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Removal of Platinum and Palladium from Wastewater by Means of Biosorption on Fungi *Aspergillus* sp. and Yeast *Saccharomyces* sp.

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Abstract: The emission of platinum group metals from different sources has caused elevated concentrations of platinum and palladium in samples of airborne particulate matter, soil, surface waters and sewage sludge. The ability of biomass of *Aspergillus* sp. and yeast *Saccharomyces* sp. for removal of Pt(IV) and Pd(II) from environmental samples was studied in this work. The pH of the solution, the mass of biosorbent, and contact time were optimized. The Langmuir and Freundlich adsorption isotherms and kinetic results were used for interpretation of the process equilibrium of Pt(IV) and Pd(II) on both microorganisms. The maximal efficiency of retention of Pt(IV) on yeast and fungi was obtained at acidic solutions (pH 2.0 for Pt(IV) and pH 2.5–3.5 for Pd(II)). The equilibrium of the biosorption process was attained within 45 min. The best interpretation for the experimental data was given by the Langmuir isotherm. Kinetics of the Pt and Pd adsorption process suit well the pseudo-second-order kinetics model. Fungi *Aspergillus* sp. shows higher adsorption capacity for both metals than yeast *Saccharomyces* sp. The maximum adsorption capacity of fungi was 5.49 mg g⁻¹ for Pt(IV) and 4.28 mg g⁻¹ for Pd(II). The fungi possess the ability for efficient removal of studied ions from different wastewater samples (sewage and road run-off water). It was also demonstrated, that quantitative recovery of Pd from industrial wastes could be obtained by biosorption using *Aspergillus* sp.

Keywords: biosorption; precious metals; selective sorbent; isotherm adsorption models; environmental samples; run-off water

1. Introduction

Platinum and palladium due to their corrosion resistance, alloying ability and unique catalytic properties are used in various chemical productions and metallurgy. The electrical conductivity and durability of these metals are exploited in electronic applications for the production of multi-layer ceramic (chip) capacitors, and plating connectors and lead frames. Components inside computers and mobile phones are linked by connectors plated with a conductive layer of precious metal [1]. The production of PC computers, mobile phones and entertainment devices generates electronic waste (e-waste) [2]. However, the most important application of Pt and Pd is connected with the production of three-way catalytic converters for car engines [3]. The emission of these metals into the environment is connected with the operation of vehicle catalysts and their recycling. Elevated concentrations of Pt and Pd have been found in samples of airborne particulate matter, road and tunnel dust, and soil close to the roads [4–6]. Discharges of anthropogenic contamination to surface waters include both atmospheric deposition and stormwater runoff. Analysis of sewage sludge, surface waters, and ditch sediments demonstrated that the anthropogenic activity has resulted in elevated concentrations of these elements in such samples [6–8]. Globally, Nuss and Blengini [9] have found that anthropogenic

fluxes of Pd and Pt induced by the EU-28 countries might be greater than the respective global natural fluxes. Therefore, methods and processes for the removal of precious metals from waste have become necessary for the creation of the sustainable world [2]. To decrease the pollution with heavy metals, many processes like adsorption, precipitation, coagulation, ion-exchange, electro-dialysis have been developed [10]. One of the modern environmentally friendly technologies for the recovery of platinum group metals is biosorption [11].

A literature survey shows that microorganisms and native biomaterials, such as industrial and agricultural wastes and compounds derived from plant and animal tissues (e.g., lignin, tannin, chitin and chitosan), have been used as effective metal sorbents [11–15]. The majority of studies devoted to biosorption of Pt and Pd have been performed on biomass derived from plants and marine organisms [16–22] with various derivatives of chitosan preferred [16–18]. Very few microorganisms (some strains of bacteria, algae, fungi) [23–30] and *Tobacco mosaic virus* [13] have been used for this purpose. The recovery of platinum by a poly(ethylenimine) (PEI) modified biomass, prepared by attaching PEI onto the surface of inactive *Escherichia coli* biomass was reported by Won et al. [23]. This sorbent was tested for the removal of Pt from wastewater collected from an industrial laboratory. In the next paper Won et al. [24] used PEI-modified *Corynebacterium glutamicum* for recovery of Pd from the hydrochloric acid solution. Different species of *Desulfovibrio*, sulfate-reducing bacteria, have an ability to remove Pd(II) at pH 3 with its further reduction to Pd(0). The potential of such bacteria was also shown for the recovery of Pt and Pd from spent automotive catalyst leachates using hydrogen as the reductant [25]. Turner et al. [28] studied the uptake of platinum group elements by marine macroalgae, *Ulva lactuca* in sea water. Algae *Chlorella vulgaris* immobilized on cellulose have been used for the selective separation of Pt and Pd from environmental matrices [29]. A sulfothermophilic red microalga, *Galdieria sulphuraria*, living in hot sulfur springs, was used for simultaneous removal of gold and palladium from model wastewater [30]. Competitive biosorption of Pt(IV) and Pd(II) by *Escherichia coli* [26] and *Providencia vermicola* [27] was studied in model solutions.

Saccharomyces sp. is a single-cell yeast being used for the biofuel, bakery and beverage industries or for the production of biotechnological products. Such biomass possesses an ability to accumulate a broad range of heavy metals under a wide range of external conditions [31]. Mack et al. [32] have studied a kinetic of the sorption of Pt by immobilized *Saccharomyces cerevisiae* under acidic conditions. Godlewska-Żyłkiewicz [33] observed the highest retention of platinum (62%–65%) and palladium (95%) on free cells of baker's yeast at pH range from 1.6 to 2.2. A solid-phase extraction procedure using yeast *S. cerevisiae* immobilized in calcium alginate beads was proposed for the determination of Pd in road dust by electrothermal atomic absorption spectrometry (ETAAS) [34]. Yeast *S. cerevisiae* immobilized on a cellulosic resin was also used for selective on-line separation of Pt(IV) from river water prior to its chemiluminescent determination [35].

The fungal microorganisms are used extensively in a variety of large-scale industrial fermentation processes and production of gluconic acid, citric acid and many enzymes [36]. Waste biomass of free and immobilized cells of *Aspergillus* was used to remove heavy metal ions, such as cadmium, lead, chromium, iron and nickel from different matrices [37–39]. The first report on the bioaccumulation of platinum and other metals by fungi was published by Moore et al. [40]. The uptake efficiency of Pt equal to 85% at pH 2–3 within 48 h was reported. It was also demonstrated that *Aspergillus sp.* immobilized on cellulose resin Cellex-T could be used as a selective sorbent for solid-phase extraction of Pt and Pd from the complex matrix of road dust [41].

In this work, the ability of biomass of *Aspergillus sp.* and yeast *Saccharomyces sp.* for biosorption of Pt(IV) and Pd(II) from chloride aqueous solutions was studied. Studies comparing different sorbents will reveal the importance of metal-biomass specificity. The pH of the solution, the mass of biosorbent, and contact time have been studied in order to find the optimal parameters for biosorption of metals. The Langmuir and Freundlich adsorption isotherms have been used for interpretation of the process equilibrium of Pt(IV) and Pd(II) on *Aspergillus sp.* and *Saccharomyces sp.* The sorption kinetics of both ions on these microorganisms was also studied. The method was tested for the removal of these

precious metals from different wastewater samples (sewage and road run-off water). Moreover, it was demonstrated that the quantitative recovery of Pd from industrial wastes (anode slime) might be obtained using fungal biosorbent.

