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# Adsorption and reduction of platinum(IV) chloride complex ions on activated carbon

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**Abstract:** The adsorption kinetics of platinum(IV) chloride complex ions on the activated carbon Norit GF40 was investigated. Experiments were carried out at different initial concentrations of Pt(IV) chloride complex ions, temperature, rate of mixing and pH. It was found that the value of activation energy of the studied process is equal to 19.7 kJ/mol. From the ICP MS analysis it was confirmed that platinum ions (Pt(IV) and Pt(II)) are removed from the solution due to the adsorption and are further reduced to the metallic state. Such mechanism was confirmed by XPS analysis which showed that on the carbon surface three forms of platinum species, i.e. Pt(0), Pt(II) and Pt(IV), exist. The presence of platinum in the solution at different oxidation states was also confirmed spectrophotometrically by identification of their characteristic absorption bands. The metallic form of Pt present on the surface of activated carbon was observed in the form of small spherical islands with the diameter not exceeding 500 nm. Those islands consist of smaller, flake-shape particles with a thickness of about 35 nm.

Key words: adsorption; platinum(IV) chloride complex ions; reduction; recovery; kinetics; activated carbon

## **1** Introduction

It is known that a lot of chemical reactions can be completed only with the help of either homogenous or heterogeneous catalysts. For an example, oxidation of carbon monoxide at room temperature [1], or Heck, Suzuki [2] and Hiyama coupling [3] reactions can be given. KÖHLER et al [4] described how properties of carbon supported palladium catalyst affect Heck reaction. However, it seems to be necessary to carry out experiments focused on designing a new catalyst with different chemical properties, i.e. more effective and more selective. Carbon-supported catalysts are often used in practice due to the chemical resistance of such materials and their low price. These features make the carbon an attractive catalyst template material. There are several methods often used to deposit catalytically active metals on carbon surface, e.g. wet impregnation [5], chemical vapor deposition CVD [6], organometallic chemical vapor deposition OMCVD [7], electrochemical

deposition [8]. These techniques are described in literature, giving excellent recipes for catalyst synthesis. Among different noble metals deposited on the carbon surface, the platinum is frequently used as a valuable and efficient catalyst [9].

AGEEVA et al [9] studied the mechanism and kinetics of the sorption process of platinum, palladium and gold complexes on the BAU activated carbon (AC). The effects of pH and initial concentration of precious metals on the adsorption equilibrium of those metals were investigated. The authors showed that in the studied process, platinum, palladium and gold complexes are sorbed probably by the ligand exchange and formation of metal–carbon complexes.

van DAM and van BEKKUM [5] studied the process of metallic platinum formation on AC. As a sorbent the Norit ROX 0.8 AC was used. The physical and chemical properties of synthesized material were analyzed using XPS and Boehm titration. They showed that platinum(IV) chloride complexes are adsorbed on activated carbon and during the impregnation process,

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platinum(IV) ions are reduced to the platinum(II) by the carbon.

The adsorption and reduction of platinum(IV) chloride complexes was also studied by CHEN et al [10]. They showed that the activated carbon fibers (ACF) used as a adsorbent reduce platinum(IV) to platinum(II) and to Pt metallic form. They also found that after sorption some amount of platinum(IV) exist on the surface in the non-reduced form. Immediately after synthesis, metallic platinum has an amorphous structure (from X-ray diffractions analysis they showed specific peaks characteristics of Pt(111), (200) and (220)).

Moreover, activated carbons are often used to precious metal recovery from dilute solutions. AKTAS and MORCALI [11] investigated the influence of temperature, amount of applied AC, shaking rate and time of adsorption on the efficiency of the platinum recovery from waste solutions containing impurities, such as Cu, Zn, Pb, Ni, Fe, Au, Ag, Rh and Pd. They showed that AC can be useful for platinum ions recovery. However, they did not show any information about adsorption kinetics, which is very important in process planning.

Our previous work [12] was focused on the gold(III) chloride complex ions recovery from acidic media (pH=1) using AC Norit GF40. It was shown that Au(III) ions are adsorbed and reduced to metallic form. Those results confirmed that AC can be useful material for gold recovery from dilute solutions where the concentration of gold ions is lower than 0.985 mg/L.

However, there are a small number of details in literature about the influence of adsorption conditions on the final material's properties, such as the total loading of metal, metal dispersion, the size and shape of obtained particles.

