Recovery of Platinum Complexes from Chloride Solutions Using Oxidized Carbon Sorbents

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Abstract

Sorption of platinum chloro complexes from solutions with the help of oxidized carbon sorbents was studied. An effect of the oxygenated surface functional groups of oxidized carbon sorbents on their sorption capacity was studied using IR spectroscopy, pH-metry, titrimetry. Sorption isotherms for H_2PtCl_6 and H_2PtCl_4 were obtained. It was established that the capacity of the sorbent with respect to H_2PtCl_6 increased by a factor of 2.4.

Key words: recovery of platinum group metals, surface functional groups, sorption, solutions of H_2PtCl_6 and H_2PtCl_4, oxidized carbon sorbents

INTRODUCTION

In connection with the fact that the consumption of platinum group metals (PGM) is increasing every year, repeated involving them in manufacturing is required. The refining of platinum group metals with the use of hydrometallurgical methods requires for obtaining a great amount of waste and cleansing platinum chloride solutions with the content of PGMs ranging from 20 to 2000 mg/L, at different stages of the process. Extracting the PGM from the refining solutions is carried out using sorption methods [1].

Carbon sorbents are used in different processes for filtering gases and fluids in the manufacture of catalysts in medicine. Furthermore, they are used for extracting PGM from technological solutions. At the same time, despite a lot of papers concerning the extraction of PGM from solutions by means of carbon sorbents [2–6], there are no accurate data in the literature indicating any influence of textural and chemical properties of these materials upon the mentioned process.

The modification of carbon sorbents allows one purposefully changing their properties. One of the ways to modify them consists in the process of oxidation. Earlier it was demonstrated that oxidation of activated carbon by atmospheric oxygen results in an increase in the sorption capacity of these materials [7, 8]. In this connection, it is interesting to know what changing properties and characteristics of carbon sorbents would affect their absorption capacity with respect to the PGM.

The aim of the present work consisted in extracting chloro complexes of platinum (II, IV) by oxidized carbon sorbents from platinum chloride solutions.

EXPERIMENTAL

In this study we used carbon material(CM) "Tekhnosorb" obtained *via* a procedure described in [9]. An average CM particle size amounted to 0.7–1.5 mm. In a similar way as in [10] we obtained samples CM-250, CM-350, CM-450, CM-500, CM-550 at temperatures of oxidation equal to 250, 350, 450, 500, 550 °C,

TABLE 1

Texture and absorption characteristics of oxidized CM samples

T, °C	A_{BET}, m²/g ($n = 8$)	ΣV, cm³/g	pH	SEC, mg-eq/g (for 0.1 M NaOH)	SEC, µg-eq/m² (for 0.1 M NaOH)	−COOH, mg-eq/g	SC, mg/g ($C_{init} = 0.02$ M)	
							Pt(II)	Pt(IV)
CM (init.)	408±4	0.147	8.9±0.4	0.65±0.01	1.575±0.1	0.42±0.02	11.5±0.8	38.7±1.1
250	410±4	0.714	8.3±0.4	0.65±0.01	1.57±0.1	0.70±0.02	9.4±1.3	50.1±0.9
350	420±5	0.729	7.5±0.5	0.66±0.01	1.61±0.2	0.72±0.02	7.6±1.2	67.2±1.3
450	422±4	0.787	5.7±0.4	0.85±0.02	2.0±0.2	0.80±0.02	6.6±0.9	95.4±1.7
500	423±4	0.884	5.6±0.4	0.8±0.03	1.87±0.2	0.77±0.02	6.4±1.1	93.3±1.9
550	424±5	1.051	5.5±0.5	0.78±0.02	1.85±0.1	0.75±0.02	6.1±1.4	90.2±0.7

Notes. ΣV is total pore volume, cm³/g; A_{BET} is specific surface area m²/g; SEC is static exchange capacity for 0.1 M NaOH solution, calculated for specific CM surface area, µg/m²; pH is the water extract pH; SC is static capacity with respect to Pt(II) and Pt(IV), mg/g.

respectively. The texture characteristics of the samples were determined using ASAP 2400 automatic volumetric adsorption unit (Micromeritics, the USA) and Sorbtometr-M specific surface area analyzer.

The specific surface area and A_{BET} and the total pore volume ΣV were calculated from the adsorption isotherms according to [11, 12]. The static exchange capacity (SEC) was determined using 0.1 M NaOH solution according to Russian Standard GOST 20255−74.

Since in the course of the CM oxidation the CM surface increased, it was necessary to determine the cause of SEC growth: whether increasing the surface containing surface functional groups (SFG), or increasing the number of the SFG on the unit surface. For this purpose, the SEC was calculated per 1 m².

