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KINETIC STUDY OF THE PHOTOELECTROCHEMICAL GOLD RECOVERY FROM DILUTED CHLORIDE SOLUTIONS

BADANIA KINETYCZNE PROCESU ODZYSKU ZŁOTA Z ROZCIEŃCZONYCH ROZTWORÓW CHLORKOWYCH METODĄ FOTOELEKTROCHEMICZNĄ

Au(III) was recovered from an acidic aqueous solution via a photoreduction technique under UV light irradiation. Titanium dioxide nanopowder was applied as a photocatalyst. Gold was deposited onto TiO_2 surface in the form of nanoparticles with average dimensions between 20 and 30 nm. The influence of the Au(III), TiO_2 and methanol initial concentrations on the reaction rate was determined. It was shown, that the rate of the gold photoreduction strongly depends on the concentration of TiO_2 and methanol. The recovery of gold from the diluted acidic solutions containing as much as 1.97 and 0.197 mg/dm^3 of Au(III) was also carried out. Obtained results suggest, that it is possible to recover about 45% of gold. Besides the losses during the filtration process due to the application of very fine TiO_2 particles, oxygen dissolved in the solution as well as the hydrogen ions may take part in parasitic reactions and thus decrease the Au yield.

Keywords: Gold, recovery, photoreduction, TiO_2, aqueous solutions

Przeprowadzono odzysk jonów Au(III) z kwaśnych, chlorkowych roztworów wodnych metodą fotoredukcji pod wpływem światła UV. Jako fotokatalizator wykorzystano proszek dwutlenku tytanu o rozmiarach nanometrycznych. W wyniku redukcji kompleksu chlorkowego Au(III), na powierzchni TiO_2 otrzymano fazę metaliczną w formie nanocząstek o rozmiarach w zakresie od 20 do 30 nm. Zbadano wpływ stężeń początkowych Au(III), TiO_2 i metanolu. Badania wykazały, że szybkość fotoredukcji Au(III) silnie zależy od stężenia dwutlenku tytanu i metanolu. Przeprowadzono również badania nad odzyskiem złota z rozcieńczonych roztworów zawierających 1.97 i 0.197 mg/dm^3 Au(III). Otrzymane wyniki wskazują, że przyjęta metoda pozwala odzyskać około 45% złota z roztworu. Niska wydajność procesu może być spowodowana stratami w procesie filtracji związanymi z zastosowaniem nanokrystalicznego TiO_2, tlenem rozpuszczonym w roztworze oraz jonami H$^+$, które mogą ulegać redukcji w konkurencyjnych, równoległych reakcjach.

1. Introduction

On one hand, increasing amount of toxic metal ions in the environment gradually becomes a serious problem for the society. On the other hand, resources of metals, especially noble metals are limited, whereas the demand for them is constantly growing. Therefore, it is necessary to develop cheap and efficient techniques for recovery of metals from wastewater. The more expensive metal is, the more cost-effective process will be. In the case of gold, there are several known techniques of its removal from aqueous solutions. Namely, sorption on activated carbon [1, 2], chemical reduction [3] or electrochemical reduction [4]. Despite the fact that they are known for many years, there are still problems with their efficiency. Electrolysis is difficult to use in the acidic media containing chloride ions due to evolution of gaseous chlorine during the process. In addition, problems with a low selectivity in systems containing other metals frequently occur. More popular method is the chemical reduction which is applied for example by one of the biggest copper plant KGHM Polska Miedź SA, where disodium disulphite is employed as a reductant. In turn, the

adsorption on activated carbon can be carried out both in alkaline and acidic media. An example can be gold recovery from cyanide or chloride complexes, respectively [2]. In alkaline media, activated carbon is used in several techniques as: carbon in pulp (CIP) [5], carbon in leach (CIL) [6] and so on. With these methods, it is possible to decrease the concentration of gold ions down to 0.01 mg/L. Unfortunately, these techniques are strenuous for the environment and lead to the production of significant amount of toxic wastes. Therefore, the need for the cheap and environmentally-friendly technique of gold recovery from the wastewater seems to be still unsatisfied.

Titanium dioxide is extensively examined towards the photocatalytic decomposition of organic pollutants in wastewater [7]. It also exhibits the redox properties enabling reduction of numerous metal ions from aqueous solution. TiO_2 is an *n*-type semiconductor with a band gap around 3.2 eV [8]. When it absorbs the photon with energy greater than the value of the gap, an electron-hole pair is generated which may take part in redox reactions at the surface of the particle. Since a

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lifetime of the charge carriers is reduced, only electron-hole pairs generated sufficiently close to the surface may take part in the redox reactions. Therefore, increased surface area is preferential for the photocatalytic behavior. The reduction of an electron acceptor from the electrolyte usually occurs via the conduction band (CB), whereas the oxidation of an electron donor via the valence band (VB). Photogenerated charge carriers may be also trapped at the surface and then the redox reactions may be realized via the surface states which are usually located in the middle of the band gap. It prevents from the recombination, nonetheless the reduction or oxidation potentials of electron and hole are reduced in comparison with the charge carriers in the conduction and valence band respectively [9].