In this work, we focused on the kinetic studies of platinum(IV) chloride complex ion deposition, followed by reduction on activated carbon (AC), and the influence of experimental deposition method on the final structure of the material. The obtained materials were analyzed by XPS and SEM to determine the size and the distribution of particles precipitated on the AC surface.

## 2 Experimental

In all experiments, commercially available activated carbon, Norit GF40 (AC), in non-modified form was used. Platinum(IV) chloride complex was obtained from metallic platinum (purity 99.99%) dissolved in aqua regia solution which was then dried several times to remove an excess of nitric acid. To set up proper pH in the system, hydrochloride acid (obtained from POCH, analytical purity) was used.

The measurements of the kinetics of platinum(IV)

chloride complex ions adsorption onto activated carbon were carried out in a thermostated glassy reactor at constant temperature ( $\pm 0.2$  °C). After the temperature of the system was adjusted, 0.5 g ( $\pm 0.001$  g) of activated carbon Norit GF40 was introduced into the aqueous solution containing platinum(IV) chloride complex ions. The total volume of the solution was equal to 300 mL. Every 10-15 min, a 3 mL-sample of solution was taken and analyzed spectrophotometrically (Shimadzu model PC 2501, Japan) to detect changes of platinum (IV) chloride ions concentration (at pH=1 molar absorption coefficient for  $[PtCl_6]^{2-}$  equals 25200 mol·L<sup>-1</sup>·cm<sup>-1</sup>, at the wavelength of 262 nm). After analysis the sample was returned back to the solution in the reactor. All experiments were carried out for three different initial concentrations and with variable mixing rate and temperature. Solution was mixed with a glass stirrer dipped into the reactor at the 2 cm-distance from the bottom of reactor. The rate of mixing was adjusted with CAT R-50D stirrer.

The XPS studies were carried out in the ultrahigh vacuum (UHV)  $(3 \times 10^{-11} \text{ Pa})$  system equipped with hemispherical analyzer (SES R4000, Gammadata Scienta, Sweden). The Mg K<sub>a</sub> source of incident energy of 1256.6 eV was applied to generating core excitation. The spectrometer was calibrated according to ISO 15472:2001. The energy resolution of the system, measured at full width at half maximum (FWHM) for Ag 3d<sub>5/2</sub> excitation line, was 0.9 eV.

Before the analysis, powder samples were pressed into indium foil. The analysis area of the prepared sample was about  $3 \text{ mm}^2$ . No gas release and no change in the sample composition were observed during the measurements.

The CasaXPS 2.3.12 software was applied for the analysis of the XPS spectra. No charge was observed for the studied catalysts, therefore no additional calibration of the spectra energy scale was applied. In the spectra, the background was approximated by a Shirley profile. The deconvolution of spectra into a minimum number of components was done by application of the Voigt-type line shapes (70:30 Gaussian/Lorentzian product).

The analytic depth of the XPS method was estimated as 10.2 nm. The calculations were performed with QUASES-IMFP-TPP2M Ver 2.2 software according to an algorithm proposed by TANUMA et al [13]. This estimation takes into account 95% of photoelectrons escaping from the surface. The experimental error of the XPS analysis is approximately  $\pm 3\%$ .

SEM analyses were carried out on Hitachi Su-70 (made by Thermo Scientific) microscope (equipped with EDS, WDS and EBSD add-on device).

Zeta potential of carbon was measured using a Zetasizer (Zetasizer Nano ZS, Malvern, England).

### **3 Results**

#### 3.1 Analysis of activated carbon by Boehm method

Before experiments, the presence of surface groups on activated carbon Norit GF 40 was analyzed by Boehm method. The details of this method can be found in Refs. [14–16]. All experiments were carried out at ambient temperature 295 K, for 7 d using 0.5 g of AC samples. Measurements were repeated three times. The average values of functional groups concentration obtained during the experiments are given in Table 1.