2. Materials and Methods

2.1. Instrumentation and Measurement Conditions

A Solaar M6 (Thermo Electron Corporation, Gloucester, UK) atomic absorption spectrometer equipped with an electrothermal atomizer (ETAAS) and a Zeeman background correction system was used. Hollow cathode lamps (CPI International, Santa Rosa, USA) were operated at a current of 10 mA for Pt and 6 mA for Pd. The absorbance signals were measured with 0.5 nm spectral bandpass at 265.9 nm and 247.6 nm for Pt and Pd, respectively. Pyrolytically coated graphite tubes were used for atomization of analytes. The time/temperature program for the Pd determination was: drying at 100 °C for 30 s, 110 °C for 20 s, ashing at 1100 °C for 20 s and atomization at 2200 °C for 3 s. The time/temperature program for the Pt determination was: drying at 100 °C for 30 s, 110 °C for 20 s, ashing at 1200 °C for 20 s and atomization at 2500 °C for 3 s.

An inoLab pH Level 1 (WTW, Weilheim, Germany) pH meter equipped with an electrode SenTix 21 (WTW, Weilheim, Germany) was used to measure the pH. A centrifuge MPW 312 (MPW Med. Instruments, Warszawa, Poland) was used for separation of biomass from the supernatant. A Hitachi Model S-3000N (Hitachi, Tokyo, Japan) scanning electron microscope equipped with an energy dispersive X-ray microanalysis (EDX) was used to detect metals in the cells.

2.2. Reagents and Solutions

Standard solutions of Pt as a hexachloroplatinic (IV) acid (30%) (POCH, Gliwice, Poland) and Pd as PdCl₂ (1 g L⁻¹) (SPC SCIENCE, Baie D'Urfé, Quebec, Canada) were used. Stock solutions of Pd(II) and Pt(IV) (1 µg L⁻¹) in 1 mol L⁻¹ HCl were prepared daily from standard solutions. The appropriate working solutions of Pd(II) and Pt(IV) used for biosorption studies were prepared by dilution with Milli-Q water (Millipore, Burlington, USA). Hydrochloric acid (37% Trace Select, Fluka, Lyon, France) and sodium hydroxide (analytical grade, Standard, Lublin, Poland) were used for adjustment of pH of solutions. Nitric acid (65% Trace Select, Fluka, Lyon, France) and hydrochloric acid (37% Trace Select, Fluka, Lyon, France) were used for digestion of samples.

A growth media were Czapek dox agar (Fluka, Buchs, Switzerland) containing sucrose (30 g L⁻¹), agar (15 g L⁻¹), NaNO₃ (3 g L⁻¹), K₂HPO₄ (1 g L⁻¹), KCl (0.5 g L⁻¹), MgSO₄·7H₂O (0.5 g L⁻¹), FeSO₄·7H₂O (0.01 g L⁻¹), Yeast extract (Fluka, Buchs, Switzerland) (a mixture of amino acids, peptides, water soluble vitamins and carbohydrates), YPG agar (Fluka, Buchs, Switzerland) and α-D-glucose (Aldrich, Hamburg, Germany).

2.3. Preparation of Cells

Aspergillus sp. isolated from the soil was prepared according to the procedure described in Reference [42]. In short, it was inoculated on solid nutrient medium onto Petri dishes and aerobically incubated at 30 °C for 72 h. The growth medium: 50 g L⁻¹ of Czapek 146 dox agar and 3.89 g L⁻¹ of Yeast extract was sterilized by autoclaving (20 min at 121 °C). *Saccharomyces* sp. (*Saccharomyces cerevisiae*, Baker's yeast, type II, (Sigma-Aldrich, Hamburg, Germany) was grown aerobically at 37 °C for 96 h in a pre-sterilized (20 min at 121 °C) solid medium containing: yeast extract, 1% (w/v); peptone, 2% (w/v); glucose, 2% (w/v) and agar, 2% (w/v). Biomass of fungi and yeast was scraped from the growth medium and then washed with 5 mL of 0.12 mol L⁻¹ HCl and 5 mL of Milli-Q water in order remove growth solution residues and to stabilize the surface activity.

2.4. Biosorption Studies

The biosorption of Pt(IV) and Pd(II) was studied under batch experimental conditions using 0.1 g of wet mass (WM) of biosorbent (fungal or yeast cells) and 5 mL of 0.1 mg L⁻¹ of Pt(IV) or

0.075 mg L⁻¹ Pd(II) solutions. The pH of Pt(IV) or Pd(II) solutions was adjusted to the desired value with 0.1 mol L⁻¹ HCl or 0.1 mol L⁻¹ NaOH. Next, 0.1 g of wet biomass was added to 5 mL of such solution. The suspension of biomass was stirred for 60 min at temperature (25 ± 1) °C on a magnetic stirrer and next centrifuged at 4000 rpm (550× g) for 10 min. Concentrations of Pd(II) and Pt(IV) in supernatants were determined by ETAAS using external calibration graph. In some cases, the pH of supernatants was also measured. The effect of initial pH on the retention of analyte on biomass was studied in the pH range from 0.5 to 11. The optimum pH of the Pt solutions was equal to 2 (for fungi and yeast), while the optimum pH of the Pd solutions was 2.5 for yeast or 3.5 for fungi. These pH values were used throughout all biosorption experiments. The effect of biosorbent dosage was studied in the range from 0.025 to 0.5 g (wet mass). The contact time was varied between 5 min and 24 h.

To examine the adsorption model, the solutions of Pt and Pd of initial concentration between 0.01 mg L⁻¹ and 20 mg L⁻¹ and optimal pH (pH 2 for Pt(IV) and pH 2.5 and 3.5 for Pd(II) on yeast and fungi, respectively) were stirred with 0.1 g of wet biomass for 45 min at 25 °C. Afterward, the samples were centrifuged at 4000 rpm for 10 min. The initial and final concentrations of Pt and Pd in solutions were determined by ETAAS. Each experiment was conducted in triplicate. In order to recalculate the obtained results for dry biosorbent mass, five portions of wet biomass (0.4 g) were dried at 60 °C overnight [37,38] and weighted. It was calculated that 0.1 g of wet biomass is equal to 0.013 g of dry biomass.

The efficiency of retention of analyte on biomass and metal uptake by biomass were calculated from the following equations [43]:

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_{exp} = \frac{V(C_0 - C_e)}{w} \quad (2)$$

where E is the efficiency of analyte retention (in %), C_0 is the initial concentration of metal in solution (mg L⁻¹), C_e is the equilibrium concentration of metal in solution after the biosorption process (mg L⁻¹), q_{exp} is the experimental equilibrium uptake (mg g⁻¹ of dry weight), V is the solution volume, and w is the dry weight of biosorbent (g).

