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KINETICS OF THE ADSORPTION OF GOLD(III) CHLORIDE COMPLEX IONS ONTO ACTIVATED CARBON

KINETYKA ADSORPCJI JONÓW KOMPLEKSOWYCH ZŁOTA(III) NA WĘGLU AKTYWNYM

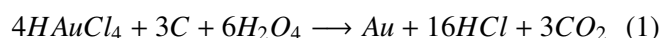
In this paper, the kinetics of $[\text{AuCl}_4]^-$ ions loading onto activated carbon (Norit GF-40) was investigated. Investigations were carried out under different initial concentration of gold(III) chloride complex ions, temperature and rate of mixing. The progress of the process was monitored spectrophotometrically. From the changes of gold(III) ions concentration the kinetic curves, were derived and consequently the rate constants for the investigated process were obtained. Also, the possible influence of gold preloaded onto carbon on the adsorption process was demonstrated.

W niniejszej pracy, przedstawiono wyniki badań kinetyki adsorpcji jonów kompleksowych $[\text{AuCl}_4]^-$ na węglu aktywnym Norit GF-40. Doświadczenia prowadzono stosując różne stężenia początkowe jonów kompleksowych złota(III) oraz różne temperatury i szybkości mieszania. Postęp procesu adsorpcji rejestrowano spektrofotometrycznie. Z zarejestrowanych zmian stężenia jonów złota(III) w roztworze otrzymano krzywe kinetyczne, z których wyznaczono stałe szybkości procesu. Badano również możliwy wpływ wstępnie osadzonego złota na peletach węgla aktywnego, na szybkość adsorpcji.

1. Introduction

Among many different methods of gold recovery from the aqueous solutions, one frequently used is the adsorption of gold(I) and gold(III) ions onto activated carbon. Recently, many authors studied such a process using different kinds of adsorbing carbon as well as adsorbed gold complex ions [1-4]. In the conducted experiments different conditions, e.g. concentration of gold(I) and gold(III) ions, amount and kind of adsorbent, temperature, rate of solution mixing, etc were applied. The best known method is the process of adsorption of cyanide gold(I) complex ions onto activated carbon [5-9]. It has still wide technological application and many factories use the cyanide methods until now. At present however, small recycling businesses, look for another, flexible technology for recovery of metals from different sources including gold. They try to apply different oxidizing systems to dissolve solid wastes and then to recover noble metals using reduction method. As an example of the system, in which gold is present in the form of complex ions, the aqueous chloride system can be given. One of the method which can be used to separate gold(III) ions from such a solution is based on

their deposition on the activated carbon surface. This chloride system has also additional interesting advantage. The gold(III) chloride complex ions after adsorption onto carbon are reduced to metallic form [10] producing gold clusters on the carbon surface. This reaction can be written as:



It seems that small "islands" of metallic gold present on the carbon surface can be applied as a potential catalysts.

Because of a few studies on the adsorption of gold(III) chloride complex ions onto activated carbon, it was decide to study kinetics of gold(III) chloride ions adsorption onto carbon NORIT – GF40 in aqueous chloride system, in which the $[\text{AuCl}_4]^-$ ions dominate.

2. Experimental technique

Measurements of the adsorption kinetics of $[\text{AuCl}_4]^-$ complex ions onto activated carbon were carried out in the thermostated ($\pm 0.2^\circ\text{C}$) glassy reactor. The scheme of the experimental setup is shown in Fig.

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1. After temperature in the system was adjusted, known amount (0.5 g) of activated carbon (Norit GF-40) in the pellets form was introduced into the aqueous solution containing chloride gold(III) complex ions. Its chosen physico-chemical parameters, such as active surface (S) and minimal and maximal bulk density ($\rho_{\min}$ i $\rho_{\max}$)

are given in Table 1. The experiments were carried out at three different temperatures, different initial gold(III) complex ions concentration in the solution, and using three different mixing rates. Values of the parameters are gathered in Table 2.