The IR spectra of the initial and oxidized CM samples were registered using Scimitar FTS 2000 FTIR spectrometer within the range of 400−4000 cm⁻¹. Changing in the pH of the aqueous extract was measured by means of the method described in [13]. The amount of SFG was determined by means of titrimetric method [13−17].

The experiments on the sorption of platinum onto oxidized carbon sorbents were carried out under static conditions at the temperature equal to 20 °C. The H_2PtCl_6 and H_2PtCl_4 solution concentration were varied within the range from 10^{-4} to 10^{-2} mol/L. The component ratio CM/solution = 1 g : 50 mL. The concentration of platinum in the initial and final solutions was determined spectrophotometrically [18] with the use of $SnCl_2$.

RESULTS AND DISCUSSION

The results concerning the texture and sorption characteristics of oxidized samples are presented in Table 1. It can be seen that the oxidation causes an increase in the sorbent surface area and total pore volume due to the removal of a less dense part of the carbon matrix and a partial gasification. Furthermore, the free pore volume determined from decane absorption exhibits a maximum value at 450 °C.

The oxidation results also in changing the pH value of the aqueous extract from pH 8.9 to pH 5.5 for the sample oxidized at 450 °C. This indicates changing the ion-exchange properties of the carbon sorbent, which is consistent with the data presented in [19], and with
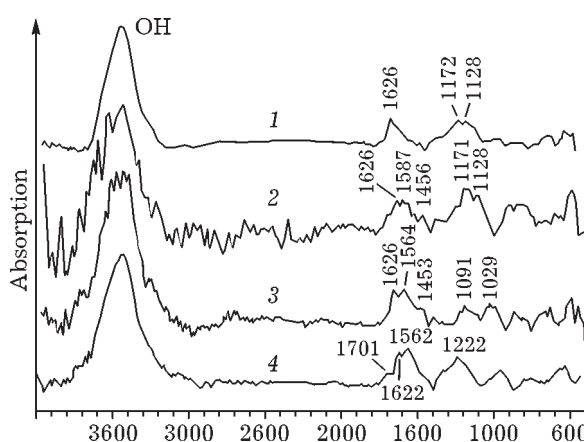

Fig. 1. IR spectra of oxidized samples CM: *1* − original, *2* − CM-250, *3* − CM-350, *4* − CM-450.

the composition of SFG on the surface of the oxidized CM samples.

At the temperature of 450 °C on can also observe an increased carboxyl group content, which is also reflected in the static absorption capacity value, especially for Pt(IV).

Studying the IR spectra of oxidized CM (Fig. 1) demonstrated that in the course of oxidation the intensity of vibration bands inherent in oxygen-containing groups exhibit a change. The IR spectrum of the initial CM exhibits an absorption band at 1626 cm^{-1} corresponding to the vibrations of the coordinated carboxyl group −COOH. For the oxidized CM, in addition to increasing the intensity of this band one can observe an increase in the intensity of bands within the regions of 1580−1560 and 1450−1460 cm^{-1}, those can be assigned to the vibrations of the ionized −COO^{-} group. The IR spectra of CM-450 sample the initial CM sample the vibration band at 1450−1460 cm^{-1} disappears, whereas the band at 1580−1560 cm^{-1} becomes more intense than the band attributed to the vibrations of the −COOH group. The IR spectrum of sample CM-450 exhibits appearing a band at 1701 cm^{-1} corresponding to the stretching vibrations of the C=O group. Consequently, the amount of ionized carboxyl groups on the surface increases after the CM oxidation.

The IR spectra demonstrate also bands in the region of 1220−1110 cm^{-1} attributed to the vibrations of −C−OH group, wherein with increasing the UM sample oxidation temperature the bands exhibit a shift towards a higher frequency region of the spectrum. So, the absorption band at 1221 cm^{-1} becomes the most intense

one for sample CM-450, which indicates that there is increasing the amount of hydroxyl groups on the surface observed. The assignment of absorption bands was performed in accordance with the procedure described in [20, 21].

There is the fact noted that the SEC value depends on the amount of carboxyl groups on the surface of the CM. The experimental data indicate that an increase in the number of carboxyl groups on the CM surface results in increasing the sorption capacity with respect to 0.1 M NaOH.

The character of curves obtained in the course of extracting platinum from 0.02 M H$_2$PtCl$_6$ solutions (Fig. 2) demonstrates a high sorption rate: for 15 min the curve reaches a plateau, the extraction level of platinum (IV) in this case amounts up to 44.7 % for sample CM-450. It should be noted that at lower concentration values, the recovery of platinum (IV) can reach 99−98.9 %.

