MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES
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PALLADIUM RECOVERY FROM WASTE PLATING SOLUTIONS USING COMMERCIAL RESIN LEWATIT TP 214

ECE ULUSER YEGÜL

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Marmara Üniversitesi Fen Bilimleri Enstitüsü Yüksek Lisans Öğrencisi Ece ULUSER YEGÜL'ün "Palladium recovery from waste plating solutions using commercial resin Lewatit TP 214" başlıklı tez çalışması, ……... tarihinde savunulmuş ve jüri üyeleri tarafından başarılı bulunmuştur.

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Ece ULUSER YEGÜL, a Master of Science student of Marmara University, Institute for Graduate Studies in Pure and Applied Sciences, defended her thesis entitled "Palladium recovery from waste plating solutions using commercial resin Lewatit TP 214", on …… and has been found to be satisfactory by the jury members.

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Marmara University Institute for Graduate Studies in Pure and Applied Sciences Executive Committee approves that Ece ULUSER YEGÜL is granted the Master of Science in Department of Metallurgical and Materials, Metallurgical and Materials Program on ……..……... (Resolution no: ……..…).

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Thank You All!

06/2021 **Ece ULUSER YEGÜL**

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TİCARİ REÇİNE LEWATIT TP 214 KULLANILARAK ATIK KAPLAMA ÇÖZÜMLERİNDEN PALADYUM GERİ KAZANIMI

Bu çalışma, Lewatit TP 214 reçinesi üzerindeki Pd(II) metal iyonlarının adsorpsiyon davranışını incelemeyi amaçlamaktadır. Pd(II) metal iyonları, değerli metal kaplama solüsyonu atıklarından elde edilen amonyum içeren asidik solüsyon içinde çözündürüldü ve bu paladyum(II) klorür atık solüsyonu kaynak solüsyon olarak seçildi. Paladyum konsantrasyonu, bir atomik absorpsiyon spektrometresi kullanılarak 600 ppm olarak belirlendi ve deneysel çalışmalar için, başlangıç çözeltileri olarak pH 4 ve 7.5 olan 60 ppm Pd(II)'lik iki stok çözelti hazırlandı. Lewatit TP 214 (yoğunluk yaklaşık 1.1 g/mL), bu çalışma için Pd(II) iyonları için seçici reçine olarak seçildi.

Bu çalışma, dört parametreyi değiştirerek bir kesikli sistemde yapılmıştır; temas süresi, sıcaklık, Lewatit TP 214 miktarı ve çözelti pH'ı. Deneylerin başlangıcında sıcaklık deney serisine göre sırasıyla 25, 40, 50 ve 60ºC'de sabit tutulmuş ve her seferinde pH 4 veya 7.5'te iki ana stok çözeltiden biri kullanılmıştır. Stok çözeltilerdeki Lewatit TP 214 miktarı sırasıyla 100, 200, 300 ve 400 mg olarak belirlendi. Kör deneylerdeki performansından sonra ve deney çalışmalarının başında ilk çözümlere eklenmiştir. Her deney sırasında, kinetik çalışma için her 15 dakikada bir alikotlar alındı. Çalışmalar, pH'ı düşürerek, sıcaklığı artırarak ve adsorban miktarını artırarak geri kazanım yüzdesinin arttığını göstermiştir.

Anahtar Kelimeler: Paladyum geri kazanımı, atık kaplama solüsyonu, iyon değişim reçinesi, Lewatit TP 214.

SUMMARY

PALLADIUM RECOVERY FROM WASTE PLATING SOLUTIONS USING COMMERCIAL RESIN LEWATIT TP 214

The aim of this study is to adsorb dissolved palladium (II) metal ions in the waste plating solution with Lewatit TP 214 commercial resin and to investigate the adsorption behavior of the resin. Pd(II) metal ions were dissolved in an acidic solution -containing ammonium- obtained from precious metal plating solution waste and, this palladium(II) chloride waste solution was selected as the source solution. The palladium concentration was determined as 600 ppm using an atomic absorption spectrometer, and for the experimental studies, two stock solutions of 60 ppm Pd(II) with a pH of 4 and 7.5 were prepared as initial solutions. Lewatit TP 214 (which has a density approximately 1.1 g/mL) was chosen as the selective resin for Pd(II) ions for this study.