 Table 1 Functional groups concentration on AC surface
 determined by Boehm method

Functional group	Amount of groups per unit of AC mass/(mmol $\cdot$ g <sup>-1</sup> )					
Carboxylic	0					
Lactone	1.33					
Phenolic	2.63					
Carbonylic	13.99					
Total alkaline groups	4.1					
Total acidic groups	17.96					

# **3.2** Spectrophotometric investigation of Pt(IV) sorption onto carbon surface

From the spectra analysis registered during platinum(IV) chloride complex ions adsorption (Fig. 1), it was found that in the range of wavelength of 225–235 nm additional absorption band with  $\lambda_{max}$ =232 nm appears. The observed band disappearing characteristics for [PtCl<sub>6</sub>]<sup>2-</sup>, together with new band appearance with a maximum at ca.  $\lambda$ =234 nm suggest that during adsorption



**Fig. 1** Change of UV-Vis spectra of platinum(IV) chloride complex ions during their adsorption onto activated carbon NORIT GF40 (Experimental conditions: Pt(IV) initial concentration  $5 \times 10^{-4}$  mol/L, mixing rate 1200 r/min, temperature 323 K)

of platinum(IV) ions, redox reaction takes place:

$$[PtCl_6]^{2^-} + R \Longrightarrow [PtCl_4]^{2^-} + P \tag{1}$$

where R is reductant and P is products of reaction.

The changes of absorbance at  $\lambda$ =262 nm, Pt(IV) chloride ions concentration vs time dependences were recorded. Using general assumption that decrease of platinum ions concentration is proportional to the amount of platinum deposited on the AC surface, kinetic curves were derived.

#### 3.3 Influence of rate of mixing

To determine the influence of the mixing rate on the kinetics of adsorption process, experiments at ambient temperature (295 K) were performed in the presence and in the absence of mixing of solution. From registered kinetic curves (Figs. 2(a) and (b)) it can be seen that the mixing has strong influence on the kinetic curves. Specific sigmoidal shape of the obtained curves (Fig. 2(a)) suggests that the process may have an autocatalytic character.

From the obtained results it can be clearly seen that the rate of disappearing of Pt(IV) ions without mixing is



**Fig. 2** Kinetic curves of platinum(IV) chloride complex ions deposition on AC at 295 K: (a) Under 'static' conditions (without mixing); (b) At mixing rate of 1200 r/min

much slower than that obtained with the mixing rate of 1200 r/min (Fig. 2(b)). Induction time for higher initial concentration is shorter than that for lower one. It is due to faster solid phase Pt appearing on carbon surface in the case of lower initial concentration, which results in the increase of reaction rate. Significant acceleration of the process was achieved after 3 d for sample with the initial concentration of platinum(IV) chloride complex ions of  $5 \times 10^{-4}$  mol/L. When  $c_{0,\text{Pt(IV)}}$  was 10 times lower, acceleration of the process was achieved after 5 d. The influence of the mixing rate on the adsorption process rate at 348 K is presented in Fig. 3. The experiments showed that the mixing rate has significant influence on the process rate.



**Fig. 3** Influence of mixing rate on observed rate constant  $(k_{obs})$  of Pt(IV) chloride complex ions adsorption

#### 3.4 Test for autocatalytic character of reaction

It was mentioned before that specific sigmoidal shape of kinetic curve (Fig. 2) may suggest autocatalytic mechanism of the process. To confirm or reject this hypothesis, 'static' studies (without mixing) of adsorption were carried out with the application of carbon impregnated before the test with  $[PtCl_6]^{2^-}$  ions. Figure 4 shows that the application of such a carbon has significant influence on the rate of adsorption. The observed rate constants increased from  $4.11 \times 10^{-6}$  h<sup>-1</sup> (for AC without impregnation) to  $2.29 \times 10^{-2}$  h<sup>-1</sup> (for AC with ca. 29.3 mg Pt on the carbon surface).

It confirms that the investigated process is accelerated and the path of complex reaction has an autocatalytic character.

## 3.5 Effect of $[PtCl_6]^{2-}$ initial concentration

It was found that the initial concentration of platinum(IV) chloride complex ions has also an influence on the rate of adsorption (Fig. 5). It can be seen that the increase of initial concentration of Pt(IV) resulted in decrease of the process. This tendency was observed for three different mixing rates.



**Fig. 4** Influence of Pt amount on activated carbon surface on kinetic curves of adsorption (Experimental condition:  $c_{0,Pt(IV)}$ =  $1.0 \times 10^{-4}$  mol/L, without mixing, temperature 348 K)



**Fig. 5** Influence of  $[PtCl_6]^{2-}$  initial concentration on observed rate constants of adsorption at different mixing rate at 348 K

#### 3.6 Effect of temperature

To determine the influence of temperature on the studied process, experiments of adsorption at different temperatures, i.e. 25, 40, 50, 60 and 75 °C, were carried out. The observed rate constants are gathered in Table 2.