At the same time, the recovery level of platinum (II) from 0.02 M solutions of H$_2$PtCl$_4$ for CM samples is low and decreases with increas-
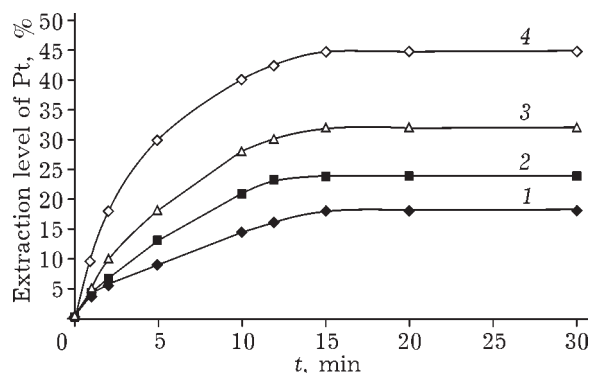

Fig. 2. Kinetic curves of sorption samples CM: 1 − CM Pt(IV), 2 − CM-250, 3 − CM-350, 4 − CM-450.
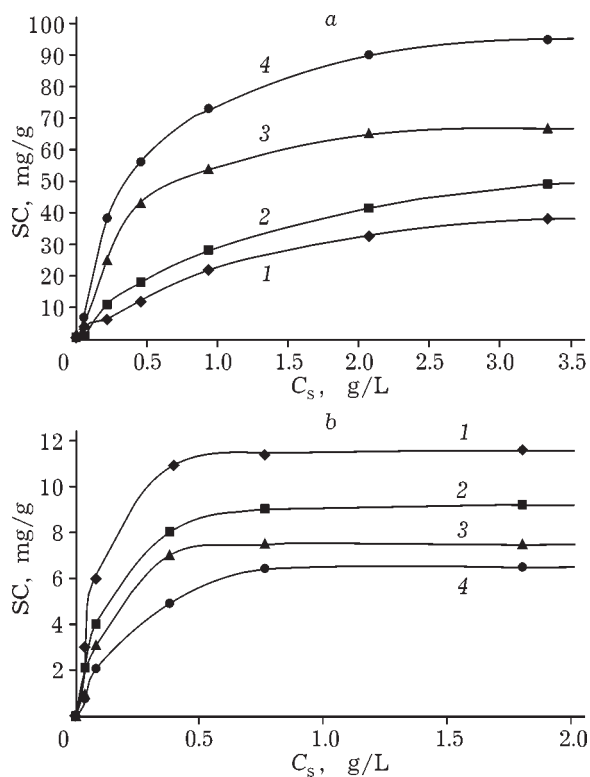

Fig. 3. Sorption isotherms for H$_2$PtCl$_6$ (a) and H$_2$PtCl$_4$ (b) inherent in CM samples: 1 − initial CM, 2 − CM-250, 3 − CM-350, 4 − CM-450.

ing the oxidation temperature. Its maximum value is equal to 5.4 %.

Figure 3 demonstrates platinum (IV, II) adsorption isotherms from the solutions of H_2PtCl_6 and H_2PtCl_4 for the samples of oxidized CM. It can be seen that the isotherms are S-shaped with a very short initial part. Such isotherms are inherent in the case when the adsorptive molecules are attracted or repulsed. In a most accurate manner, these isotherms could be described by the Freundlich equation, which corresponds to a multilayer adsorption from solutions onto heterogeneous surfaces [22]. However, according to [23], within a high concentration there can be observed deviations between experimental and theoretical capacity values.

CONCLUSION

1. Using the IR spectroscopy technique, it was demonstrated that increasing the temperature of CM oxidation results in changing the composition of SFG as well as in increasing the amount of carboxyl and hydroxyl groups.

2. A dependence of the static absorption capacity with respect to Pt(IV) on the amount of carboxyl groups on the surface of oxidized CM has been revealed. The static absorption capacity with respect to Pt(IV) in H_2PtCl_6 solution for CM-450 sample amounted to 95 mg/g, that is 2.4 times greater than the static capacity value for a non-oxidized specimen. At the concentration values equal to 10^{-4} M H_2PtCl_6 the platinum recovery level amounts to 99.9 %. Under these conditions, Pt(II) from the solution of H_2PtCl_4 almost could not be extracted, therefore the CM-450 samples selective with respect to H_2PtCl_6.

It could be supposed that the CM-450 sample is promising to a considerable extent as a sorbent for the extraction of H_2PtCl_6 from platinum chloride solutions.

Acknowledgement

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