The experiments were performed in a controlled batch system to examine four parameters; contact time, temperature, amount of Lewatit TP 214, and solution pH. At the start of the experiments, the temperature was kept constant at 25, 40, 50, and 60°C based on the experiment series, respectively, and each time one of two main stock solutions at pH 4 or 7.5 was used. The amount of Lewatit TP 214 into the stock solutions was 100, 200, 300, and 400 mg, respectively. After its performance in the blank tests, these amounts were added into the initial solutions at the beginning of the experimental studies. During each experiment, aliquots were taken every 15 min for the kinetic study. The studies showed that the recovery performance was higher at lower pH, higher temperature, and higher amounts of the adsorbent.

Keywords: Palladium recovery, waste plating solution, ion exchange resin, Lewatit TP 214

SYMBOLS

C_0 : The initial Pd concentration in the solution (mg/L)

C_t : The final Pd concentration in the solution at the end of the experiment (mg/L)

t : The adsorption time (min)

q_t : The adsorption amount at time t (mg/g)

q_e : The adsorbed amount of Pd per unit mass of the sorbent (mg/g)

k_1 : Pseudo-first-order rate constant (min^{-1})

k_2 : Pseudo-second-order rate constant (g/mg min)

k_p : Intra-particle diffusion rate constant (mg/g $min^{1/2}$)

R^2 : The correlation coefficients for intra-particle diffusion

V : Volume (L)

m : Mass (g)

C_e : The equilibrium Pd concentration (mg/L)

E_a : Activation energy (KJ/mol)

K_F : Freundlich constant (mg/g)

K_L : Langmuir constant (L/g)

n : Dimensionless exponent of Freundlich equation

k : Rate constant

R : Gas constant

T : Temperature (K)

A : Frequency or pre-exponential factor

q_m : Maximum amount of the adsorbed Pd per unit mass of sorbent (mg/g)

Q_{max} : Maximum adsorption capacity of a material

ABBREVIATIONS

ppm : Particles per million

EU : Europe

PGM : Platinum group metals

PGE : Platinum group elements

ELP : Electroless plating

EDTA : Ethylene Diamine Tetraacetic Acid

PEI : Polyethylenimine

AAS : Atomic absorption spectrometer

PFO : Pseudo-first-order

PSO : Pseudo-second-order

IP : Intra-particle

SSE : Sum of squared errors

DFT : Density theory

BET : Brunauer, Emmett, and Teller model

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1. INTRODUCTION

The demand growth for the recycling of platinum group metals for the last decade induced research studies, primarily, in the EU, in order to balance the offer for these metals, thus to convert a single use material as secondary sources into a valuable renewable resource including plating solutions, spent automotive and chemical industry catalysts, military equipment, electronic scrap, ore dressing plant tailings, and exhausted nuclear fuel [1].

Ion Exchange resins play an essential role in the separation process of precious metals, i.e., platinum group elements (PGEs), silver and gold. Therefore, the selective ion exchange resins comprised of anion, chelating and cationic with chelating groups were used in the industry. Especially basic ion exchange resins were applied widely in the recovery, separation, concentration, adsorption of noble metal ions due to their high affinity [2]. In one of the previous studies, the utilization of Lewatit MP 500 and Lewatit MP 500A (type-I) as strongly basic anion exchange resins for Pd (II) adsorption in the chloride solutions (NaCl-HCl). The contact time, HCl concentration, and macro component inclusion (NaCl) were investigated. This study showed that the chloro-complex of Pd (II) had a high chemical affinity for the type-I exchangers, and the adsorption efficiency increased with higher contact time, but the augmentation of HCl and NaCl decreased the Pd (II) uptake [2].