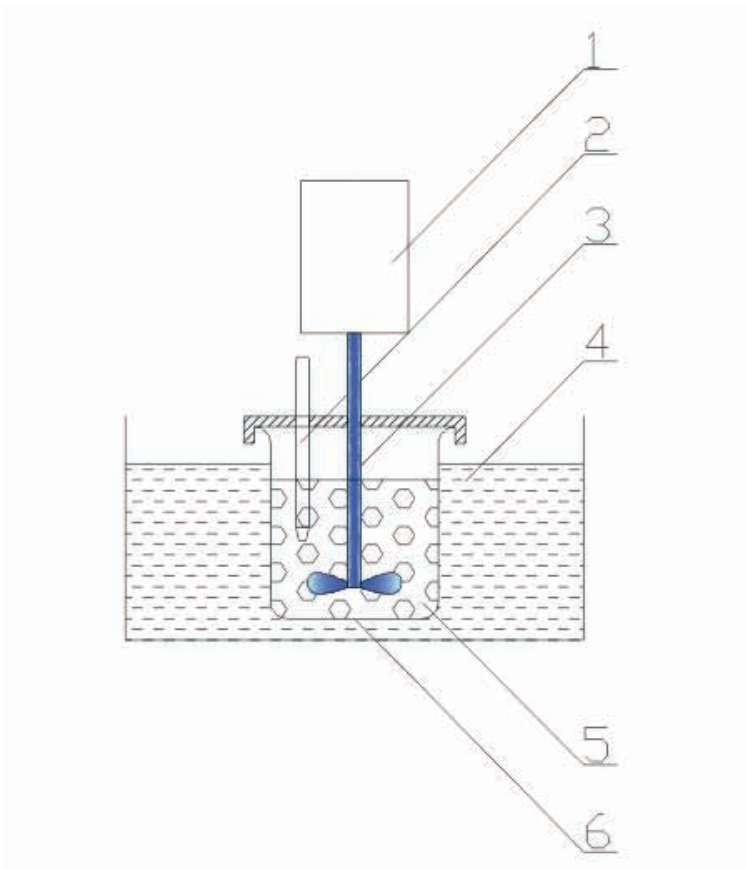


Fig. 1. Scheme of the system used to study the adsorption of gold(III) complex ions onto activated carbon 1 – Drive of the mixer, 2 – Thermometer, 3 – Mixer, 4 – Aqueous jacket, 5 – Au(III) solution containing activated carbon, 5 - Reactor

Physical-chemical parameters of Norit GF-40 carbon pellets TABLE 1

S[m ² /g]	1340
$\rho_{\min}$ [cm ³ /g]	0,174
$\rho_{\max}$ [cm ³ /g]	0,294

Values of the parameters changed during experiments TABLE 2

Initial concentration of [AuCl ₄] ⁻ , $C_{0,[AuCl_4]^-}$ [M]	Mixing rate, V [rpm]	Temperature, T [°C]
$5 \cdot 10^{-4}$	1200	75
$1 \cdot 10^{-4}$	600	50
$5 \cdot 10^{-5}$	200	25

During experiments, with chosen for the given test time interval (i.e. every 10 or 20 min., depending on the whole process duration), samples of solutions were collected from the reacting solution. At the static tests (adsorption measurements carried out in the ambient temperature, without mixing of the solution), time intervals between sample withdrawals ranged from 24 to 48 hours. Collected samples were analyzed spectrophotometrically to detect the changes of $[\text{AuCl}_4]^-$ ions concentration (spectrophotometer Shimadzu PC 2501, Kyoto, Japan). From the analysis of the spectra of solutions (measurements done at the wavelength $\lambda = 315$ nm), the decrease of the gold(III) ions concentrations during the reaction was determined. An example of changes of the band intensity, characteristic for the $[\text{AuCl}_4]^-$ ions during the studied process is shown in Fig. 2. Obtained results were used to derive kinetic curves ($[\text{AuCl}_4]^-$ concentration vs. time – an example is given in Fig. 3, and the amount of Au loaded onto carbon vs. time), to which kinetic equa-

tions were fitted using TCCurve software [11]. From the obtained equations, values of the rate constants were derived. Because the experimental technique (spectrophotometry) we used is able to determine only the amount of gold(III) dissolved in the solution, it was not possible to prove if gold(III) adsorbed ions are completely reduced on the carbon surface. We assumed that after contact with carbon surface the whole adsorbed gold(III) complex ions were reduced to the metallic form. Consequently, it was assumed that the rate of decreasing of gold(III) ions concentration is equal to the rate of metallic gold deposition onto carbon surface.