Modeling of the isotherm data was attempted using the Langmuir [44] and Freundlich [45] models, which are represented by the following equations:

$$\text{Langmuir model : } q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (3)$$

$$\text{Freundlich model : } q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

where q_e is the amount of adsorbed metal (mg g⁻¹), C_e is the equilibrium (final) concentration of the metal in solution (mg L⁻¹), q_{max} is the maximum monolayer sorption capacity (mg g⁻¹), b is the Langmuir equilibrium constant (L mg⁻¹), K_F is an empirical constant that provides an indication of the adsorption capacity of biomass, and n is the Freundlich constant, that indicates the intensity of adsorption.

The sorption isotherms were plotted by varying the analyte uptake (q) by biosorbents to the final concentration of Pt or Pd in solution after the biosorption process (C_e).

Kinetic models are used to identify the adsorption mechanism type in a studied system. Moreover, kinetics studies are necessary to define the optimum conditions for the metal removal process. The pseudo-first and pseudo-second-order models are most often used for studies of biosorption kinetics of platinum group metals [27].

Linear pseudo-first-order model used in this study was:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

Linear pseudo-second-order model was:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where q_t and q_e (mg g^{-1}) are the amounts of adsorbed ion a given time and at equilibrium state, respectively, k_1 —is the first-order kinetic rate, k_2 —is the second-order kinetic rate ($\text{g mg}^{-1} \text{min}^{-1}$).

2.5. SEM-EDX Analysis

Scanning electron microscopy with energy dispersive X-ray (SEM-EDX) provides information about the presence of various elements in the biosorbent. In this work, 5 mL of Pt(IV) or Pd(II) solutions of 20 mg L^{-1} ($100 \text{ }\mu\text{g}$) were added separately to 0.1 g (wet mass) of fungal cells and gently stirred for 72 h. Next, the cells were centrifuged and the supernatant was discarded. Before SEM-EDX analysis all samples were frozen in liquid nitrogen.

2.6. Samples Used for Recovery Studies

Samples of sewage were obtained from the sewage treatment plant in Bialystok (Poland). Samples of road run-off were taken from the retention reservoir at the ring road of Bialystok. Pt (100 ng mL^{-1}) and Pd (75 ng mL^{-1}) was added to the samples and left for 2 h for equilibration. Then samples were filtered through PVDF discs ($0.45 \text{ }\mu\text{m}$, Whatman, Maidstone, Wielka Brytania), adjusted to the required pH with 0.1 mol L^{-1} HCl and stirred with 0.1 g of wet biomass for 2 h. The biomass was separated by centrifugation (10 min, 4000 rpm), washed with 0.01 mol L^{-1} HNO_3 and digested in quartz crucibles with concentrated HNO_3 on a laboratory heater. The digested samples were diluted appropriately with MQ water before determination of metals by ETAAS.

The samples of anode slime (200 mg) obtained from the Institute of Non-Ferrous Metals in Gliwice (Poland) were digested in Teflon vessels in a closed digestion microwave system ETHOS PLUS (Milestone, Sorisole, Italy) with 8 mL of *aqua regia*. The residue was separated and solutions were transferred into quartz crucibles and evaporated at a hot-plate near to dryness with concentrated HCl ($3 \times 2 \text{ mL}$) and next diluted with Milli-Q water to 15 mL. Samples were filtered through PVDF filters, adjusted to the required pH and stirred with 0.1 g of wet biomass for 2 h. Next, the biomass was separated by centrifugation (10 min 4000 rpm) and concentrations of Pt and Pd in supernatants were determined by ETAAS.

3. Results and Discussion

3.1. Effect of pH on Biosorption

The effect of an initial pH on the biosorption of Pt(IV) and Pd(II) on fungal and yeast biomass was studied at the pH range from 0.5 to 11.0 (Figure 1). The highest efficiency of biosorption of Pt(IV) ions on yeast cells was observed at the pH range from 1.8 to 3.5, while on fungal cells was nearly quantitative (90%–96%) at the pH range from 2.0 to 11.0. The maximal efficiency of biosorption of Pd(II) ions on yeast (85%) was obtained at a very narrow range of pH from 2.0 to 3.0. Low biosorption of analyte occurred both in a strong acidic medium and in solutions of pH above 4.0. The biosorption of Pd(II) on fungal cells reached the highest values at a pH range of 4.0–11.0. In all cases, the biosorption of Pt(IV) and Pd(II) was lower in strong acidic solutions (at $\text{pH} < 1.8$). It is apparent that different attractions are responsible for biosorption of metals on the studied microorganisms. Further experiments on biosorption of Pt(IV) ions were performed at pH 2 on yeast and fungal cells, while of Pd(II) ions at pH 2.5 on yeast and pH 3.5 on fungal cells.

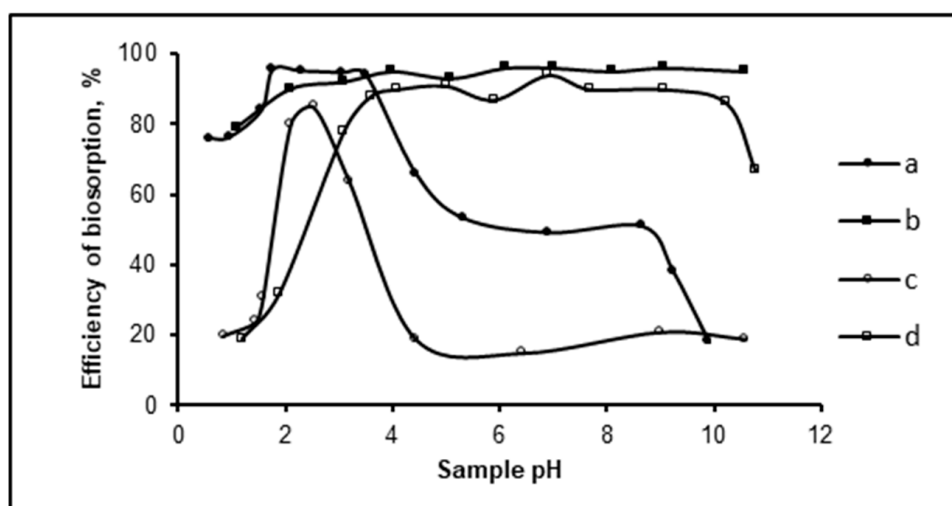


Figure 1. Influence of sample pH on the efficiency of biosorption of Pt (0.1 mg L^{-1}) and Pd (0.075 mg L^{-1}) on yeast *Saccharomyces* sp. and fungi *Aspergillus* sp. (contact time 60 min): a—Pt(IV) on yeast; b—Pt(IV) on fungi; c—Pd(II) on yeast; d—Pd(II) on fungi.