In one patented work, Pt, Pd, and Rh were extracted through reduction of gases, extraction of solvents, electrowinning, or PGM adsorption from waste infiltration solutions for recovery [1]. As an alternative technique to conventional methods, they presented higher selectivity, thus better refining. Lewatit MP 600 WS and Purolite S985 were also studied in detail. The resins with the thiouronium-functional group were successfully tested for several adsorption studies in the literature survey. Similarly, Lewatit TP-214 [3,5], Lewatit SPC 118 [4], UCP 118 [4], Duolite GT-73 [3,5], Purolite S920 [5], Srafion NMRR, and Monivex are one of the few thiouronium-functionalized resins, and their behaviors were investigated comprehensively in several articles [1-5]. In addition to all the above-mentioned studies, Duolite A6 [6], Duolite A7 [6], Duolite A 30 B [6], Varion AP [6], Lewatit M 600 (in gel form) [7], Amberlyst A26 (microporous) [7] and acrylic Amberlite IRA 458 (in gel form) [7], Amberlite IRA 958 (macroporous) [7], also Lewatit

MonoPlus TP-220 [8], Lewatit AF 5 [9] and Lewatit MP 62 [10] were other chelating resins used in several significant works in the literature survey.

In one of the latest studies, the Pd (II) adsorption performance of the macroporous resin Lewatit TP 214 was explored by fluidized mode and batch mode. It was found that one hour of fluidization was enough for the complete removal of palladium even in an excess quantity of solution, the capacity of maximum adsorption was 20 mg/g. Following trials using several stock solutions at different concentrations to eliminate Pd (II), the hydrochloric and perchloric acids mixture provided 98% recovery [11].

In another study, Lewatit MonoPlus TP 214 was used for Pd (II) adsorption from hydrochloric acid solutions. The Pd (II) adsorption was finished in 21 h, and according to the Langmuir model, maximum recovery was 241.1 ± 11.6 mg/g [12].

A similar study also conducted to investigate the gold adsorption performances of activated rice husk and Lewatit TP 214. A gold chloride solution which contains 100 ppm Au^{3+} was prepared synthetically for the experiments. According to the results of the study, the adsorption performance of Lewatit TP 214 was higher than the activated rice husk, and the activation energy of activated rice husk was higher than the Lewatit TP 214 [13].

In a more former study, chelating ion exchangers (Lewatit TP 214 and Purolite S 920) were compared with cationic ion exchangers (Chelite S and Duolite GT 73). They were used to recover Pd (II) chloro-complexes from chloride solutions. The effect of the hydrochloric acid and sodium chloride concentrations on the performance of Pd (II) recovery was investigated. One of the other parameters was the contact time. After the experiments, adsorbed Pd (II) amounts, capacities of the resins, the distribution coefficients of weight and bed were estimated to determine the best resin. According to the results, Lewatit TP 214 was the best resin for the Pd (II) recovery, followed by Purolite S 920, Chelite S, and Duolite GT 73, respectively [5].

In one study, Lewatit TP 214 compared with Amberlyst A21 to find out which resin is better on Pd (II) recovery from electroless plating (ELP) solutions which were prepared synthetically. The researchers aimed to determine the effect of protonation, solution complexity, pertinent functional groups, and the speciation on the adsorption and desorption characteristics. The parameters of the experiments were pH, contact time, and quantity of resins. After the experiments, the results were compared with the kinetic calculations and eventually, it was seen that Lewatit TP 214 had a better performance than Amberlyst A21 as an adsorbent. Also, it is found that these resins have higher Pd (II) adsorption capacity from aqueous media than ELP systems, because EDTA and ammonia have a preventative role on adsorption sites of the exchangers [14].

Several studies conducted using Lewatit TP 214 for adsorption of platinum [15,16] and gold [17, 18, 19] resin showed successful performance even compared to natural sorbents produced using rice husk, pistachio nutshell, and activated pistachio nutshell.

