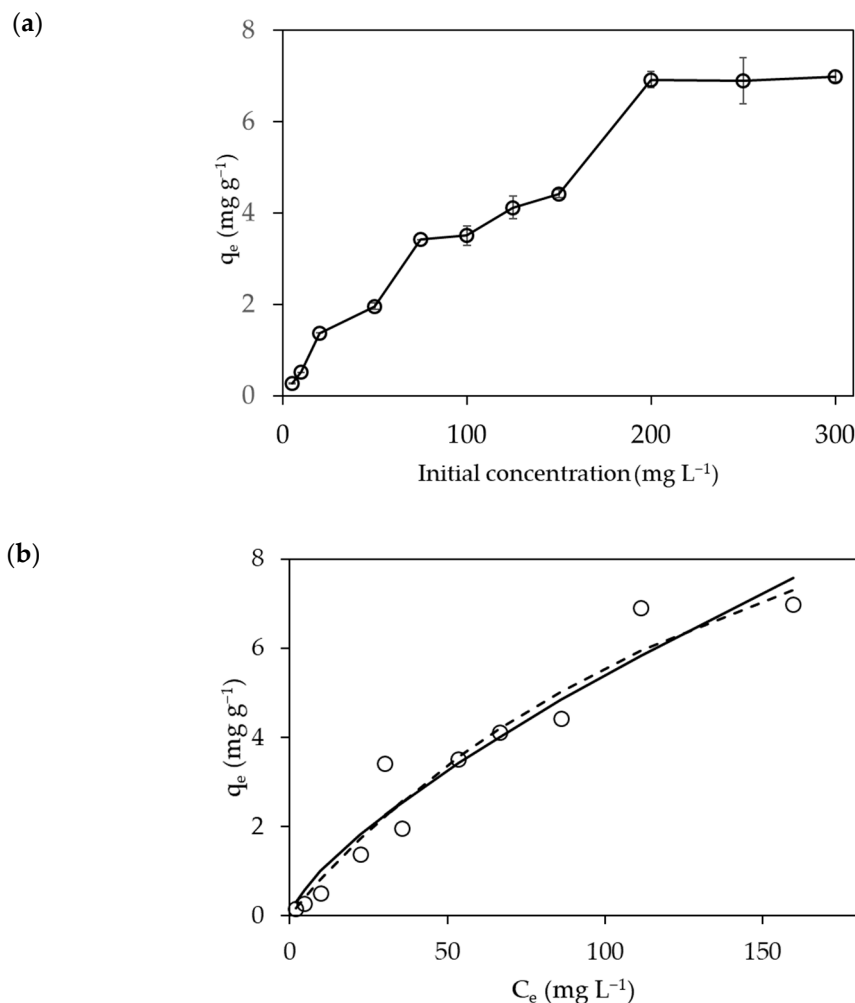


Figure 8. (a) Total adsorbed cisplatin vs. initial concentration of Si-DTC. (b) Adsorption isotherm plot calculated with Langmuir (solid line) and Freundlich (dashed line) models.

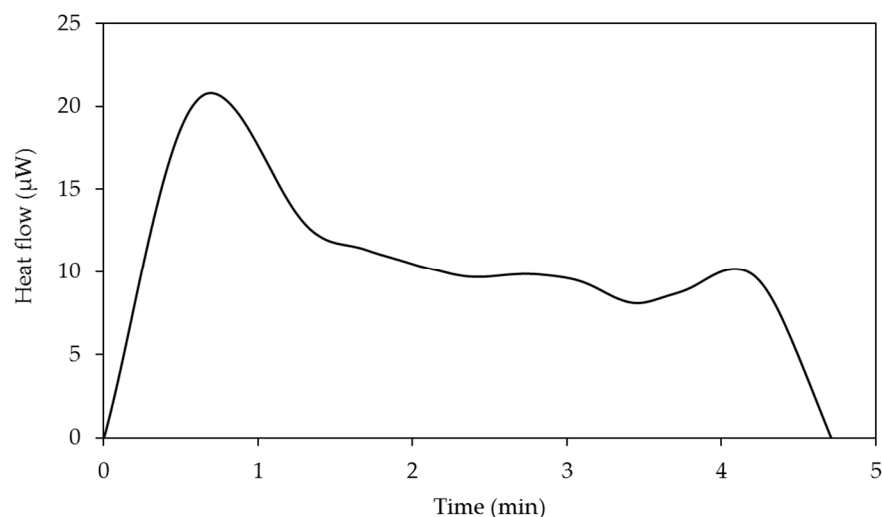
Equilibrium data were fitted using the Freundlich and Langmuir isotherm models (Table S1) [81,82]. Both models gave a good fit (Figure 8b), although the Langmuir isotherm gave a slightly better performance (Table 2). The obtained maximum loading was $15.6 \pm 4.7 \text{ mg g}^{-1}$ of cisplatin. This value is much lower than the 150 mg g^{-1} reported by Farias et al. [59], who employed cryogels to recover cisplatin. However, in that case the conditions were quite different, with much longer equilibration times (up to 48 h) and higher starting cisplatin concentration ($250\text{--}2000 \text{ mg L}^{-1}$). Lastly, the target species were different, as in [59] the stock solutions were prepared in pure water (i.e., in the absence of chloride) and thus a mixture of aqua-species was likely to be present.