Several researchers have also investigated the effect of pH on the biosorption of Pt(IV) and Pd(II) using different microbial mass and comparable results have been reported (Table 1). For instance, biosorption of Pt(IV) [32,33] and Pd(II) [33] on free cells of baker's yeast was maximal in acidic media. The similar effect of pH on the Pd(II) biosorption was observed on yeast immobilized in calcium alginate. The biosorption of Pd(II) ions on this sorbent reached the highest values at a pH range 1.0–2.5 and significantly decreased for less acidic solutions [34].

During the course of the experiments, the pH of the suspensions before and after the biosorption process of each metal was also measured. It was found that the pH of Pt(IV) and Pd(II) solutions incubated with both microorganisms at pH 2–2.5 slightly increased ($\Delta\text{pH} \sim 0.14$), while the pH of suspension incubated without metal ions maintained almost constant ($\Delta\text{pH} \leq 0.05$). A dissimilar effect was observed during biosorption of Pd(II) ions by fungal cells (at pH 3.5), as the pH of suspension decreased by 0.4 pH unit, while the pH of suspension incubated without metal ions decreases only by 0.3 pH unit. These phenomena should be discussed in terms of reactions of Pt(IV) and Pd(II) ions in aqueous solutions.

It is known that the chemical form of platinum group metals in solutions at the equilibrium state depends on the medium type, the concentration of chloride ions and temperature. In strong acidic media anionic chlorocomplexes of Pt(IV) (as PtCl_6^{2-}) and Pd(II) (as PdCl_4^{2-}) predominate. With the decrease in solution's acidity, the proceeding aquation and hydrolysis reactions cause a formation of different aquachloro- and aquahydroxocomplexes of platinum and palladium ($\text{PtCl}_5(\text{H}_2\text{O})^-$, PdCl_4^{2-} , $\text{PdCl}_3(\text{H}_2\text{O})^-$, PdCl^+ and $\text{Pd}(\text{OH})_2$), as was shown in References [19,46]. Additionally, the chemical composition and acidity of the solution influence the activity and accessibility of functional groups present at the surface of the cell's wall.

Table 1. Biosorption conditions and parameters of isotherm adsorption models of Pd(II) and Pt(IV) on various microorganisms.

Microorganism	Biosorption Conditions	Parameters of Equilibrium Isotherm Models		Application	Ref.
		Langmuir	Freundlich		
<i>Tobacco mosaic virus</i>	Sample pH: 5–5.5 contact time: 1 h biomass: 0.038 g L ⁻¹ temperature: 50 °C	(Pd) R ² : 0.95 q _{max} : 368.21 mg g ⁻¹ b: 0.36 L mg ⁻¹	-	Standard solutions	[13]
<i>Tobacco mosaic virus-wild</i>		(Pd) R ² : 0.98 q _{max} : 312.87 mg g ⁻¹ b: 0.12 L mg ⁻¹			
<i>Escherichia coli</i>	Sample pH: 3 contact time: 24 h biomass: 0.09 g temperature: 25 °C	(Pd) R ² : 0.991 q _{max} : 141.1 mg g ⁻¹ b: 0.014 L mg ⁻¹	-	Standard solutions	[14]
Polyallylamine hydrochloride modified <i>Escherichia coli</i>		(Pd) R ² : 0.969 q _{max} : 265.3 mg g ⁻¹ b: 0.042 L mg ⁻¹	-		
Polyethylenimine (PEI)-modified <i>Escherichia coli</i>	Sample pH: extremely acidic condition contact time: 60 min biomass: 0–1.8 g temperature: 25 °C	(Pt) R ² : 0.965 q _{max} : 108.8 mg g ⁻¹ b: 0.0014 L mg ⁻¹	(Pt) R ² : 0.952 K _F : 1.465 L g ⁻¹ n: 1.835	ICP wastewater	[23]
<i>Escherichia coli</i>	Sample pH: 1.2 contact time: 24 h biomass: 0.06 g temperature: 25 °C	(Pd) R ² : 0.962 q _{max} : 38.87 mg g ⁻¹ b: 0.48 L mg ⁻¹ (Pt) R ² : 0.991 q _{max} : 45.65 mg g ⁻¹ b: 0.58 L mg ⁻¹		Single and binary standard solutions	[26]
<i>Desulfovibrio desulfuricans</i>	Sample pH: 3 contact time: 20 min biomass: 0.0015 g temperature: 30 °C	(Pd) q _{max} : 125.0 mg g ⁻¹ b: 1.21 L mg ⁻¹ (Pt) q _{max} : 62.5 mg g ⁻¹ b: 0.50 L mg ⁻¹	(Pd) K _F : 69.7 L g ⁻¹ n: 4.24 (Pt) K _F : 24.2 L g ⁻¹ n: 3.43	Standard solutions	[25]

Table 1. Cont.

Microorganism	Biosorption Conditions	Parameters of Equilibrium Isotherm Models		Application	Ref.
		Langmuir	Freundlich		
<i>Desulfovibrio fructodivorans</i>		(Pd) q_{\max} : 119.8 mg g ⁻¹ b: 0.12 L mg ⁻¹	(Pd) K_F : 10.4 L g ⁻¹ n: 2.35		[25]
		(Pt) R ² : q_{\max} : 32.3 mg g ⁻¹ b: 1.17 L mg ⁻¹	(Pt) K_F : 20.3 L g ⁻¹ n: 7.12		
<i>Desulfovibrio vulgaris</i>		(Pd) q_{\max} : 106.3 mg g ⁻¹ b: 0.66 L mg ⁻¹	(Pd) K_F : 41.9 L g ⁻¹ n: 3.73		[25]
		(Pt) q_{\max} : 32.1 mg g ⁻¹ b: 0.42 L mg ⁻¹	(Pt) K_F : 16.8 L g ⁻¹ n: 5.92		
<i>Providencia vermicola</i>	Sample pH: 4 contact time: 3 h biomass: 0.075 g temperature: 30 °C	(Pd) R ² : 0.95 q_{\max} : 119 mg g ⁻¹ b: 0.1 L mg ⁻¹	(Pd) R ² : 0.78 K_F : 1.27 L g ⁻¹ 1/n: 1.07	Single and binary standard solutions	[27]
		(Pt) R ² : 0.97 q_{\max} : 30.2 mg g ⁻¹ b: 0.13 L mg ⁻¹	(Pt) R ² : 0.72 K_F : 0.16 L g ⁻¹ 1/n: 1.06		
<i>Saccharomyces</i> sp.	Sample pH: (Pd) 2.5, (Pt) 2 contact time: 45 min biomass: 0.1 g (wet), 0.013 g (dry) temperature: 25 °C	(Pd) R ² : 0.9874 q_{\max} : 0.042 mg g ⁻¹ b: 0.0204 L mg ⁻¹	(Pd) R ² : 0.797 K_F : 0.095 L g ⁻¹ n: 1.630	Standard solutions	This study
		(Pt) R ² : 0.9860 q_{\max} : 0.185 mg g ⁻¹ b: 0.0068 L mg ⁻¹	(Pt) R ² : 0.975 K_F : 0.286 L g ⁻¹ n: 1.505		
<i>Aspergillus</i> sp.	Sample pH: (Pd) 3.5, (Pt) 2 contact time: 45 min biomass: 0.1 g (wet), 0.013 g (dry) temperature: 25 °C	(Pd) R ² : 0.9823 q_{\max} : 4.277 mg g ⁻¹ b: 0.0021 L mg ⁻¹	(Pd) R ² : 0.805 K_F : 2.842 L g ⁻¹ n: 1.485	Run-off water, sewage, anode slime	
		(Pt) R ² : 0.0010 q_{\max} : 5.488 mg g ⁻¹ b: 0.0006 L mg ⁻¹	(Pt) R ² : 0.962 K_F : 1.766 L g ⁻¹ n: 1.164		