**Table 2** Observed rate constants ( $k_{obs}$ ) for adsorption process of  $[PtCl_6]^{2^-}$  ions on activated carbon NORIT GF40 in aqueous solution obtained at different temperatures under conditions of  $c_{0,Pt(H)} = 1.0 \times 10^{-4} \text{ mol/L}, \text{ pH=1}$ 

=0,Ft(IV) = · · · · · ·	nei, 2, pri 1	
$T^{-1}/\mathrm{K}^{-1}$	$\ln(k_{\rm obs}/{\rm s}^{-1})$	Standard deviation
0.00287	-7.66996	0.0459
0.003	-7.88335	0.02363
0.0031	-8.2041	0.01449
0.00319	-8.44411	0.04906
0.00336	-8.77064	0.06631
0.00287	-7.66996	0.0459

From the obtained results the activation parameters of the process were calculated. Using linear form of Arrhenius dependence,

$$\ln k_{\rm obs} = \ln A - \frac{E_{\rm a}}{RT} \tag{2}$$

and graphical method (Fig. 6),  $E_A$  and A were determined (Table 3).



**Fig. 6** Arrhenius dependence for sorption of platinum(IV) chloride complex ions on activated carbon NORIT GF40 under experimental conditions of  $[PtCl_6]^{2-}$  initial concentration  $5.0 \times 10^{-5}$  mol/L, mixing rate 200 r/min

**Table 3** Parameters in Arrhenius equation for adsorption process of  $[PtCl_6]^{2-}$  ions on activated carbon NORIT GF40

$E_{\rm a}/(RT)$	$E_{\rm a}/{\rm kJ}$	$\ln (A/s^{-1})$	$A/s^{-1}$
2370.159	19.7	-0.836	0.4335

#### 3.7 Influence of pH on adsorption kinetics

The influence of pH value in the range of 1-4 on the process of adsorption was investigated. To adjust pH, hydrochloride acid was used in the system. It was found that the change of pH from 0 to 1 has no influence on the reaction rate. In turn, pH change from 1 to 2 results in the change of the rate constant from  $0.0415 \text{ s}^{-1}$  to 0.0707 $s^{-1}$ . Moreover, UV-Vis spectra of the system at pH=2 did not show any isosbestic points under such conditions. The observed changes may be connected with the change of zeta potential of Norit GF40. Our studies indicate that in the pH range of 0 and 2 the activated carbon has positive value of  $\zeta$  (Fig. 7). At higher pH value, its surface exhibits negative charge. These changes may influence the electrostatic interaction between platinum(IV) chloride complex ions and AC, resulting in the inhibiting of adsorption process.

#### 3.8 XPS studies

The XPS studies were performed on the samples of NORIT GF40 after adsorption experiments conducted at



**Fig. 7** Influence pH on zeta potential for activated carbon Norit GF40 at temperature 298 K

348 K, mixing rate of 1200 r/min and the Pt(IV) initial concentration of  $5.0 \times 10^{-4}$  mol/L.

The analysis of the surface showed small differences in compositions of carbon, nitrogen and oxygen (Table 4) compared with the reference sample. Significant difference was registered in the content of phosphorus (four times larger compared with reference substrate). The experiments material (Pt/AC) contained 0.17% (mole fraction) platinum. The lower content of oxygen on the composite surface suggests either possible oxidation of surface groups or Pt adsorption on the groups containing oxygen.

 Table 4 Surface composition of carbon substrate (reference material) and AC after Pt(IV) chloride complex ions adsorption

Q	Surface composition/%							
Sample	С	0	Р	Ν	Cl	Pt		
Reference material (Norit GF40)	89.3	9.2	1.2	0.3	-	-		
Pt/AC	90.6	8.0	0.3	0.3	0.6	0.17		

The C 1s line was deconvoluted into 5 components (Fig. 8, Table 5). The maximum intensity (*A*) at binding energy (BE) of 284.6 eV was assigned to C—C lattice carbon. Then, four peaks of lower intensity at 286.0, 287.1, 289 and 291.1 eV were ascribed to the carbon bonded with hydroxyl groups C—OH (*B*), carbonyl groups C—OH (*C*), carboxyl groups COOH (*D*) and, so-called shake-up satellite [13,16,17], respectively.

