

Supporting Information:

Palladium(II) chloride complex ions recovery from aqueous solutions using adsorption on activated carbon.

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Experimental:

Stability constants are given in the table below.

Table S1 Stability constants of chosen Pd(II) complexes

Reaction	Formation constants	reference
$PdCl_4^{2-} + 4HCN \rightleftharpoons Pd(CN)_4^{2-} + 4Cl^- + 4H^+$	$\beta_6=63.0$	1
$PdCl_4^{2-} + OH^- \rightleftharpoons [PdCl_3OH]^{2-} + Cl^-$	$\beta_1=16.34$	2
$[PdCl_3OH]^{2-} + OH^- \rightleftharpoons [PdCl_2OH_2]^{2-} + Cl^-$	$\beta_2=20.19$	
$[PdCl_2OH_2]^{2-} + OH^- \rightleftharpoons [PdClOH_3]^{2-} + Cl^-$	$\beta_3=23.04$	
$[PdClOH_3]^{2-} + OH^- \rightleftharpoons [PdOH_4]^{2-} + Cl^-$	$\beta_4=26.29$	

To determine the distribution of various complexes, pH dependent stability diagram was calculated. The obtained results are shown in Figure. S1.

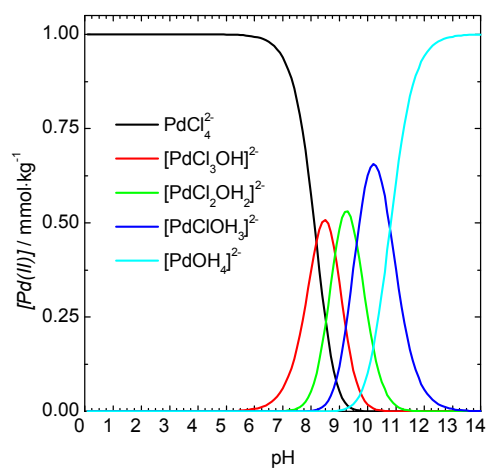


Figure. S1 Distribution of complexes as a function of pH. Chloride ions concentration $0.1 \text{ mol} \cdot \text{kg}^{-1}$.

Spectrophotometric determination of Pd(II) molar absorption coefficient.

To determine the concentration changes of Pd(II) chloride complexes with time, the spectrophotometric method was used in this study. As the reference material for spectrophotometric measurements, the solvents ($0.1 \text{ mol} \cdot \text{kg}^{-1} \text{ HCl}$) was used. The concentration change can be derived from the recorded absorbance. The UV-Vis spectra of Pd(II) chloride complex ions recorded for different concentrations are shown in Figure S2 A. It is seen that three absorption peaks are visible for the wavelengths of 233, 279 and 447 nm. The intensity of these peaks is proportional to the concentration of Pd(II) chloride complex ions, the relation is described by Lambert-Beer law.

$$A = \varepsilon \cdot l \cdot [\text{PdCl}_4^-] \quad (1)$$

where

A – absorbance, arbitrary unit

ε – absorption coefficient, $\text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{kg}$

l- optical path length, cm (in our experiment $l=1\text{cm}$)

However, to calculate the concentration of Pd(II) complex ions in the solution from the measured absorbance the molar absorption coefficient ε is required.

They were found to be $208.2 \pm 5.2 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{kg}$, $8113.4 \pm 59.1 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{kg}$ and $24338.7 \pm 764.8 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{kg}$ for the wave lengths 447nm, 279nm and 223nm, respectively. The coefficients were determined at the temperature 298K, in which all analysis were made.

Similar work was done with the Pd(II)-Cl-H₂O complexes complexes obtained by dissolution of Pd(II) in 1M HClO₄. For seven known concentrations of Pd(II) (see Figure S2 C) the absorbance at wavelengths 209 and 413nm was determined. Next, the molar absorption coefficients were derived directly from the obtained linear relationship Abs v.s. Pd(II) for the given wavelengths (Figure S2 D). They were found to be $12801 \pm 154 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{kg}$, $110.4 \pm 6.4 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{kg}$ for the wave lengths 209nm, and 413nm, respectively. The coefficients were determined at the temperature 293K, in which all analysis were made.