The high biosorption of platinum and palladium on yeast cells at pH range from 1.8 to 3.0 occurs probably through electrostatic attractions between the protonated functional groups of the sorbent and their anionic chlorocomplexes. It was reported that the zeta potential of *Saccharomyces* sp. immobilized on cone biomass was positive at pH 2.0 and the overall surface of the biomass was negatively charged at the pH values between 3.0 and 7.0 [47]. Other studies [48] have shown, that the surface of free cells of yeast was negatively charged for pH higher than 3.5 favoring adsorption of cationic species. Lower sorption of Pt(IV) and Pd(II) observed in strong acidic medium is an effect of competing of chloride ions and anionic chlorocomplexes of platinum and palladium present in the solution for the protonated functional groups of yeast's cell wall. The results presented above imply that the biosorption mechanism could be based on electrostatic attractions between analytes and microorganisms. In our former studies [35] platinum was efficiently (83%) removed from immobilized yeast with 3 mol L⁻¹ NaCl, showing that ion-exchange mechanism could be also involved in the metal binding to biomass. However, in our opinion, other kinds of interactions may also participate in biosorption of Pt, as above 91% of platinum was recovered from the same sorbent with an acidic solution of thiourea [34]. A complex mechanism, likewise, initial non-specific sorption of platinum ions due to electrostatic attractions between protonated sorbent and platinum anions followed by chemical sorption of Pt(IV) by *S. cerevisiae* was suggested by Mack et al. [32]. Kim et al. [26] stated that primary amines present in the biomass are responsible for selective biosorption of Pd(II) and Pt(IV) by *E. coli*. Moreover, the affinity of amines toward the Pd(II) was much higher than for Pt(IV) ions.

The attractions between Pt(IV), Pd(II) and fungi cells are also complex in their nature including electrostatic attractions of anionic complexes to the positively charged amino groups (at a lower pH range) and complexation of neutral or cationic forms of their aqua- and aquahydroxochloro-complexes to functional groups of cell wall from neutral and basic solutions. The effect of modification of a fungal cell wall by acidic solution has to be also considered. The initial studies (data not shown) were performed on the effect of modification of fungal cells (washing with MQ water, washing with 0.12 mol L⁻¹ HCl and next MQ water, boiling with 0.5 mol L⁻¹ NaOH and next washing with MQ water) on the biosorption of platinum and palladium. The experiments showed that biosorption of both metals from solutions of pH > 4 on the fungi washed with water and modified with NaOH was significantly lower (biosorption efficiency from 5% to 40%) than on the fungi modified with an acid solution (biosorption efficiency > 90%). The efficient retention of Pt and Pd on fungi treated by each procedure occurred from solutions of pH 2–4. These results cannot be easily compared to literature data as the research on biosorption of precious metals on fungi is mainly focused on gold [9]. Gold and other heavy metals, e.g., copper, cadmium and lead, are retained on *Aspergillus* sp. biomass in weakly acidic or neutral pH [2,37–39]. Hence, in our further work, in order to achieve better selectivity of removal of precious metals from samples containing other metals, the studies were carried out at pH 2.0 for Pt(IV) and 3.5 for Pd(II). At pH ≥ 3 biosorption of Pd(II) ions in the form of PdCl⁺ and Pd(OH)₂ species [19] may occur. The increase of the concentration of H⁺ ions in cells suspension after the biosorption process suggests that Pd(II) ions could be bound by an ion-exchange mechanism.

3.2. Effect of Contact Time and Biomass Dosage

The effect of contact time on the biosorption of Pt(IV) and Pd(II) ions on yeast and fungal biomass was studied in the range from 5 min to 24 h. About 60% of Pd(II) was taken up by yeast within the first 10 min, and after 45 min the amount of biosorbed Pd(II) reached a constant value of 90.1% ± 0.7%. The biosorption of Pt(IV) on yeast was faster, as above 93% of the initial amount of ions was retained within 5 min of contact time. These results are consistent with the results of Mack et al. [32], who observed the rapid platinum removal during the first 5 min. Next, the process, identified as chemical sorption, was much slower. The efficiency of biosorption of Pd(II) and Pt(II) on fungi within 15 min reached 97% and 91%, respectively. Figure 2a reveals that over 80% of biosorption of both ions occurred within 15–20 min and the equilibrium was attained within 45 min. The reproducibility of the biosorption process (n = 6) on fungal biomass was 89.0 ± 1.4% for Pt(IV) and 96.0 ± 3.8% for

Pd(II), while on yeast biomass was $94.1 \pm 1.6\%$ for Pt(IV) and $84.3 \pm 4.7\%$ for Pd(II). There was no remarkable change in the amount of metal taken up after 24 h of contact time. The time required to reach the biosorption equilibrium of other metals ions on fungi *Aspergillus* sp. [37–39] and yeast *Saccharomyces* sp. [47–49] was longer than that found in this work. The equilibrium time between platinum or palladium and moss biomass was comparable [21] but this time was much longer for other biomaterials (in the range 24–96 h) [17,20,22]. In practice, a sorbent with a faster uptake is better for the removal of metals.

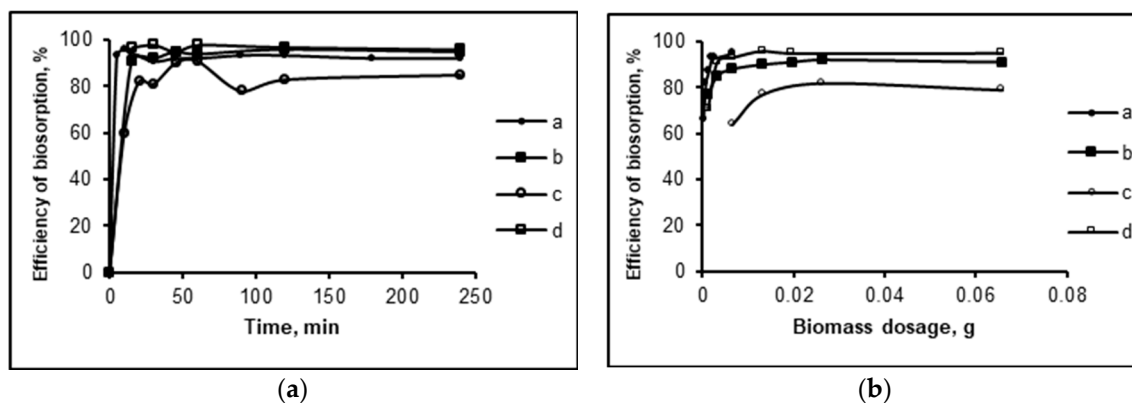


Figure 2. Dependency of the efficiency of biosorption of Pt (0.1 mg L^{-1}) and Pd (0.075 mg L^{-1}) at optimal pH conditions on *Saccharomyces* sp. and *Aspergillus* sp. on (a) contact time (b) biosorbent mass (contact time 45 min); a—Pt(IV) on yeast; b—Pt(IV) on fungi; c—Pd(II) on yeast; d—Pd(II) on fungi.