The application of titanium dioxide in the gold recovery was already investigated. Borgarello *et al.* [10] demonstrated the possibility of selective separation and recovery of Au(III), platinum(IV) and rhodium(III) in chloride media under AM1 simulated sunlight. Mohamed *et al.* investigated the kinetics of a light induced formation of gold nanoparticles onto TiO_2 using the stopped-flow method and indicated an autocatalytic growth of the gold deposit [11]. Also, gold recovery from spent cyanide plating baths was investigated [12]. Moreover, there are numerous reports concerned with the photoreduction of other metals onto TiO_2 *e.g.* platinum, rhodium, silver, lead, mercury, nickel, chromium, copper and iron [9, 10, 13-16].

The aim of this work was to determine the kinetics of the gold photoreduction onto TiO_2 *i.e.* the influence of the titanium dioxide, Au(III) and methanol initial concentrations on the reaction rate as well as the applicability of this technique in gold recovery form diluted acidic waste solutions.

2. Experimental

The gold chloride complex was obtained by a dissolution of 19.69 g of metallic gold (Mennica Polska SA, purity 99.99%) in the mixture of hydrochloric and nitric acid. The crystals of tetrachloroauric acid were crystallized and subsequently dissolved in the concentrated hydrochloric acid in order to remove the excess of nitric acid. Such a procedure was repeated several times. Finally obtained crystals were dissolved in water and used in further experiments.

Photoreduction of $AuCl_4^-$ ions was performed on the Evonik P25 TiO_2 powder, which is a mixture of anatase and rutile with specific surface area determined by BET equal to 50 ± 15 m^2/g and approximated tapped density 130 g/dm^3. The band gap was determined using a diffuse reflectance spectroscopy. The sample was ground in a mortar with a spectrally pure barium sulfate in 1:50 weight ratio, $BaSO_4$ pellet was employed as a 100% reflectivity standard. Reflectance spectrum was recorded on a Lambda 950 (Perkin Elmer, USA) spectrophotometer equipped with the 150 mm integration sphere. The flatband potential value of titanium dioxide powder was determined from the electrochemical impedance spectra recorded on a Autolab PGSTAT 302N potentiostat in 0.1 M KNO_3 under nitrogen, pH was equal to 5. Impedance spectra were recorded in the frequency range between 100 kHz and 10 mHz for each potential step equal to 100 mV from 1 V to −0.5 V vs. Ag/AgCl saturated electrode.

The photoreduction experiments were performed as follows. TiO_2 was suspended in 0.1M HCl with methanol, then the solution containing Au(III) was added. Methanol was used as a holes scavenger in the system. Reaction mixture was vigorously stirred and illuminated at 375 nm using LED illuminator (Instytut Fotonowy, Poland), radiant flux density was equal to 517 mW/cm^2. Next, the suspension was filtered through the 50 nm filter (Milipore, φ47mm, RC) and the Au(III) concentration in the filtrate was determined spectrophotometrically (Shimadzu U-2501 PC) at 314 nm. The influence of TiO_2, Au(III) and CH_3OH initial concentrations on the reaction rate was evaluated. In order to determine the gold concentration in the solutions containing trace amount of gold, (below the detection level of the UV-VIS technique), an ICP-MS (ELAN 6100, Perkin Elmer) was applied.

The presence of metallic gold deposited onto TiO_2 was confirmed by different techniques, namely UV-VIS (the effect of surface plasmon resonance), X-ray diffraction (Rigaku Miniflex II diffractometer with Cu Kα radiation, λ =0.15406 nm) and scanning electron microscopy (Hitachi SU 70). The particle size distribution was calculated using ImageJ software.

3. Results and discussion

3.1. Determination of the electronic structure of applied TiO_2

In order to explain the mechanism of the photoreduction reaction, one should evaluate the electronic structure of the applied semiconductor *i.e.* the conduction band edge potential which may be regarded as the reduction potential of an electron in the conduction band and the value of the band gap. Diffuse reflectance spectroscopy is a very suitable method for determination of the latter for the powdery samples. On the basis of a measured reflection spectrum of TiO_2 dispersed in $BaSO_4$, the value of the band gap was determined as equal to 3.34 ± 0.05 eV. The corresponding absorption edge lies between 366 and 377 nm. Obtained value is in a good agreement with the literature data, where the value of the band gap for bulk anatase equals to 3.2 eV and for rutile is equal to 3.05 eV [8]. However, due to the thermal fluctuations, structural disorder as well as the surface states, semiconductor may absorb photons slightly below the absorption edge within a so called Urbach tail region [17]. Detailed description of the applied procedure may be find in our previous work [18]. Electrochemical impedance spectroscopy (Mott-Schottky analysis) is frequently applied to determine the type of conductivity, the flatband potential and the density of donors of TiO_2 made by Ti anodization [19, 20]. In the case of powders only determination of the conduction band edge potential as well as the type of conductivity was possible. TiO_2 is the *n*-type semiconductor and the flatband potential is equal to -0.35 ± 0.01 V vs. SHS at pH = 5. It depends on the pH and decreases with the increasing pH with 59 mV per pH unit [21]. Therefore, at the pH equal to 1, the flat band potential is higher and equals to -0.114 ± 0.01 V. Taking into account the *kT/e* correction for 298 K gives -0.140 ± 0.01 V. Detailed description of the applied procedure is given in our previous work [18].