Another study focused on Pd adsorption with commercial exchangers from the rhenium containing sulfuric acid solutions. There were several resins used to investigate the Pd adsorption performance. The best exchanger was TP 214 and followed by D 4384, TP 207, AN 105, CS-PTFE, A170, MN 202, MP 62, and VP-14KR, respectively. After the experiments, recovered Pd eluted from the exchangers with 8% ammonia and/or 4 mol/L hydrochloric acid [20].

There are some examples in which bacteria are also used in researches for the recovery of precious metals. Escherichia coli bacteria, also known as E. coli, was used in one of them. E. coli was found to absorb Pd (II) and Pt (IV) metals in single, and bimetal systems at different metal concentrations, and even more selectively absorbed Pd(II) metal in bimetal systems. This performance of E. coli has also been compared with Lewatit TP 214 and Amberjet 4200 ion exchange resins. TP 214 absorbed Pd(II) metal more selectively in the bimetal system, just like E. coli, and such a particular situation was not observed in Amberjet 4200 [21].

Polyethyleneim (PEI) was cross-linked with another bacterium, Corynebacterium glutamicum, and a new biosorbent was obtained. With the experiments, its performance on adsorption and recovery of palladium was investigated. Experiments were also carried out with different commercial resins such as Amberjet 4200 Cl, TP 214, SPC-100, and

SPS-200 for comparison. It has been determined with the Langmuir model that the biosorbent produced has a better performance than SPC-100 and SPS-200 [22].

The adsorption of Pd(II) in chloride solution with Lewatit MonoPlus MP-500 was investigated. During the experiments, different amounts of NaCl and HCl were added to the solutions. The effects of both the ionic strengths of the solutions and the NaCl concentration on the adsorption were investigated. As a result, it has been determined that MP-500 can perform adsorption under these conditions, but increasing the amount of HCl in the solution reduces the performance of Pd(II) adsorption due to competition between Pd(II) and Cl^- [23].

In another study with Lewatit MonoPlus TP 214, a 92% and 96% efficiency were obtained in Pt and Pd recovery, respectively, and the method investigated was successfully applied to the particles emitted from automobile catalysts [24].

Upon recovery of Pd(II), a study was conducted with Amberlite IRA958 and Dowex Marathon MSA commercial exchangers and compared to Lewatit TP214, and Amberlyst A21 studied in previous studies. It has been found that Dowex MSA is more efficient than IRA958, despite the use of less amount and shorter contact time. Dowex MSA was the best absorbent compared to the results of other studies. Amberlyst A21 was determined as the best option considering cost-efficiency [25].

2. BACKGROUND

2.1. Uses and applications

The discoverer of palladium metal is William Hyde Wollaston. Wollaston, who dissolved platinum in aqua regia to purify it in 1803, while continuing his experiment, discovered a new white metal, palladium [26].

Palladium is a PGM because it is rare in the world. Despite the continental tenor potential in South Africa, where the platinum group elements are mostly found, palladium production in Russia is higher [26-27]. Other metals in the platinum group are rhodium, iridium, ruthenium, osmium, and platinum. These metals have great importance for industries because their usage areas are developing technology [28].

Palladium is used as an alloying element in the jewelry industry. Also, since it is a white metal, it has also been used in light-colored plating or decolorating processes. PGMs are used as catalysts in the Automobile Industry. The aim is to reduce nitrogen oxides, unburned hydrocarbons and carbon monoxide. Catalytic convertors of automobiles contain 0.08% Pt, 0.04% Pd and 0.005-0.007% Rh [28]. Besides, it is also used in the electronics, medical and chemical industries [26]. Palladium has also been used in the dental industry since the late seventies. It is possible to use it as a dental crown and bridge alloy since it can be easily alloyed with many metals and has a high corrosion resistance [29]. Pd is also used in the electronics industry, due to its corrosion resistance, electrical conductivity, chemical resistance, hardness, and high melting point. Palladium, rhodium, platinum, and ruthenium are the most commonly used elements in the plating industry. It is used as a catalyst for the production of hydrogen peroxide and nitric acid. Palladium catalysts are also used to synthesize organic compounds such as acetaldehyde, caprolactam, vinyl acetate, toluene diisocyanates, nitrobenzene, cyclohexane [30].