A small difference was observed in component contents for lattice carbon and carbonyl groups in substrate and composite. The composite showed a larger amount of lattice carbon compared with pure substrate. It suggests the reduction of the composite surface confirmed by lower concentration of carbonyl groups.



Fig. 8 Deconvolution of C1s core excitation for carbon material

The O 1s core excitation indicated four electronic states of oxygen (Fig. 9, Table 6). Peak A at BE of 530.9 eV was assigned to oxygen in hydroxyl groups, peak B at 531.9 eV to oxygen in carbonyl groups and/or in water, peak C with maximum intensity at 533.3 eV to single bonded oxygen in organic species and the peak D at approximately 535.4 eV to single bonded oxygen in organic compounds [13,16,17]. The shake-up satellites (Sat.) at above 537 eV indicated the presence of organic systems containing unpaired electrons [17].

The O 1s spectra for carbon substrate and the composite showed a lower amount of carbonyl group B at the composite surface. On the other hand, the larger peaks C and D indicated more electronegative (i.e. cyclic or conjugated bond systems) surrounding of the lattice oxygen. The latter was confirmed by a larger shake-up satellite found in O 1s spectrum of the composite.

The Pt 4f core excitation was deconvoluted into two doublets that indicated the presence of two electronic states of platinum in the composite sample (Fig. 10). The main Pt  $4f_{7/2}$  core excitation *A* at 72.4 eV (71.3%) was



Fig. 9 Deconvolution of O 1s core excitation for composite material

assigned to metallic form of platinum or partly reduced platinum(IV) complex, e.g. Pt(II). The lower Pt  $4f_{7/2}$  peak *B* at 74.1 eV (28.7%) was ascribed to [PtCl<sub>6</sub>]<sup>2-</sup>, which confirmed that part of the platinum complexes remained unreduced after the adsorption process or they were adsorbed at the carbon substrate in their native form.

#### 3.9 SEM analysis

For SEM analysis, a sample of activated carbon (NORIT GF40) containing about 25% (mass fraction) of platinum was used. Platinum deposition on the activated carbon surface was carried out under following conditions: initial concentration of platinum(IV) chloride complex ions of  $5 \times 10^{-4}$  mol/L, temperature of 348 K, mixing rate of 1200 r/min, pH=1, initial mass of AC of 0.1g. A view of external surface of Norit GF40 after adsorption is presented in Fig. 11.

The observed small white islands can be platinum particles. High resolution SEM observations show that the obtained particles are smaller than 500 nm and have specific flaked shape. The width of these flakes is

Table 5 Components of C 1s core excitation for carbon substrate (reference material) and AC after Pt(IV) chloride complex ions adsorption

	A		В		С		D		Sat.	
Sample	BE/	Composition/								
	eV	%								
Norit GF40	284.6	74.8	286.0	9.7	287.1	9.0	289.0	6.5	291.1	-
Pt/AC	284.6	76.1	285.9	10.0	287.0	7.8	289.0	6.1	291.2	_

Table 6 Components of O 1s core excitation for carbon substrate (reference material) and AC after Pt(IV) chloride complex ions adsorption

	A		В		С		D		Sat.	
Sample	BE/	Composition/								
	eV	%								
Norit GF40	530.9	13.7	531.9	33.6	533.3	45.5	535.4	7.2	537.7	-
Pt/AC	530.7	12.5	532.0	29.4	533.5	48.7	536.0	9.4	538.7	-



Fig. 10 Deconvolution of Pt 4f core excitation for composite material



Fig. 11 SEM image of platinum particles deposited on NORIT GF40 carbon surface

#### 30-35 nm (Fig. 12 (a)).

The view of the Pt/AC sample after annealing process is shown in Fig. 12(b). The process was carried out at 973 K in a sealed silica ampule for 12 h. After this time, the sample was cooled down for 5 h to room temperature. Apparently, temperature has an influence on particles shape. Our studies showed that annealing process changed the shape of obtained particles from flake-shape to spheres.

XRD analysis (Fig. 13(a)) shows that the obtained Pt/AC materials have an amorphous structure. After annealing (Fig. 12(b)), the presence of characteristic peaks of platinum was observed.

### 4 Mechanism of adsorption process

It is suggested that the studied process consists of several stages, which can be described according to the following scheme.