Thanks to the spectroscopic measurements, the energetic scheme of a semiconducting particle in contact with the solution containing gold was determined (Fig. 1). When the semiconducting particle comes into a contact with the electrolyte without illumination, charge transfer occurs until Fermi level of electrons in the solid equilibrates with the reduction potential of the redox species in the electrolyte (which in fact is equivalent to the Fermi level of electrons in solution). Upon illumination, an electron from the valence band is promoted to the conduction band. Fermi level is split into two quasi levels, one for electrons and one for holes. Since the former occurs at lower potential than the reduction potential of gold, there is a driving force which let electrons from the conduction band reduce the $AuCl_4^-$ species to Au. Reduced gold is deposited onto the surface of TiO_2 particle. The Fermi level of such hybrid material will be located slightly below the conduction band edge potential of the semiconductor [22]. The electron at such potential is still able to reduce gold ions from the electrolyte. In order to ensure the efficient cathodic reaction (*i.e.* to avoid a recombination of photogenerated electron-hole pair), methanol was applied as a hole scavenger. At first step it is oxidized to the $^\bullet CH_2OH$ radical by a hole from the valence band. Next, the radical injects the electron to the conduction band and formaldehyde is produced. This phenomenon is known as a current doubling effect, since from one photon arise two electrons [9].
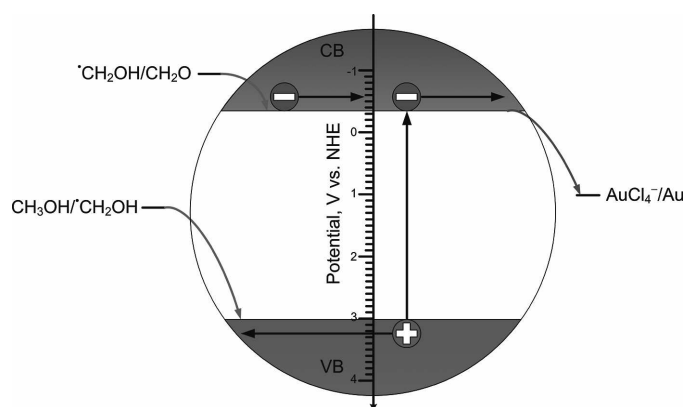

Fig. 1. The energetic scheme of the TiO_2 particle in contact with the electrolyte containing gold and methanol as a hole scavenger. The arrows represent the electron transfer (blue – reduction of gold, red – oxidation of the hole scavenger). The formal reduction potentials of employed species are marked on the figure. CB indicates the conduction band whereas VB the valence band

The presence of the gold nanoparticles onto the TiO_2 surface was confirmed using different techniques. First of all, the absorption spectra of the samples before filtration indicated the presence of Au. In Fig. 2 there is a peak at 587 nm which origins from the surface plasmon resonance of the gold nanoparticles. The wavelength of this peak depends on the dimensions of the gold deposit as well as its shape. Therefore, it changes with the reduction time and concentrations of the reagents. The surface plasmon resonance effect is also manifested by changing colors of the colloids after reduction (Fig. 6).
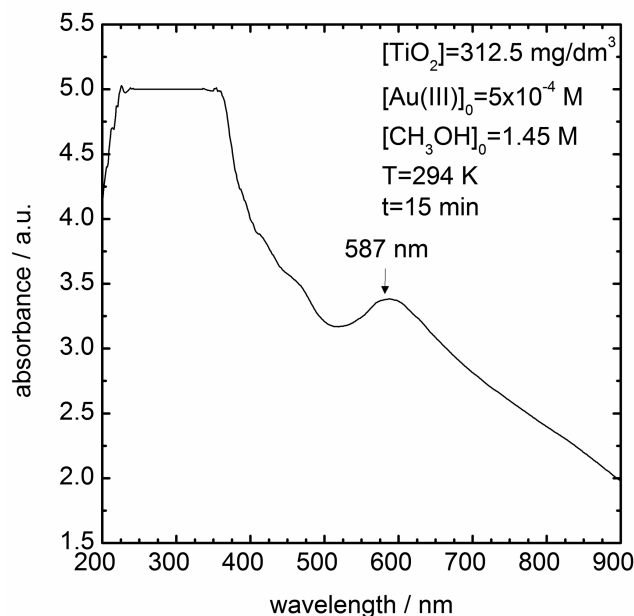

Fig. 2. The absorption spectrum of the sample containing colloid of TiO_2 with deposited gold nanoparticles