The influence of biomass dosage on Pt(IV) and Pd(II) biosorption was studied in the range of 0.001–0.066 g of dry mass (0.025–0.5 g of wet mass) (Figure 2b). The biosorption efficiency of both ions increases along with the increasing mass of biomass to a value of 0.013 g (0.1 g of wet mass). This is probably an effect of a higher number of binding sites on the surface of the biosorbent. The efficiency of biosorption was constant in the range of 0.013–0.066 g of biomass dosage demonstrating the formation of an equilibrium between the ions bound to the biosorbent and those remaining in the solution.

3.3. Biosorption Isotherms

The equilibrium biosorption isotherm is of importance in the design of sorption systems. The Langmuir isotherm is based on the monolayer adsorption on the active sites of the adsorbent. The Freundlich isotherm explains the adsorption on a heterogeneous (multiple layers) surface with uniform energy. Although the empirical models cannot provide any mechanistic understanding of the adsorption phenomena, these models may be used to conveniently estimate the maximum uptake of precious metals from experimental data.

The experimental sorption isotherms obtained under optimal conditions and the sorption isotherms predicted by the Langmuir and Freundlich models along with the determination coefficients (R^2) are shown in Figure 3. The calculated Langmuir and Freundlich parameters are listed in Table 1. The values of R^2 , which were found to be above 0.982, indicating that the biosorption of Pt and Pd on the fungi and yeast biomass is consistent with the Langmuir model. In other words, monolayer adsorption took place at the binding sites of both microorganisms. Both types of microorganisms have a higher affinity for Pd(II) than for Pt(IV) ions. The highest affinity of the sorbent for the sorbate was observed between the yeast and the Pd(II) ions (the highest b constant). Fungi *Aspergillus* sp. show a higher adsorption capacity than yeast *Saccharomyces* sp. for both metals. According to the Langmuir model, the fungi achieved a maximum platinum uptake of 5.488 mg g^{-1} that was 30-fold higher than that of the yeast biomass (0.185 mg g^{-1}). The specific palladium sorption capacity of fungi (4.277 mg g^{-1}) was 100-fold higher than that of yeast. This is most likely related to the composition of the cell wall of *Aspergillus* sp., which enhances the adsorption capacity. As can be seen, fungi exhibit an advantage in the removal

of Pt and Pd compared with yeast. Hence, further studies were performed on *Aspergillus* sp. cells. The specified sorption of Pt(IV) and Pd(II) to fungi cells was confirmed by EDX analysis (Figure 4b,c). The signal of Pt is seen at 2 keV and Pd at 2.8 keV and 0.2 keV (covered by the peak of C).

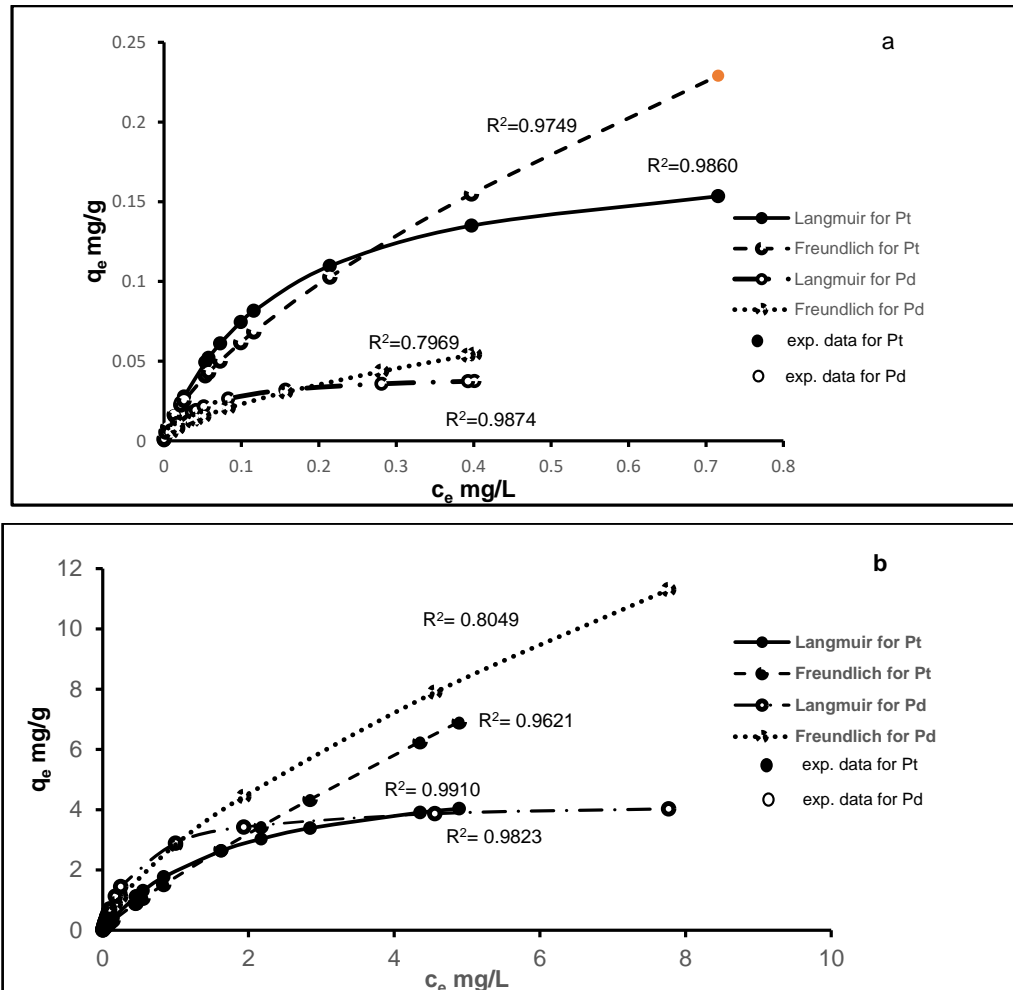
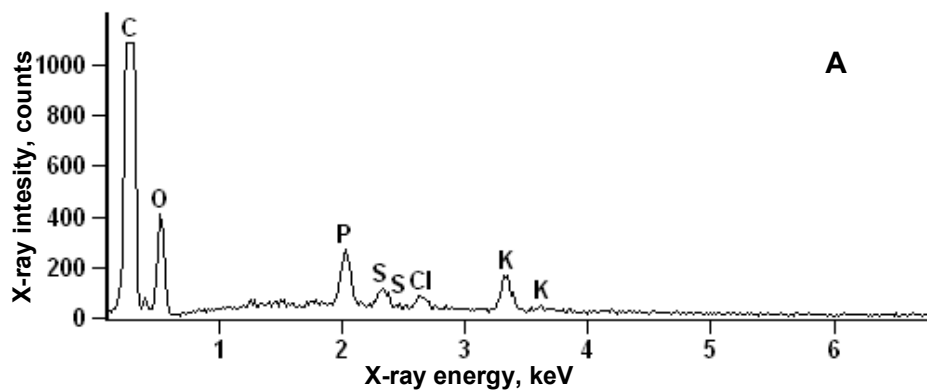


Figure 3. Sorption isotherms of Pt and Pd on (a) *Saccharomyces* sp. and (b) *Aspergillus* sp. Biosorption of Pt on yeast and fungi at pH 2, biosorption of Pd on yeast at pH 2.5, on fungi at pH 3.5, dry biomass 0.013 g, contact time 45 min.