Table 2. Parameters of the Langmuir and Freundlich models.

		Value	R ²
Langmuir	K _L (L mg ⁻¹)	0.0055 ± 0.0025	0.944
	b (mg g ⁻¹)	15.6 ± 4.7	
Freundlich	K _F (mg g ^{-1/n})	0.19 ± 0.08	0.935
	n	1.38 ± 0.17	

3.4. Calorimetric Study

The measured heat flow in the calorimeter upon addition of a solution of cisplatin, associated with the adsorption experiment of Si-DTC suspensions, is shown in Figure 9. The positive sign in the thermogram corresponds to an exothermic process. The enthalpy of adsorption (ΔH_{ads}), obtained by dividing the area of the peak in Figure 9 by the moles of adsorbed cisplatin, was -25.8 ± 0.1 kJ mol⁻¹. This value is similar to those previously obtained for the adsorption of metal ions by complexation on surface-modified materials [39,53].

**Figure 9.** Thermogram of the adsorption calorimetric experiment (positive sign: exothermic).

3.5. Study of Desorption of Platinum from Si-DTC

Recycling the adsorbed platinum could be useful from an economic point of view and open the road to new applications of the Si-DTC material. Therefore, desorption experiments were carried out in various media to find out the most effective solution for removing cisplatin from Si-DTC. A solution with cisplatin and Si-DTC was washed with various solutions, specifically, 0.1 M and 0.5 M HCl, 0.1 M HNO₃ and 0.1 M NaCl in acetate buffer. The recovery percentages of cisplatin for each condition studied are presented in Table 3.

Table 3. Percentage of total platinum recovery by desorption.

Condition	Concentration (M)	Recovery %
HCl	0.1	60 ± 2
	0.5	42 ± 5
HNO ₃	0.1	48 ± 10
NaCl-acetate buffer	0.1	47 ± 0.1

The desorption experiment began with strong acids such as hydrochloric or nitric acid, which have been widely studied in the literature to recover platinum species [83]. First, an experiment was carried out at a concentration of 0.1 M for both acids. A better percentage of

desorption (recovery) occurred with HCl (60%). This percentage is comparable with results obtained by other authors under similar conditions [48]. Another procedure employed NaCl (0.1 M) in HAc/NaAc buffer medium at pH 3.5, as reported in the literature [59]. However, recovery was lower than with HCl (0.1 M).

4. Conclusions

In this paper, dithiocarbamate-modified silica gel was synthesized as a new cisplatin sorbent in a two-step process and tested. FT-IR and TGA results confirmed that the dithiocarbamate units were immobilized onto the surface of the modified silica gel. The functionalized silica gel was thus shown to be an effective and promising sorbent for the removal of cisplatin from aqueous solutions. The effect of various parameters such as sorbent dose, solution pH, initial volume, and contact time on the sorption process were investigated. Based on the results, the maximum removal of cisplatin by Si-DTC sorbent was obtained at pH 6 with an adsorbent mass/volume ratio of 2 mg mL^{-1} . The kinetics of adsorption are characterized by a rapid initial step followed by slow increase. The kinetic study showed that the adsorption fitted well with the pseudo-first-order kinetic model. This is likely related to the slow ligand substitution in cisplatin [72]. Both the Freundlich and Langmuir isotherms modeled the experimental data with satisfactory accuracy, with the latter producing a slightly better fit. The maximum loading value determined by the Langmuir fit for Si-DTC results was 15.6 mg g^{-1} at $25 \text{ }^\circ\text{C}$. This value is lower than that previously found for cryogel adsorbents [59], but we should take into consideration the fact that the adsorption conditions (contact time, initial concentration, preparation of the solution containing cisplatin) were very different.

Isothermal titration calorimetry indicated that the adsorption process was weakly exothermic, thus it is favored at low temperatures. In addition, a good recovery of platinum was achieved with a single treatment using a strong acid.

Overall, this study demonstrated that a low-cost material, Si-DTC, specifically designed to target platinum can be employed to remove cisplatin from contaminated aqueous samples with good performance and at a low initial concentration (0.5 mg L^{-1}). As the adsorption appears to occur through surface metal complexation, the original pharmaceutical drug is degraded (i.e., the cisplatin ligands are lost) and thus no longer active. This work opens the way to the further and larger-scale development of a low-cost material which can bind to platinum and thus be used for decontaminating aqueous solutions polluted with cisplatin, with the added advantage of the ability to recover precious metals from a generic liquid sample.

Supplementary Materials: The supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr11020472/s1>, Figure S1: Calibration curve for the determination of cisplatin concentration in water (NaCl 0.9% *w/v*). Absorbance was measured at $\lambda = 300 \text{ nm}$; Figure S2: Calibration curve for the Pt(DDTC)₂ complex determined in dichloromethane. Absorbance was measured at $\lambda = 347 \text{ nm}$; Figure S3: Effect of volume variation at constant mass on adsorption capacity; Table S1: Formulas of the isotherm models employed in this work.

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