The presence of the gold deposit was also confirmed independently by the X-ray diffraction technique (Fig. 3). The intense peak from gold (111) plane is observed at 37.5 deg.
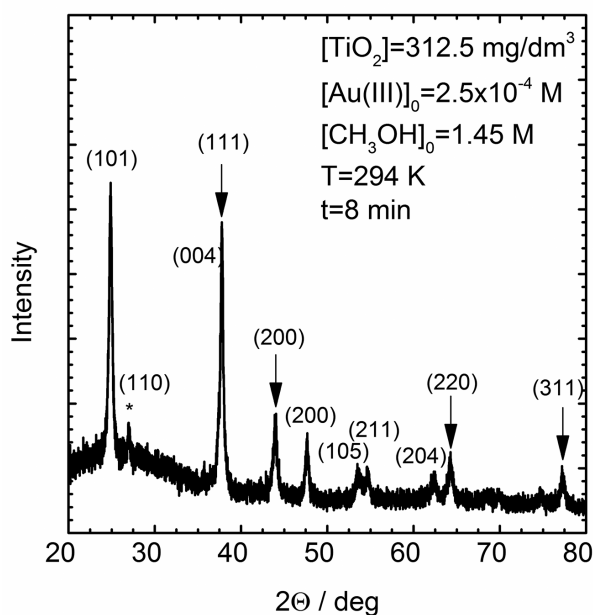

Fig. 3. X-ray diffraction pattern of the gold deposit onto TiO_2. The arrows indicate the peaks originated from the gold deposit, whereas the asterisk indicates the presence of rutile

The samples were also investigated using the scanning electron microscope (Fig. 4). It may be concluded, that the gold deposit is evenly distributed over the semiconducting material, and the average radius of the obtained nanoparticles is between 20 and 30 nm. The EDS analysis indicated the presence of only Ti, O, Au and C elements, where the latter originated from the applied carbon-made conductive substrate. Table 1 presents the detailed results of this analysis.
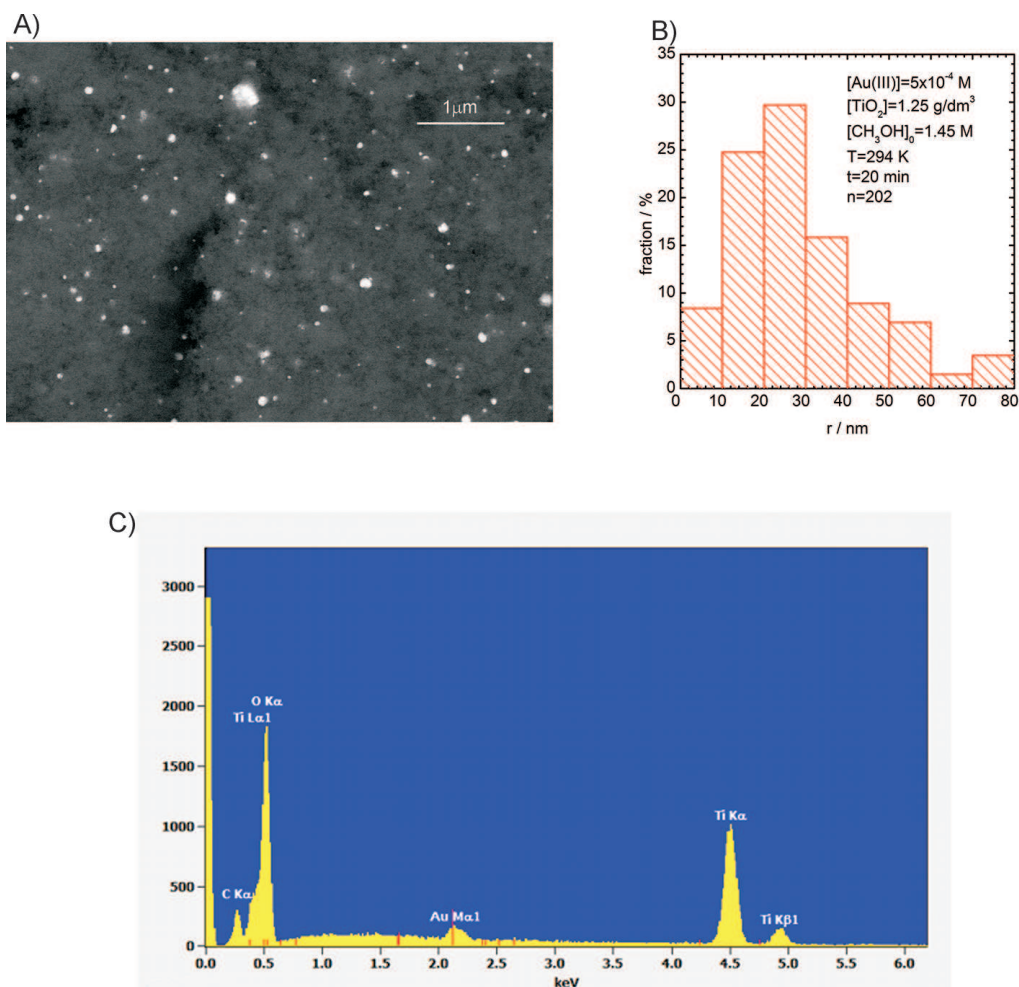
A)

B)

[Au(III)]=5x10^{-4} M
[TiO$_2$]=1.25 g/dm^3
[CH$_3$OH]$_o$=1.45 M
T=294 K
t=20 min
n=202

C)

Fig. 4. The microphotography (A), the size distribution (B) and the EDS analysis (C) of the gold deposit onto TiO$_2$

TABLE 1

The result of the EDS analysis of the sample

Element	Weight %	Atomic %
C	3.07	6.51
O	41.05	65.25
Ti	52.34	27.78
Au	3.54	0.46
Total	100	100

3.2. Kinetic studies – dark processes

The effect of the adsorption of Au(III) chloride complex ions onto the TiO$_2$ surface in the presence of methanol as well as the dark gold reduction by methanol was investigated. Obtained results are shown in Fig. 5. Methanol does not reduce gold in the absence of TiO$_2$ at the ambient temperature. After addition of titanium dioxide, Au(III) concentration decreased by 8% (after 3.5 hours). This effect was ascribed to the AuCl$_4^-$ adsorption onto TiO$_2$.