(a)

Figure 4. Cont.

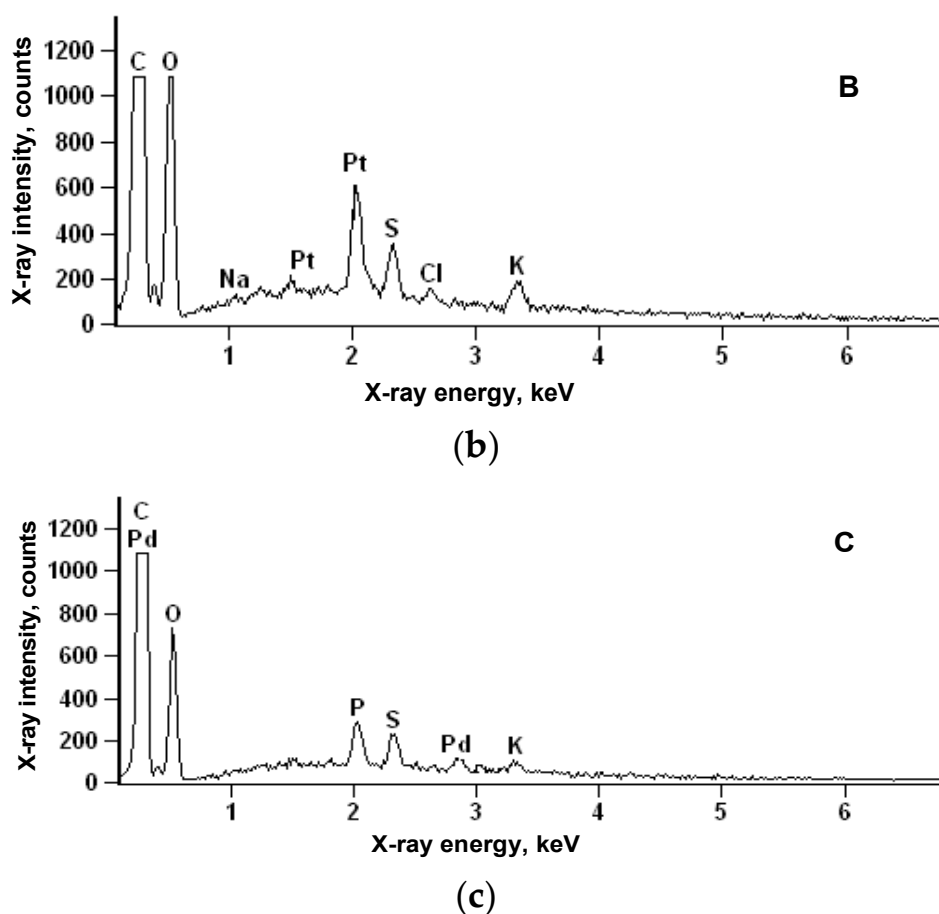


Figure 4. SEM-EDS spectra of (a) free fungi cells, (b) fungi after incubation with Pt(IV), (c) fungi after incubation with Pd(II).

The review of biosorption conditions and parameters of isotherm adsorption models of Pd(II) and Pt(IV) on various microorganisms as well as results obtained in this work are given for comparison in Table 1. As can be seen, the maximum biosorption capacities of fungi observed in our experiment are lower in comparison with the sorption capacities of other microorganisms. However, the time required to obtain the equilibrium of the biosorption process was shorter than in other works.

3.4. Biosorption Kinetics

In order to complete evaluation of the sorption mechanism of examined biomaterials, the kinetic parameters of the sorption process were determined. For this purpose, sorption studies of Pt or Pd ions were carried out under optimal conditions using 0.1 g (wet biomass) of the currently tested biosorbent. The applied concentration of Pt was 0.1 mg L^{-1} , while Pd was 0.075 mg L^{-1} . Every 15 min an appropriate amount of the tested suspension was taken and the current content of the studied ion was determined. The pseudo-first (PFO) and -second (PSO) models of adsorption kinetics were assumed and checked [50]. Basic kinetic parameters such as the amount of adsorbed metal ions at equilibrium (q_e) and the adsorption rate constants (k_1 and k_2) were determined experimentally using the graphical dependence of $\log(q_e - q_t)$ vs. t for the PFO and $1/q_t$ vs. $1/t$ for the PSO models of adsorption kinetics. The suitability of experimental data to the assumed model of adsorption kinetics was determined based on the regression coefficient. The obtained kinetic parameters of examined processes are presented in Table 2.

The obtained data show that the kinetics of the Pt and Pd adsorption process suit well the pseudo-second order kinetics model. This means that rate-limiting step most likely involves chemical interactions leading to the binding of metal ions to the adsorbent surface such as, among others, ion

exchange or complexing processes [50]. This conclusion confirms results obtained by the examination of adsorption isotherms. The mass of adsorbed ion at equilibrium state calculated for the dry mass of biosorbent was $7.819 \times 10^{-2} \text{ mg g}^{-1}$ and $5.864 \times 10^{-2} \text{ mg g}^{-1}$ for Pt and Pd ions, respectively.

Table 2. The kinetic parameters of Pt and Pd adsorption by examined biosorbents (q_e —the amount of adsorbed ion at equilibrium state (mg g^{-1}), k_1 —the first order kinetic rate (min^{-1}); k_2 —second order kinetic rate ($\text{g mg}^{-1} \text{ min}^{-1}$).