During the experiments every test was repeated twice. The surface of carbon pellets before and after adsorption process as well as morphology of gold precipitated onto activated carbon were observed using optical microscope (Nikon, model Eclipse LV 150) and atomic force microscope (NT-MDT, NTEGRA).

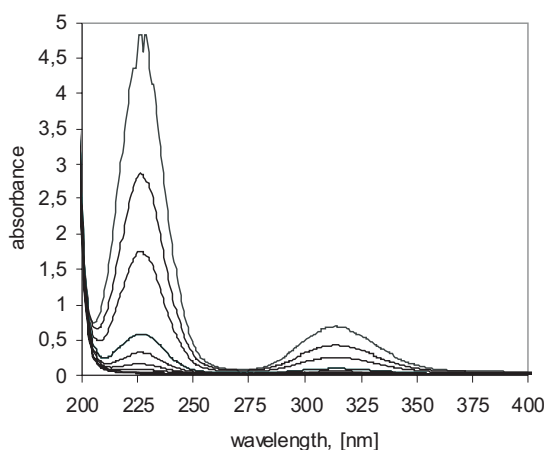


Fig. 2. An example of spectra of the solution containing gold(III) chloride complex ions after different adsorption duration time. Conditions: temperature = 75°C, $V = 600$ rpm., $C_{0,[\text{AuCl}_4]^-} = 1 \cdot 10^{-4}$ M

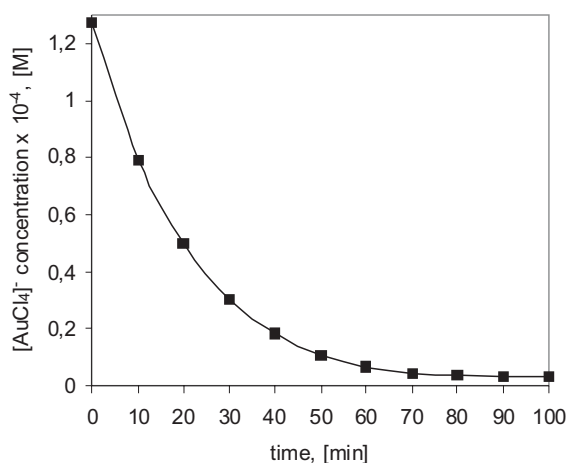


Fig. 3. An example of experimentally obtained kinetic curve vs. time. Conditions: temperature = 75°C, $V = 600$ rpm., $C_{0,[\text{AuCl}_4]^-} = 1 \cdot 10^{-4}$ M

3. Results

a) Effect of temperature on the rate adsorption.

At first, the influence of temperature on the rate and efficiency of the adsorption process was studied. Examples of kinetic curves obtained at chosen temperature (25, 50 i 75°C), constant mixing rate ($V = 1200$ rpm) and initial concentration of $[AuCl_4]^-$ ions ($C_{0,[AuCl_4]}$) equal to $5 \cdot 10^{-4}$ M are shown in Fig. 4.