[Au(III)]$_0$=5x10^{-4} M
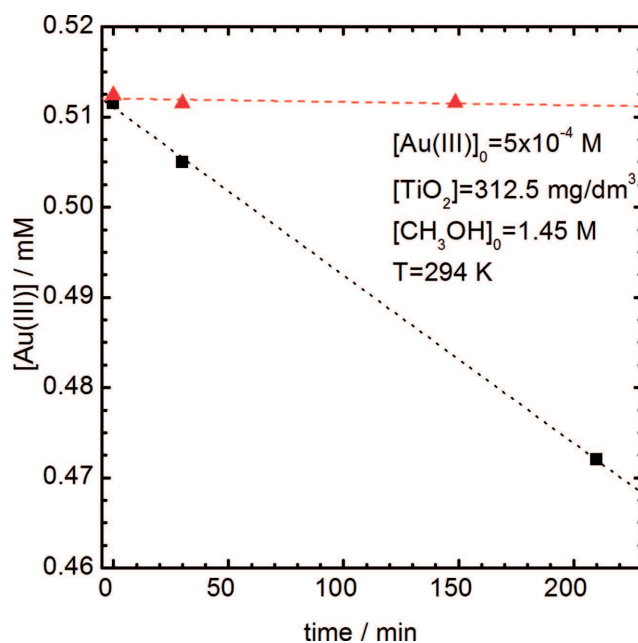[TiO$_2$]=312.5 mg/dm^3
[CH$_3$OH]$_0$=1.45 M
T=294 K

Fig. 5. The kinetics of the Au(III) removal from the solution in the dark. Black squares indicate the adsorption in the presence of methanol, red triangles correspond to the reduction of gold by methanol in the absence of TiO$_2$

3.3. Kinetic studies under UV-Vis illumination – the influence of the initial TiO_2 concentration

The rate of Au(III) ions photoreduction may be described as follows (Eq. 1):

$$\frac{d[AuCl_4^-]}{dt} = k\left[AuCl_4^-\right]^\alpha [TiO_2]^\beta [CH_3OH]^\gamma \qquad (1)$$

where α, β and γ are the reaction orders in respect to the Au(III), TiO_2 and CH_3OH concentrations respectively, and k is the rate constant. At first, the influence of the initial concentration of titanium dioxide on the rate of recovery of the Au(III) ions was investigated. Obtained kinetic curves have exponential character, which suggests first-order reaction. Therefore, measured data were approximated with Eq. 2, and the observed rate constant $k_{obs(1)}$ was determined from each fit:

$$[Au(III)] = [Au(III)]_0 \cdot e^{-k_{obs(1)} \cdot t} \qquad (2)$$

where $k_{obs(1)}$ has the form:

$$k_{obs(1)} = k\left[AuCl_4^-\right]^\alpha [CH_3OH]^\gamma \qquad (2a)$$

Obtained results as well as the pictures of Au loaded TiO_2 suspensions are gathered in Fig. 6.
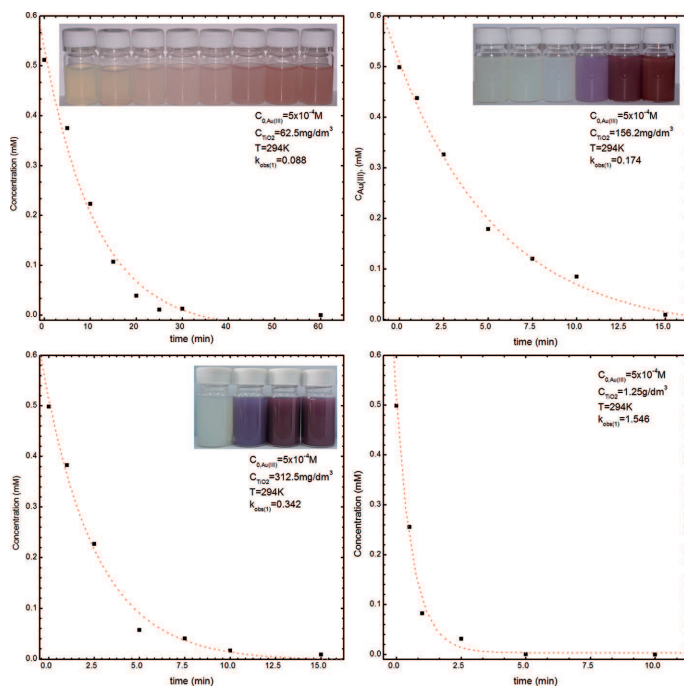

Fig. 6. The influence of the initial concentration of TiO_2 in the solution on the kinetics of the photoreduction of the Au(III) ions

One may see, that the rate of the Au(III) recovery strongly depends on the amount of applied TiO_2. For the highest concentration of the semiconductor the process is finished after about 10 minutes, whereas for the lowest one it takes more than 3 times longer. The coloration of the obtained colloids indicates the plasmon surface resonance effect (see also Fig. 2). At the lower concentration of TiO_2 more photons passes through the reaction vessel without generation of the electron-hole pairs. It also depends on the intensity of incident light and the geometry of the reaction vessel. The dimensions of the semiconducting particles also affect the number of electrons (and holes) reaching the interface [21]. Observed reaction is heterogeneous, therefore simply the greater surface area, the more active centers on the surface and faster reaction.