In case of Pd(II) stripping from AC after adsorption, $1 \text{ mol} \cdot \text{kg}^{-1}$ of HCl or $1 \text{ mol} \cdot \text{kg}^{-1}$ of HClO₄ was used. In case of HClO₄ application, significant changes in UV-VIS spectrum is observed. This is related with the formation of Pd(II)-Cl-H₂O complexes³. Recorded UV-Vis spectra for this system are shown in supplementary materials Figure S2 C

Consequently, at first, we determined the molar adsorption coefficient for palladium(II) chloride complex ions. For five known concentrations of Pd(II) the absorbance at wavelengths

233, 279 and 447 nm was determined. Next, the molar absorption coefficients were derived directly from the obtained linear relationship Abs v.s. $[PdCl_4^{2-}]$ for the given wavelengths (supplementary materials Figure S2 B).

It should be noted that absorption coefficient in fact depends on temperature⁴. However, all spectrophotometric measurements were performed at temperature of 298K. The applied spectrophotometer is equipped with thermostated measurement cell. Thanks to that it was possible to cool down each sample rapidly just before the measurement, and after that to return the sample to the reactor.

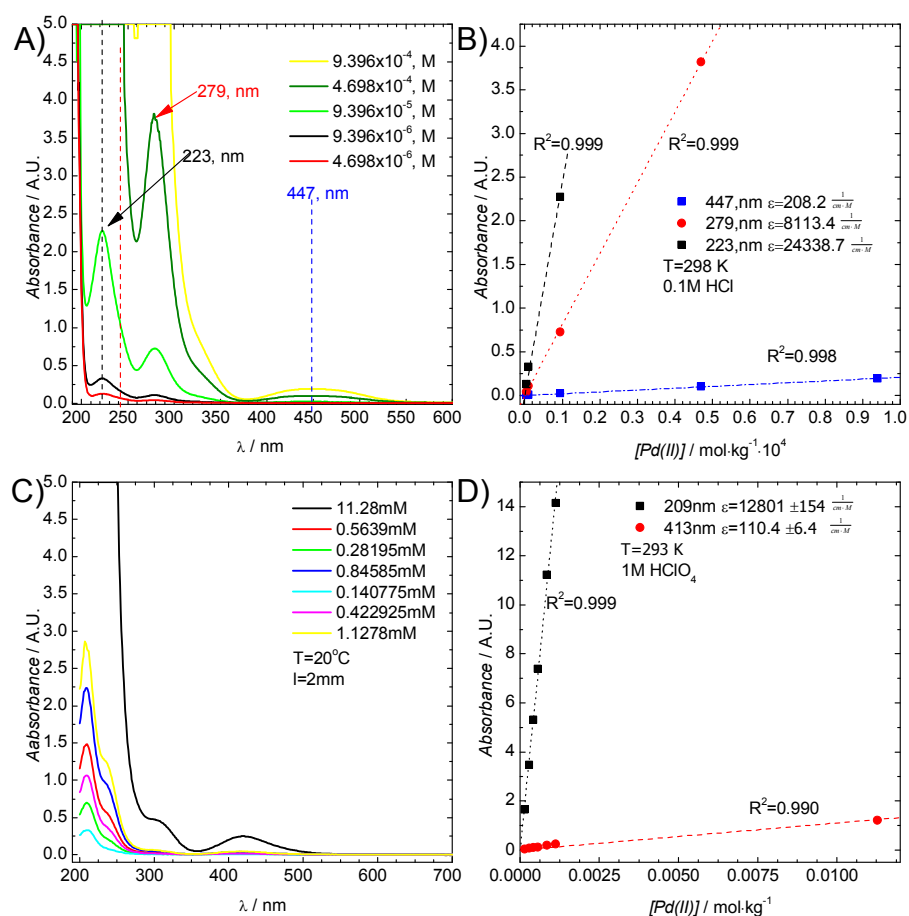


Figure S2 A) spectra of palladium(II) chloride complex ions for five different initial concentration, B) graphical determination of palladium(II) chloride complex ions molar absorption coefficient at temperature $T=298$ K, $[\text{Cl}^-]=0.1$, $\text{pH}=1$, C) spectra of palladium(II) aqua - chloride complexes ions for seven different initial concentrations,

D) graphical determination of palladium(II) chloride complex ions molar absorption coefficient at temperature T=293 K, [Cl⁻]=0, pH=0

They were found to be $208.2 \pm 5.2 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{kg}$, $8113.4 \pm 59.1 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{kg}$ and $24338.7 \pm 764.8 \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{kg}$ for the wave lengths 447nm, 279nm and 223nm, respectively. The coefficients were determined at the temperature 298K, in which all analysis were made.