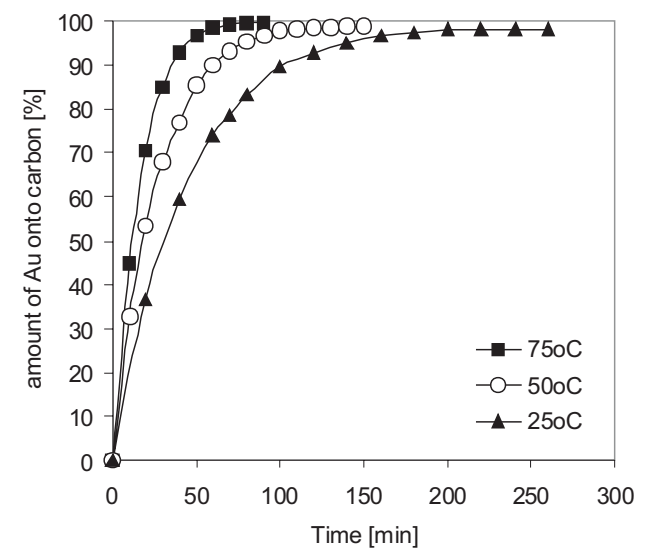


Fig. 4. Temperature influence on the rate of adsorption process and reduction of gold(III) complex ions on the Norit GF-40 active carbon. Conditions: $V = 1200$ rpm., $C_{0,[AuCl_4]} = 5 \cdot 10^{-4}$ M

The rate constants k_{obs} gathered in Table 3 were derived by fitting experimentally obtained dependencies $C_{0,[AuCl_4]}$ vs. time with the equation

TABLE 3

Values of the rate constants of adsorption and reduction of $[AuCl_4]^-$ complex ions onto the Norit GF-40 active carbon at different temperature conditions

Initial concentration of $[AuCl_4]^-$ $C_{0,[AuCl_4]}$ [M]	Rate of mixing V [rpm.]	Temperature T [°C]	Observed rate constant of reaction k_{obs} [min ⁻¹]
$5 \cdot 10^{-4}$	1200	25	0.02308
		50	0.03839
		75	0.06051

$$C_{t,[AuCl_4]} = a + C_{0,[AuCl_4]} \exp(-k_{obs}t) \tag{2}$$

where: k_{obs} – observed rate constant of the process studied, t – time in [min], $C_{0,[AuCl_4]}$ – initial concentration of the $[AuCl_4]^-$ ions, a – constant factor in equation generated during fitting procedure which was found to produce

the best fit to the experimental data. Altogether ca. 40 curves were produced with the correlation coefficient $r^2 = 0,999$ which suggests that accepted equation (2) is in good agreement with the experimental data. Using Arrhenius dependence and applying graphical method to k_{obs} values gathered in Table 3, the activation energy of the process was found to be equal to $E = 245,5 \left[\frac{J}{mol} \right]$ (Fig. 5).

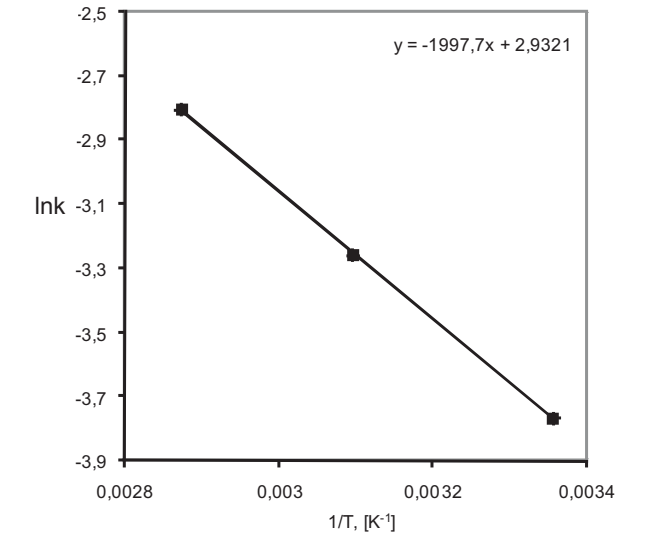


Fig. 5. Arrhenius ($\ln k$ vs. $1/T$) dependence for the adsorption and reduction process of the $[AuCl_4]^-$ complex ions

After experiments the presence of metallic gold on the surface of the carbon pellets is also detected. Examples of samples before and after adsorption process are shown in Fig. 6 and Fig. 7, respectively.