Fig. 7 shows the linear dependence between the observed rate constant $k_{obs(1)}$ and the amount of applied TiO_2 which confirms, that the reaction is first order in respect to the titanium dioxide concentration. Therefore, the expression for the reaction rate (Eq. 1) may be formulated as follows (Eq. 3):

$$V_0 = k\left[AuCl_4^-\right]^\alpha [TiO_2][CH_3OH]^\gamma \qquad (3)$$

This observation is contrary to the results of Borgarello et al. [10]. They found, that the rates of reduction of gold are almost independent on the amount of applied TiO_2. However, the concentrations of titanium dioxide in their case were 0.2, 1 and 2 g/dm^3 whereas in our case they were lower (i.e. 0.06, 0.16, 0.31 and 1.25 g/ dm^3). In addition, they used almost 2.5 times lower concentration of Au(III). Therefore, there was significant excess of semiconductor in comparison with gold, in such a case its influence on the reaction rate could be negligible.
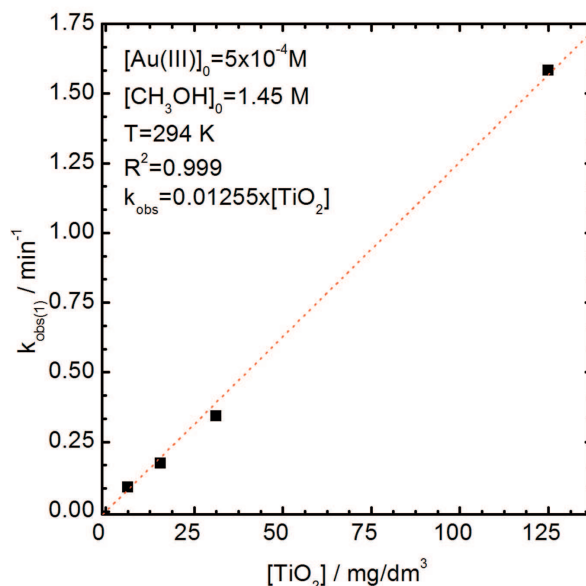

Fig. 7. The influence of the initial concentration of TiO_2 on the observed rate constant

3.4. Kinetic studies – the influence of the initial concentration of Au(III)

The influence of the initial concentration of Au(III) on the rate of its recovery was also investigated. Initial rate method was applied to determine the order of the reaction in respect to the Au(III) initial concentration. Equation 3 may be transformed as follows:

$$V_0 = k_{obs(2)}\left[AuCl_4^-\right]^\alpha \qquad (4)$$

where:

$$k_{obs(2)} = k\,[TiO_2][CH_3OH]^\gamma \qquad (5)$$

Equation 4 can also be written in the logarithmic form:
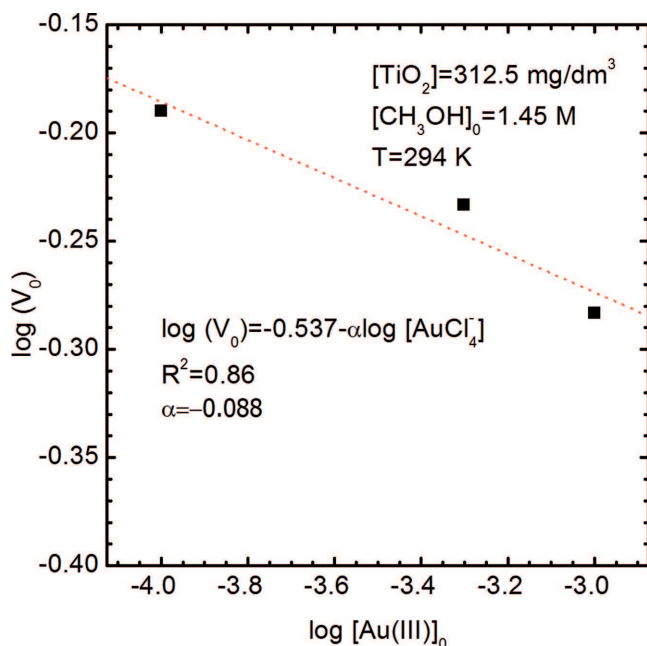
$$\log V_0 = \log k_{obs(2)} + \alpha \log\left[AuCl_4^-\right] \qquad (6)$$

Fig. 8. Determination of the order of the reaction in respect to gold by the graphical method

Fig. 9. The influence of the initial concentration of methanol on the observed rate constant

From the slope of the linear fit shown in Figure 8 the value of the reaction order (α) in respect to the Au(III) initial concentration was determined as close to 0. Such a result is rather surprising, since the kinetic curves in the Fig. 6 suggested, that the reaction order in respect to the Au(III) concentration should be equal to 1. It may indicate, that the observed effect (*i.e.* $\alpha \approx 0$) is only factitious and the reaction is inhibited by too low concentration of methanol.