Studied Ion	Microorganism	Pseudo-First Order Kinetics Model		Pseudo-Second Order Kinetics Model	
Pt	<i>Saccharomyces</i> sp.	q_e	4.670×10^{-3}	q_e	4.601×10^{-3}
		k_1	8×10^{-5}	k_2	830.173
		R^2	0.145	R^2	0.999
	<i>Aspergillus</i> sp.	q_e	0.358×10^{-4}	q_e	4.122×10^{-3}
		k_1	2.2×10^{-3}	k_2	210.474
		R^2	0.373	R^2	0.999
Pd	<i>Saccharomyces</i> sp.	q_e	1106.0	q_e	3.188×10^{-3}
		k_1	5.1×10^{-3}	k_2	226.254
		R^2	0.515	R^2	0.990
	<i>Aspergillus</i> sp.	q_e	3.218×10^{-3}	q_e	3.092×10^{-3}
		k_1	2×10^{-4}	k_2	280.620
		R^2	0.491	R^2	0.996

3.5. Recovery of Platinum and Palladium from Wastes

The presence of matrix components of the samples, inorganic ions as well as organic matter, may influence the specific biosorption of analyte. Hence, in this work, the recovery of platinum and palladium ions from samples containing complex matrix was studied. As the content of Pt and Pd in samples of crude sewage obtained from municipal sewage treatment plant and road run-off was not determined, they were spiked with different amounts of analytes and left for equilibration. Next, they were pretreated and analyzed according to the procedure described in Section 2.6. The efficiencies of retention of analytes and their recoveries from biomass were calculated and the results are given in Tables 3 and 4.

Table 3. Application of fungi *Aspergillus* sp. for separation of Pt(IV) from various samples (sample pH 2, mass of biosorbent 0.1 g, contact time 2 h, washing agent: $0.01 \text{ mol L}^{-1} \text{ HNO}_3$, $n = 3$).

Sample Type	Pt(IV) Amount, μg	Retention \pm SD, %	Recovery \pm SD, %
Standard solution	100	89.1 ± 1.1	70.9 ± 2.5
	200	81.3 ± 0.8	65.3 ± 4.3
	500	68.1 ± 6.0	66.5 ± 4.3
	1000	56.5 ± 1.7	51.3 ± 5.2
Road run-off	0.5	95.6 ± 0.9	68.9 ± 2.1
	100	90.7 ± 0.7	62.9 ± 6.2
	200	82.0 ± 0.9	51.2 ± 0.1
	500	70.7 ± 5.9	50.9 ± 4.7
	1000	47.4 ± 0.0	-
Sewage	0.5	62.3 ± 7.5^a	37.5 ± 3.4^a
	0.5	89.4 ± 0.5	82.7 ± 3.4
	1000	36.7 ± 0.0	-
Anode slime	1.2^b	-	74.8 ± 5.7

^a mass of biomass 0.013 g , ^b constituent content of anode slime: Pt— $6 \mu\text{g g}^{-1}$, Ag—40%, Pb—30%, Sb—1%–3%, Se—1%–2%, Cu—1%–2%, S—6%, Au— $200 \mu\text{g g}^{-1}$, Pd— $7 \mu\text{g g}^{-1}$.

Table 4. Application of fungi *Aspergillus* sp. for separation of Pd(II) from various samples (sample pH 3.5, mass of biosorbent 0.1 g, contact time 2 h, washing agent: 0.01 mol L⁻¹ HNO₃, n = 3).

Sample Type	Metal Amount, µg	Retention ± SD, %	Recovery ± SD, %
Standard solution	1000	98.1 ± 0.2	95.2 ± 3.3
Road run-off	0.5	93.7 ± 0.2	98.8 ± 3.4
	1000	99.4 ± 0.0	82.4 ± 4.8
Sewage	0.5	99.4 ± 0.3 ^a	95.8 ± 5.1 ^a
	0.5	91.2 ± 1.0	86.4 ± 1.1
	1000	88.6 ± 0.9	65.7 ± 6.2
Anode slime	1.4 ^b	-	97.9 ± 7.7

^a mass of biomass 0.013 g, ^b constituent content of anode slime: Pd—7 µg g⁻¹, Ag—40%, Pb—30%, Sb—1%–3%, Se—1%–2%, Cu—1%–2%, S—6%, Au—200 µg g⁻¹, Pt—6 µg g⁻¹.

The mean efficiency of retention of Pt (500 ng) from sewage on 0.013 g of fungal biomass was about 60%. Therefore, higher biomass dosage (0.1 g) was used in further experiments. It was observed that the efficiency of biosorption of the same amount of Pt on higher biosorbent mass from sewage samples increased to 89% and from run-off samples achieved 95%. The recovery of Pt from digested fungal biomass was lower, in the range of 69%–82%, indicating that part of the Pt(IV) ions was non-specifically bound to the cells' surface. For 20 mL of standard and samples solutions containing Pt content in the range of 100–500 µg, the retention efficiency was in the range 95%–70%, while the recovery was in the range 70%–50%, decreasing with increasing Pt concentration (Table 3). The retention of analyte from samples containing 1000 µg of Pt decreased to about 57% from standard solutions and even below 50% for complex samples. In this case, the platinum uptake was only about 2.8 mg g⁻¹, not exceeding the maximal capacity of the sorbent. Probably the biosorption of high amounts of Pt was restricted by some factors. Competition between Pt and other ions, organic matter in sewage and road run-off samples, cannot be neglected.

Under the same conditions the recovery of Pd from biomass for all samples type was quantitative (Table 4). These results proved that Pd was specifically bound to fungal cells and no competition in biosorption was observed.

Owing to the presence of valuable metals and metalloids in the anode slime, products obtained from electrolytic refining of copper, numerous approaches have been made by the researchers to extract them following metallurgical routes [51]. The samples of anode slime were digested and pretreated according to the procedure described in Section 2.6. The content of Pt in anode slime determined by XRF method was 6 µg g⁻¹, while the content of Pd was 7 µg g⁻¹.

The experiment has shown that the recovery of precious metals from fungal biomass was excellent for Pd (97.9 ± 7.7%, n = 3) and good for Pt (74.8 ± 5.7%, n = 3). In this work, the biomass was digested by means of high temperature in concentrated acid. The obtained results show that the biomass of fungi can be applied for the quantitative recovery of palladium from wastewater and industrial samples. As for the recovery of precious metals from biomass an incineration process could be used [24], we also plan to examine the efficiency of this process in the future.

4. Conclusions

Yeast *Saccharomyces* sp. and fungi *Aspergillus* sp. have been used to investigate the biosorption of trace amounts of Pt(IV) and Pd(II) from chloride solutions in a batch system. The maximal efficiency of retention of Pt(IV) on yeast and fungi was obtained at pH 2.0 ± 0.2. The biosorption of Pd(II) was performed at pH 2.5 ± 0.2 on yeast, and pH 3.5 ± 0.2 on fungi. The biosorption process is very fast as the equilibrium was attained within 45 min. The best interpretation for the experimental data was given by the Langmuir isotherm and pseudo-second-order kinetics model. Fungi *Aspergillus* sp. show a higher adsorption capacity for both metals than yeast *Saccharomyces* sp. The maximum adsorption capacity of fungi was 5.49 mg g⁻¹ for Pt(IV) and 4.28 mg g⁻¹ for Pd(II). This microorganism was used for efficient removal of Pt and Pd from environmental samples (sewage, road run-off). The method

could be also applied for the recovery of Pd from industrial samples (anode slime). The results revealed that, although this new biosorbent has a relatively low capacity, it is a promising candidate for removal of palladium from contaminated aquatic environments and industrial wastes. If the amount and value of metal recovered and if the biomass is plentiful, metal loaded biomass can be incinerated thereby eliminating further treatment.

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