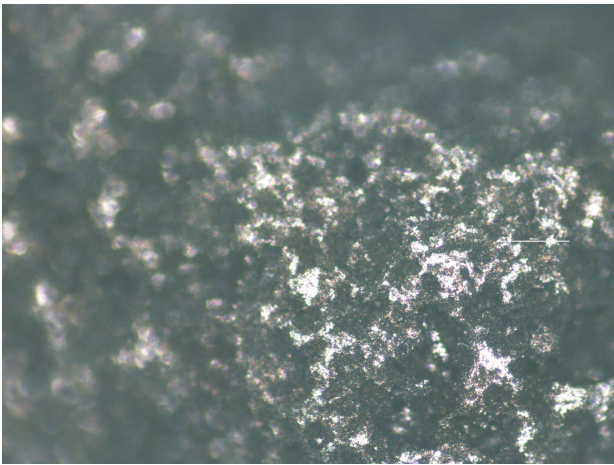


Fig. 6. Norit GF-40 carbon pellets before the adsorption process of gold(III) chloride complex ions

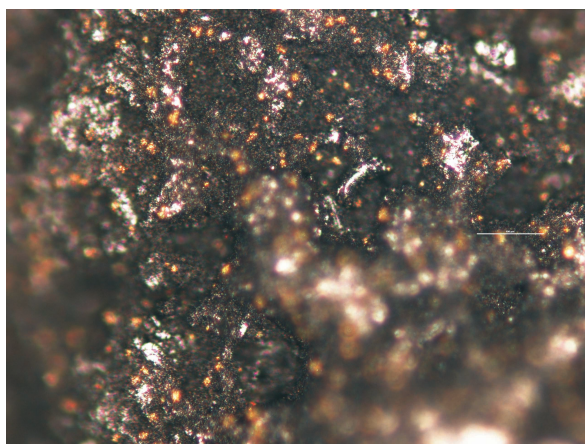


Fig. 7. Picture from optical microscope of local concentrations (islands) of metallic gold on the surface of the NORIT G-40 after adsorption of gold(III) chloride complex ions and their further reduction from optical microscope obtained. Experimental conditions: $V = 1200$ rpm., temperature = 50°C , $C_{0,[AuCl_4]^-} = 5 \cdot 10^{-5}$ M

Analysis of the carbon pellets surface after adsorption process shows, that metallic gold does not create uniform deposit, but exists in the form of local conglomerates (islands). With increasing of the gold(III) initial concentration in the solution, the islands transform into bigger bulk precipitates. Analysis of the morphology of precipitated gold performed with the atomic force microscope showed, that on the carbon surface, Au metallic clusters are present and their size is in the range from ca. 150 nm to ca. 500 nm (Fig. 8).

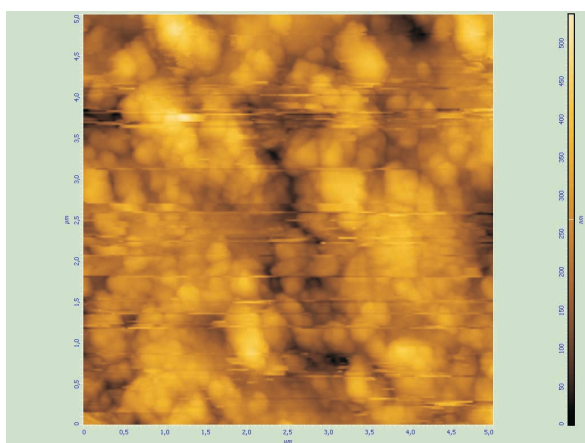


Fig. 8. AFM picture of local concentrations (islands) of metallic gold onto surface of the NORIT GF-40 after adsorption of gold(III) chloride complex ions and their reduction. Sizes of the clusters are from ca. 150 nm to ca. 500 nm

b) Effect of the mixing rate.