3.5. Kinetic studies – the influence of initial concentration of methanol

The influence of the initial concentration of CH_3OH on the reaction rate is presented in Fig. 9. One may conclude, that in the range between 2.75 and 4M of methanol for the given concentrations of TiO_2 and Au(III) the rate constant does not change. It suggests, that there is an optimal hole scavenger concentration. For its lower values, the anodic reaction *i.e.* the methanol oxidation may be the rate-limiting step, which was observed when the influence of the initial gold concentration was investigated.
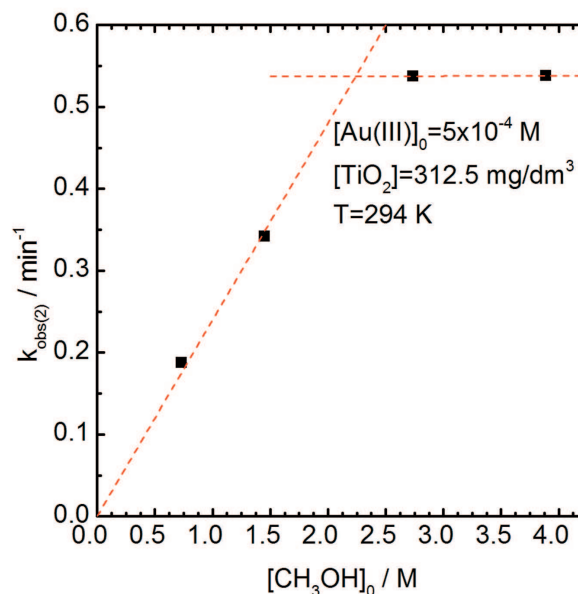
Linear character of dependency of $k_{obs(2)}$ is seen in the range from 0 to about 2.2M. It suggests that in this range, order of the reaction in respect to methanol equals to 1. Above this concentration, the mechanism of the reaction is probably different.

3.6. Gold recovery from dilute solutions – test

In order to determine the applicability of the photoreduction process in the case of the treatment of the metallurgical wastes, the yield of the gold recovery from diluted solutions was determined. The average concentration of gold in waste-water (KGHM Polska) is equal to 5 mg/dm³. In this work the gold recovery was performed using more diluted solutions *i.e.* containing 0.197 and 1.97 mg/dm³. 0.197 g of TiO_2 and 1 cm³ of methanol were applied and the total volume of the each sample was equal to 1 dm³. The samples were illuminated for 1 hour at radiant flux density 517 mW/cm² and vigorously stirred. Subsequently, suspensions were filtered through the 50 nm filter. The filtrate was analyzed on ICP-MS, while the Au loaded TiO_2 (Au@TiO_2) was leached with 25 cm³ of *aqua regia* and again the filtrate was analyzed to determine the amount of recovered gold. The results are gathered in the Table 2.
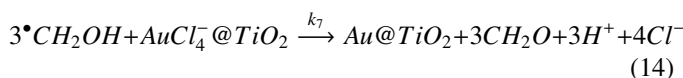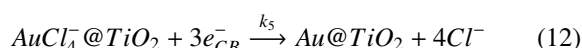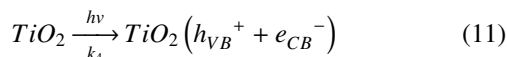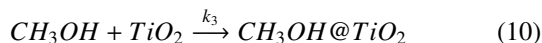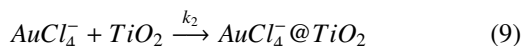
TABLE 2

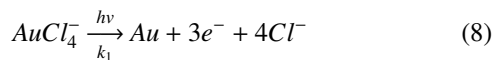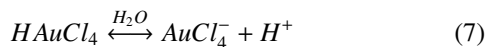Gold recovery from dilute solutions

Initial Au(III) concentration	Au(III) concentration in the filtrate after photoreduction	Au(III) concentration in the filtrate after Au@TiO_2 leaching	Photoreduction yield	Leaching yield	Net yield of the process
mg/dm³	mg/dm³	mg/dm³	%	%	%
1.97	0.81	0.89	59	77	45
0.197	0.05	0.08	73	58	42