**Fig. 12** SEM images of platinum particles deposited on AC carbon surface: (a) Directly after synthesis; (b) After annealing at 973 K



**Fig. 13** XRD patterns of analyzed sample Pt/AC: (a) Directly after synthesis; (b) After annealing process

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1) Adsorption of platinum(IV) chloride complex ions on the AC surface is as follows:

$$[PtCl_6]^{2^-} + C_{surf} \xrightarrow{k_1} [PtCl_6]^{2^-}_{surf}$$
(3)

2) Reduction of adsorbed platinum(IV) chloride complex ions is as follows:

$$[PtCl_6]_{surf}^{2-} + C_{organic} + H_2O \xrightarrow{k_2} [PtCl_4]_{surf}^{2-} + 2HCl + CO$$
(4)

where  $[PtCl_6]_{surf}^{2-}$  and  $[PtCl_4]_{surf}^{2-}$  are platinum(IV) and platinum(II) ions, respectively, adsorbed on the activated carbon surface;  $C_{surf}$  denotes carbon atoms at the surface area of AC;  $C_{organic}$  is carbon as a component of functional groups whose existence was confirmed by XPS studies (Fig. 9) and Boehm titration. Reduction reaction of  $[PtCl_6]^{2-}$  to  $[PtCl_4]^{2-}$  on the activated carbon surface was also suggested by van DAM and van BEKKUM [5].

3) Further reduction of platinum(II) chloride complex ions to metallic form Pt confirmed by XPS studies is as follows:

$$[PtCl_4]^{2-}_{surf} + C_{organic} + H_2O \xrightarrow{k_3} Pt + 2HCl + 2Cl^- + CO$$
(5)

It was also determined that except metallic platinum, ca. 30% of initial concentration of platinum(IV) chloride complex ions is not reduced.

4) Autocatalytic character of Pt(IV) reduction, suggested from 'static' studies in the presence of metallic platinum particles adsorbed on the AC surface, is as follows:

$$[PtCl_6]^{2^-} + Pt + 2H_2O + C_{\text{organic}} \xrightarrow{k_4} 2Pt + 6Cl^- + 4H^+ + CO_2$$
(6)

## **5** Discussion

Platinum(IV) chloride complex ions in aqueous solution are adsorbed on the carbon surface and then are reduced to metallic form by functional groups on the carbon surface [5]. The ability of carbon surface oxidation by the H<sub>2</sub>PtCl<sub>6</sub> was also suggested in Ref. [16]. Taking into consideration both of these facts, a small amount of metallic platinum may significantly accelerate the reduction reaction of Pt(IV) and Pt(II) ions. Electrons can be transferred through the activated carbon into catalyst (metallic platinum), where platinum(IV) and platinum(II) chloride complexes are adsorbed and further reduced to metallic state, Pt(0). This mechanism may have a confirmation in the low value of activation energy determined in the studied system. Our observations (SEM analysis) also suggest that metallic platinum exists on the external surface of the AC pellets only. In this case, autocatalytic reduction of platinum complex ions is strongly undesirable because it leads to the further growth of Pt particles and decrease of metal dispersion on the carbon surface.

Taking into account mechanism of Pt(IV) ions adsorption and their further reduction (Eqs. (3)–(6)), we constructed kinetic models of this process with assumption that surface reactions, Eqs. (4) and (5), take place relatively fast compared with the physical adsorption of platinum (IV) complex ions ( $k_2$  and  $k_3$ >> $k_1$ ) and isolation conditions (large excess of reductant compares with precursor concentration). With such assumption the model of the autocatalytic process can be simplified and described as follows:

$$[PtCl_6]^{2-} \xrightarrow{k_{1,obs}} Pt$$
(7)

$$[PtCl_6]^{2-} + Pt \xrightarrow{k_{4,obs}} 2Pt + products$$
(8)

The differential kinetic equations describing the rate of adsorption-reduction process of Pt(IV) ions have the following form:

$$\frac{dc([PtCl_6]^{2^-})}{dt} = -k_{1,obs}c([PtCl_6]^{2^-}) - k_{4,obs}c([PtCl_6]^{2^-})c(Pt)$$
(9)

and after analytical solution, the integral equation describing Pt(IV) ions consumption from the solution in time has the form:

$$c([PtCl_6]^{2^-}) = \frac{\frac{k_{1,obs}}{k_{4,obs}} + c_0([PtCl_6]^{2^-})}{1 + \frac{k_{1,obs}}{k_{4,obs}} \cdot \exp\left[\left(k_1 + k_4 c_0([PtCl_6]^{2^-})\right)t\right]} (10)$$