In order to determine how the rate of mixing may influence the adsorption kinetics of the $[AuCl_4]^-$ ions onto activated carbon, experiments were carried out using three different mixing rates (200, 600 i 1200 rpm.). Examples of experimentally obtained kinetic curves (weight

% of adsorbed gold vs. time) for the chosen experimental conditions and initial concentration of gold(III) $C_{0,[AuCl_4]^-} = 5 \cdot 10^{-4}$ M are shown in Fig. 9. Values of the rate constants determined from these curves are given in Table 4.

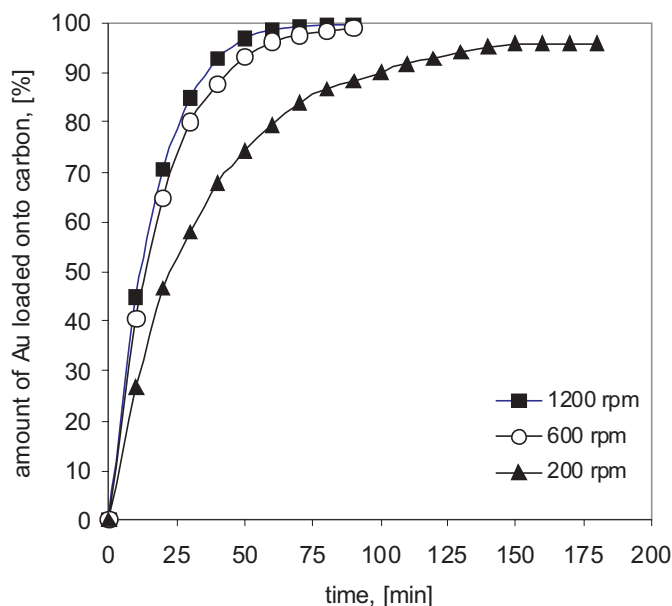


Fig. 9. Effect of the rate of mixing on the shape of kinetic curves during adsorption of gold(III) chloride complex ions onto activated carbon Norit GF-40. Conditions: initial concentration of $[AuCl_4]^- = 5 \cdot 10^{-4}$ M, $C_{0,[AuCl_4]^-} = 5 \cdot 10^{-4}$ M, temperature 75°C

TABLE 4
Values of the rate constants of adsorption and reduction process of $[AuCl_4]^-$ ions onto activated carbon Norit GF-40 at different rates of the solution mixing

Initial concentration of $[AuCl_4]^-$ $C_{0,[AuCl_4]^-}$ [M]	Rate of mixing V [obr/min]	Temperature T [K]	Observed rate constant of reaction k_{obs} [min^{-1}]
$5 \cdot 10^{-4}$	200	358	0.02483
	600		0.03202
	1200		0.06051

It can be seen, that significant influence on the kinetics of adsorption appears when the rate of mixing exceeds 600 rpm. The rate constant changes in nonlinear way (Fig. 10) from 0.02483 min^{-1} at 200 to 0.06051 min^{-1} at 1200 rpm, respectively. This dependence can be described by the empirical equation:

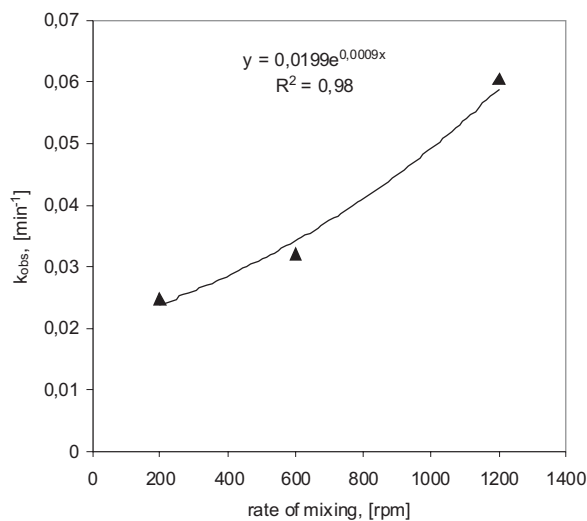


Fig. 10. Effect of the rate of mixing on the rate constant of adsorp-

tion process of gold(III) chloride complex ions onto activated carbon Norit GF-40. Conditions: initial concentration $[AuCl_4]^- = 5 \cdot 10^{-4}$ M, temperature 75°C

$$k_{obs} = 0.0199\exp(0.0009 \cdot V) \tag{3}$$

where, k_{obs} and V are observed rate constant and rate of mixing, respectively.

c) Effect of the initial concentration of gold(III) on the adsorption rate.