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Langmuir isotherm determination:

The Langmuir isotherm can be written as follows:

$$\Theta = \frac{c_r}{K_L + c_r} \quad (2)$$

where:

K_L – constant coefficient

c_r – equilibrium concentration of the absorbed substance

Θ – surface coverage

In the typical case, the eq. (2) is used in the following form:

$$\frac{C_r}{C_0 - C_r} = \frac{K_L}{x_0} + \frac{C_r}{x_0} \quad (3)$$

where:

x_0 - maximum amount of Pd(II) adsorbed in the case of full coverage by the monolayer.

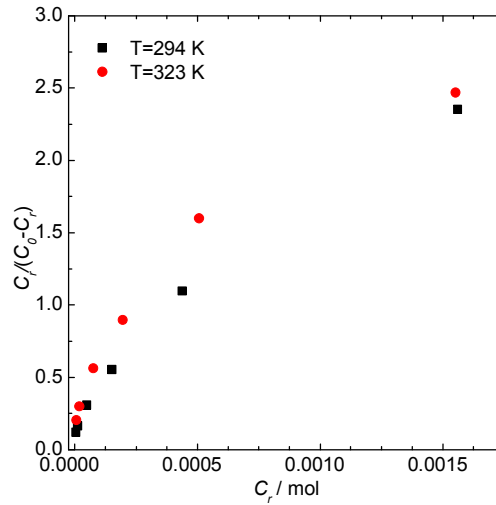


Figure S3 Langmuir isotherm determined for two different temperatures

Thermodynamics of adsorption.

Moreover, assuming, that the adsorption process can be written in the form of a chemical reaction:



the concentration ratio

$$K^* = \frac{[PdCl_4^{2-}]_{ads}}{[PdCl_4^{2-}]_{soln}} \quad (5)$$

K^* can be calculated from our experimental data. In this equation:

$[PdCl_4^{2-}]_{soln}$ is concentration of palladium(II) chloride complex ions in the solution, after achieving an equilibrium state in the system.

$[PdCl_4^{2-}]_{ads}$ is given by eq. (6).

The corresponding amount of Pd(II) adsorbed onto activated carbon can be calculated from the mass balance:

$$[PdCl_4^{2-}]_{ads} = [PdCl_4^{2-}]_0 - [PdCl_4^{2-}]_{soln} \quad (6)$$

where indexes 0 and *soln* correspond to the initial and the equilibrium concentrations. The capital letter K^* denotes the apparent equilibrium constant.

It is observed that an increase of Pd(II) chloride complex ions initial concentration results in a decrease of K^* . The influence of initial concentration of Pd(II) chloride complex ions on

the apparent equilibrium constant is shown in Figure S4. However, it can also be seen, that for the concentration above $1 \times 10^{-3} \text{ mol} \cdot \text{kg}^{-1}$ the apparent equilibrium constant calculated from eq. (5) does not change. Therefore, the K^* values for the initial concentration above $1 \times 10^{-4} \text{ M}$ should correspond to the equilibrium state between adsorbed species and the solution. Consequently, initial concentration of $[\text{PdCl}_4^{2-}]$ given in main text in Table 3 corresponds to this concentration ratio for which K^* is constant. The question is, if the suggested equilibrium (4) corresponds to the species assumed to take part in the adsorption process. Consequently, the final product of this reaction must be identified.

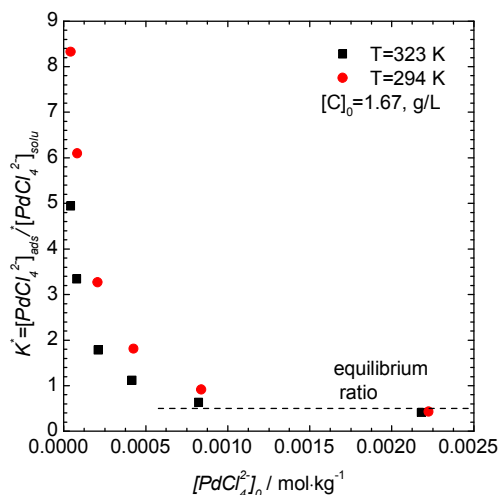


Figure S4 The influence of Pd(II) initial concentration, on the apparent equilibrium constant.

References

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4. Wojnicki, M.; Rudnik, E.; Szablowska, M.; Partyka, J., Spectrophotometric analysis of acidic copper(II) sulfate(VI) solutions. *Przem. Chem.* **2015**, 10, 1692-1696.