4. Discussion

Taking into account the obtained results, the following set of reactions may be suggested in order to explain the mechanism of the observed phenomena:

$$HAuCl_4 \overset{H_2O}{\longleftrightarrow} AuCl_4^- + H^+ \tag{7}$$

$$AuCl_4^- \xrightarrow[k_1]{hv} Au + 3e^- + 4Cl^- \tag{8}$$

$$AuCl_4^- + TiO_2 \xrightarrow{k_2} AuCl_4^-@TiO_2 \tag{9}$$

$$CH_3OH + TiO_2 \xrightarrow{k_3} CH_3OH@TiO_2 \tag{10}$$

$$TiO_2 \xrightarrow[k_4]{hv} TiO_2\left(h_{VB}^+ + e_{CB}^-\right) \tag{11}$$

$$AuCl_4^-@TiO_2 + 3e_{CB}^- \xrightarrow{k_5} Au@TiO_2 + 4Cl^- \tag{12}$$

$$CH_3OH + h_{VB}^+ \xrightarrow{k_6} {}^\bullet CH_2OH + H^+ \tag{13}$$

$$3{}^\bullet CH_2OH + AuCl_4^-@TiO_2 \xrightarrow{k_7} Au@TiO_2 + 3CH_2O + 3H^+ + 4Cl^- \tag{14}$$

Gold reduction by light (Eq. 8) is a known process [23]. To confirm, that in the studied system such a reaction did not take place, the solution containing only Au(III) ions was irradiated at 375 nm. After 1h its concentration was unchanged, therefore it can be assumed that $k_1 \approx 0$.

Adsorption of both $AuCl_4^-$ and CH_3OH species onto TiO_2 (Eqs. 9 and 10) facilitates the charge transfer processes between the semiconductor and the electron donors and acceptors. Due to the positively charged surface of TiO_2 (measured zeta potential is equal to 35 mV at pH equal to 1), the adsorption of $AuCl_4^-$ ions should be favorable. The adsorption of methanol is also possible [25]. Equation 8 in turn describes the semiconductor excitation and the electron-hole pair generation which is the ultrafast process.

The next three reactions (Eqs. 12, 13 and 14) describe the Au(III) reduction via the electrons from the CB, methanol oxidation via the holes from the VB and electron injection to the CB from $^\bullet CH_2OH$ radical with subsequent Au(III) reduction respectively. The rates of reactions (12) and (13) are equal, and the electrons will not be generated if the holes are not consumed. Otherwise, the particles would be charged up and the reaction would be stopped [21].

Amount of TiO_2 applied in experiments was in excess. For insufficiently high concentration of methanol, zero value of the reaction order in respect to Au(III) was found. However, since this effect is rather factitious, first order differential equation in respect to Au(III) may be postulated as follows:

$$\frac{d[Au(III)]}{dt} = -k_5 \cdot [Au(III)]_0 \cdot [TiO_2]_0 \cdot [CH_3OH]_0 \tag{15}$$

As a solution of this differential equation, exponential function is obtained:

$$[Au(III)] = [Au(III)]_0 \cdot e^{-k_{obs} \cdot t} \tag{16}$$

under assumption:

$$k_5 \cdot [TiO_2]_0 \cdot [CH_3OH]_0 = k_{obs} \tag{17}$$

Proposed equation (16) is in good agreement with the measured kinetic curves.

The net yield of the gold recovery may be affected by several factors. First of all certain amount of gold loaded material could pass through the filter, therefore the photoreduction yield could be underestimated while the leaching yield may be overestimated for the bigger amount of gold in the solution. Utilization of the more coarse semiconductor will make the filtration easier, but it may decrease the reaction rate due to the lower surface area. Nevertheless, the net yield of the process may be limited by two factors: first, is the slow kinetics of the gold reduction at such low Au(III) concentrations. The second are parasitic reactions. Since the pH of the solution was equal to 1, there is the driving force for the H_2 evolution ($\Delta G^0 \approx -15$ kJ/mol). In addition, gold may behave as a catalyst for the hydrogen evolution which was observed by Mohamed *et al.* [11]. In addition, the solutions were in equilibrium with air, therefore certain amount of oxygen dissolved and may be reduced on either TiO_2 or Au deposit. The formal potential of the O_2 reduction to $HO_2^\bullet$ radical at pH=0 is equal to 0.12 V [25] that suggests a possibility of such reaction. However, it is difficult to evaluate the value of the oxygen reduction potential, since the concentration of the $HO_2^\bullet$ species is unknown. This radical may be further reduced to H_2O_2 and the mechanism depends on the light intensity [21]. Hydrogen peroxide in turn may oxidize the gold deposit. The remedy for these problems is to rise pH, then reduction potentials for both hydrogen and oxygen will be shifted towards more negative values. Purging the solution with the neutral gas will also decrease the concentration of dissolved oxygen. Another possibility is to find a semiconductor, which assures the reduction potential of the electron in the conduction band to be higher than the reduction potentials of both hydrogen and oxygen, and still lower than that of gold.

5. Conclusions

The kinetics of the gold recovery from illuminated (at wavelength 375nm using LED illuminator, Instytut Fotonowy, Poland) aqueous solutions using titanium dioxide nanopowder was determined. It was found, that the initial concentrations of titanium dioxide and methanol have a significant influence on the reaction rate. With respect to the initial gold concentration, first order kinetics was postulated which describes well the obtained kinetic curves. The recovery of about 45% of gold from diluted acidic solutions containing as much as 1.97 and 0.197 mg/dm^3 of Au(III) was demonstrated. Removal of oxygen from the solution as well as the pH increase should result in the improvement of the yield of recovery. On the other hand, application of other semiconductor (*i.e.* with more positive conduction band edge potential) could be an alternative solution. Application of more coarse semiconductor particles should also decrease the losses during the filtration.

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