The influence of the initial concentration of $[AuCl_4]^-$ ions on their adsorption rate was also studied. The results obtained for the chosen experimental conditions, (mixing rate $V = 1200$ rpm and temperature $= 75^\circ\text{C}$) are shown in Fig. 11. Determined values of the rate constants are gathered in Table 5.

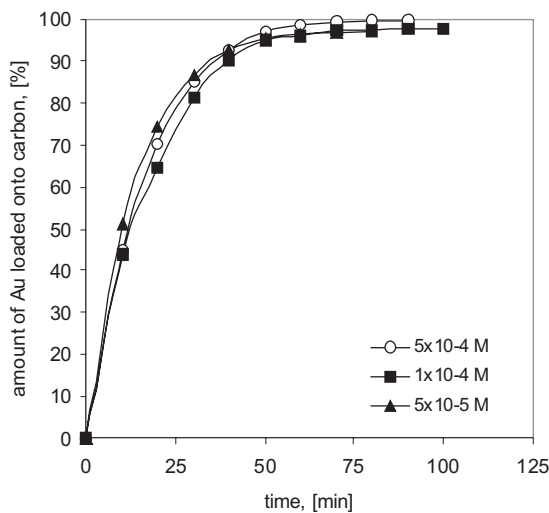


Fig. 11. Effect of initial concentration of $[AuCl_4]^-$ complex ions on the rate of their adsorption onto activated carbon Norit G-40. Conditions: rate of mixing $V = 1200$ rpm, temperature 75°C

TABLE 5
Values of the rate constants of adsorption and reduction process of $[AuCl_4]^-$ complex ions onto activated carbon Norit GF-40, at different initial concentration of catalysts Au in the solution

Initial concentration of $[AuCl_4]^-$ ions $C_{0,[AuCl_4]}$ [M]	Rate of mixing V [obr/min]	Temperature T [°C]	Observed rate constant of reaction k_{obs} [day ⁻¹]
$5 \cdot 10^{-4}$	1200	75	0.03839
$1 \cdot 10^{-4}$			0.04678
$5 \cdot 10^{-5}$			0.04433

Obtained values of k_{obs} indicate that in the range of applied conditions, initial concentration of $[\text{AuCl}_4]^-$ ions $C_{0,[\text{AuCl}_4]^-}$ has no influence on the rate of their adsorption, and consequently their reduction to metallic form. All experimental results are very similar (average value of k_{obs} is equal $0.04316 \text{ [min}^{-1}\text{)]}$.

d) The influence of preloaded gold onto carbon on adsorption kinetics.

The experiments were carried out in the system, in which pellets obtained earlier during dynamic experiments were used. The aim of this part of work was to

find out if the presence of gold on the carbon surface may influence the adsorption reaction. For comparison, identical experiments were done on carbon without gold deposition on the surface. Measurements were carried out at there different initial amount of metallic gold on the surface of preloaded carbon pellets, at constant temperature 25°C , and without mixing. Obtained relations between the amount of gold loaded onto carbon and time are compared in Fig. 12. Derived rate constants and experimental conditions are given in Table 6. The results indicate that the presence of gold on carbon surface increases the rate of the adsorption process.