where  $k_{1,obs}$  denotes the cumulative rate constant of Pt(IV) ions adsorption, and  $k_{4,obs}$  is the observed rate constant of autocatalytic reduction of platinum(IV) complex ions by the functional groups presented on the carbon surface. From the fitting of Eq. (10) to the experimental results (Fig. 2(a)) we obtained the high correlation ( $R^2=0.98$ ) between the experimental points and the fitted curve.  $k_{1,\text{obs}}$  and  $k_{4,\text{obs}}$  were found to be  $9.87 \times 10^{-5} \text{ d}^{-1}$  and 5 682.55 d<sup>-1</sup>, respectively. Such a result does not negate the suggested model of Pt(IV) ions reduction described with Eqs. (7) and (8). The 'sensitivity' of  $k_1$  for mixing rate suggests that the diffusion of Pt(IV) ions to the surface of activated carbon plays an important role in the rate of the adsorption process. From Fig. 3 significant influence of mixing rate in the range of mixing rate 200 to 600 r/min can be clearly seen, which indicates the diffusion limited process for such mixing rate value. In the range of mixing rate of 900-1200 r/min the change of the adsorption rate is negligible, suggesting that in this range of mixing rate, the process is kinetically controlled.

Based on the observation we concluded that reaction (3) can be expressed as a following differential equation:

$$-\frac{dc([PtCl_6]^{2^-})}{dt} = k_{obs} \cdot c([PtCl_6]^{2^-})$$
(11)

which is valid under the assumption:

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$$k_{\rm obs} = k_1 \cdot c(C_{\rm surf}) \tag{12}$$

The solution of equation (11) can be expressed as

$$c([PtCl_6]^{2^-}) = c_0([PtCl_6]^{2^-})exp(-k_{obs} \cdot t)$$
 (13)

Equation (13) was used to derive rate constant  $(k_{obs})$ with a good correlation index in the range of 0.980-0.999.

## **6** Conclusions

1) It was found that the activated carbon Norit GF40 is an effective adsorbent of platinum(IV) chloride ions in aqueous solution as well as efficient reductant of these complex ions in such environment.

2) Adsorption as well as reduction process is controlled by diffusion. Thus, the rate of the process can be controlled by the change of mixing rate. However, it should be pointed out that changing of mixing rate has influence not only on diffusion but also on the adsorption rate on external surface of activated carbon. Changing the temperature may cause another change of diffusion and adsorption processes as well as the reduction rate within the pores of activated carbon. However, the stages of the overall process cannot be separated during our experiment.

3) The suggested mechanism of  $[PtCl_6]^{2-}$  ions adsorption and their further reduction is complex and has several steps. The limiting step of the process is the adsorption of platinum(IV) ions on the AC surface, controlled by diffusion. The second important step due to the final product creation is autocatalytic reduction of platinum(IV) ions to the metallic particles.

4) All observed platinum particles have specific flake-shape and amorphous structure. The mean value of particle thickness was estimated as 35 nm.

5) It is possible to change the particles shape by annealing. After this process, the obtained particles indicate crystal structure typical of metallic platinum.

6) Temperature has influence on the adsorption process. The value of activation energy was found to be 19.7 kJ/mol.

7) It is worth noting that functional groups presented on the carbon surface play an important role in the Pt(IV) complex ions reduction. It seems that modification of a number of functional groups on the carbon surface would significantly change the rate of the process and influence the morphology of the final product.

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# 活性炭对铂(IV)氯络离子的吸附与还原

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摘 要:通过在不同的铂(IV)氯络离子初始浓度、温度、搅拌速率和 pH 下进行的实验,研究活性炭吸附铂(IV) 氯络离子的动力学。结果表明,吸附过程的活化能为 19.7 kJ/mol。等离子体质谱分析结果表明,Pt(IV)、Pt(II)离 子被活性炭吸附并进一步还原为金属铂,从而从溶液中分离出去。XPS 分析结果证实在活性炭的表面存在 3 种形 式的 Pt,即 Pt(0)、Pt(II)和 Pt(IV)。XPS 光谱的特征吸收峰解析证实在溶液中存在不同氧化态的 Pt。在活性炭的 表面观察到球形岛状的金属 Pt,其直径不超过 500 nm。这些球形岛状铂由厚度为 35 nm 左右的片状粒子组成。 关键词:吸附;铂(IV)氯络离子;还原;回收;动力学;活性炭

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