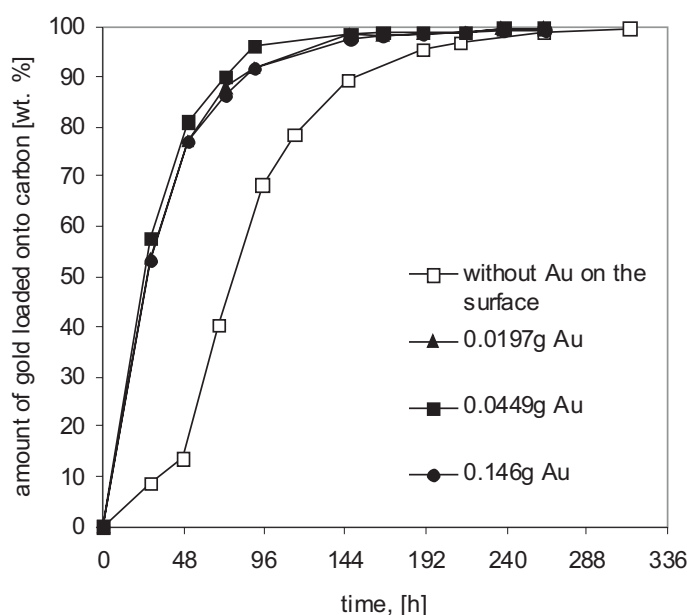


Fig. 12. . Comparison of kinetic curves (amount of gold(III) adsorbed onto activated carbon in wt. % vs. time), obtained from the static studies for different amount of metallic gold preloaded on the carbon pellets. Initial concentrations of $[\text{AuCl}_4]^-$ was $C_{0,[\text{AuCl}_4]^-} = 5 \cdot 10^{-5} \text{ M}$, temperature 25°C

TABLE 6

Values of the rate constants of adsorption and reduction process of $[\text{AuCl}_4]^-$ complex ions onto activated carbon Norit GF-40 obtained under in static conditions (without mixing), in the system with the addition of different amount of Au catalyst

Amount of added Au catalyst m_{Au} [g]	Rate of mixing V [obr/min]	Temperature T [$^\circ\text{C}$]	Observed rate constant of reaction k_{obs} [day $^{-1}$]
0.146	0.00	25	0.6890
0.0449			0.7782
0.0197			0.6841

4. Conclusions

During this study the influence of temperature, rate of mixing and initial concentration of gold complexes on the rate of adsorption process was investigated. During the experiments the kinetic curves were obtained under general assumption that the amount of the reduced complex ions is equal to the amount of gold deposited onto carbon surface. From the obtained results the following conclusions can be drawn:

1. It was found that the activated carbon Norit GF-40 is the effective adsorbent of $[\text{AuCl}_4]^-$ ions as well as an efficient reductant of these complex ions. In all experimental tests, the reduction degree was at least 95%.
2. Temperature (T) increases the process. The rate constants changed from $0.02308 \text{ [min}^{-1}\text{]}$ at 25°C to 0.06051

[min⁻¹] at 75°C. The value of the activation energy is equal to $E = 245,49 \left[\frac{J}{mol} \right]$. The function $k_{obs} = f(T)$ is found to be:

$$k_{obs} = 18.7 \exp \left(-1997.7 \frac{1}{T} \right) \quad (4)$$

3. The rate of solution mixing (V) has also the influence on the rate constant. The increase of V gives nonlinear change of the rate constant of [AuCl₄]⁻ adsorption-reduction process. This dependence is found to be:

$$k_{obs} = 0.0199 \exp(0.0009 \cdot V)$$

4. The change in initial concentration of gold complexes in the solution practically does not influence the rate of gold deposition.

5. The dependence of k_{obs} on temperature, rate of mixing and initial concentration suggests that the rate controlling step is not the chemical reaction. It seems it is diffusion process which controls deposition of gold onto surface.

6. Pre-deposited gold onto carbon surface accelerates the reaction. It may suggest autocatalytic behavior. However, it seems that the amount of gold on the surface (in the applied range) has no influence on the rate. If this problem is connected with the diffusion controlling the process it will be a subject of further study.

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- [9] H. C. Hughes, H. G. Linge, *Hydrometallurgy* **22**, 57-65 (1989).
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