2.2. The Chemical and Physical Properties of Palladium

Palladium is an element with an atomic number of 46 and an atomic weight of 106.42 g [31]. It takes place in the 10th group, the 5th period on the periodic table. It exists in the solid phase at room temperature. Palladium's melting point is 1828.05 K (1554.9°C, 2830.82°F), boiling point is 3236 K (2963°C, 5365°F). Its density is 12.023 g/cm^3.

2.3. Adsorption Theory and Kinetic Models

In order to understand and investigate the adsorption phenomenon, it is necessary to examine the adsorption kinetics. Because the speed of adsorption is determined by kinetics. The surface properties of the adsorbent, the concentration and flow of the solution are the factors that affect the kinetics. The most important kinetic models in examining the relationship between the adsorbent and the adsorbed substance are the Pseudo-First-Order (PFO), Pseudo-Second-Order (PSO), Elovich and Intra-particle (IP) models. The most commonly used models are PFO and PSO models. The error level - correlation coefficient (R^2) or Sum of Errors (SSE) have a role in the selection of the best model for the process. Recently, linear forms have been preferred in studies on adsorption kinetics. For this reason, a linear PSO model is often used instead of the PFO model [33]. The supplementary information related to several adsorption kinetics models is given in following Chapter 4.

Adsorption occurs when the adsorbed material binds to the surface of the adsorbent. Adsorption technology has been preferred for many years because of its simplicity. Also, since it is an environmentally friendly application, it is also used in water/waste water treatment plants. There are three basic mechanisms of adsorption; chemical adsorption which occurs by chemical bonding, physical adsorption which occurs by van der Waals forces and ion exchange. Having knowledge about these mechanisms is very important for adsorbent selection and planning the adsorption process. In order to understand the adsorption mechanisms, it is necessary to analyze the characterization of the adsorbent before and after the adsorption process. Moreover, calculations of adsorption equilibrium data, and density functional theory (DFT) should be performed for this purpose [34]. The isotherm models are the most used method in adsorption data modeling. Since knowing the maximum capacity of adsorbents is very important to evaluate the adsorption process, a great advantage is obtained with using this method. Some isotherm models which used in research on adsorption are: Linear, Langmuir, Freundlich, Sips, Temkin, and BET (Brunauer, Emmett and Teller). Lots of these models are experimental that are not sufficiently supported theoretically, that's why they are not useful to understand the mechanisms. Therefore, it is recommended to examine the derivatives of these models [34].

The Langmuir isotherm was first used to investigate gas and solid phase adsorption on activated carbon. According to this model, adsorption takes place in only one layer on the surface. Therefore, the adsorption process is limited by the surface area of the adsorbent. On the other hand, Freundlich isotherm is used to explain multilayer and reversible adsorption. The Sips isotherm is the combined form of these two isotherms. It approaches Freundlich isotherm when the adsorbent concentration is low, while it approaches the single layer assumption of the Langmuir isotherm when the adsorbent concentration is high [35].

In the classification of isotherms, the number of model parameters and also their shapes were also effective. But some of the researchers suggest that these isotherms theoretically should not be classified according to their number of parameters. There are four shapes of the isotherms; S, L, H, and C, respectively [34].

It may not always be possible to classify the adsorption models according to their shapes. Because most of the solid-liquid systems are L-shaped. For this reason, it is recommended to classify the isotherms according to their physical meanings. Most of the researchers preferred the linear regression method because it is both simple and useful [34].

The point to be considered here is that dependent or independent variables may be affected during linearization and cause calculation errors. To avoid these errors, nonlinear regression can be used instead of linear regression. Of course, this method is more complex and difficult than the linear regression method. New studies are necessary to understand and examine nonlinear isotherms [34].

A study has been performed to classify correctly the adsorption isotherms mentioned above. First, the physical meaning of these isotherms has been investigated. Then, statistical analysis was performed and a software was developed to solve nonlinear isotherms [34]. The supplementary information related to several adsorption isotherms is given in following Chapter 4.

3. MATERIALS & METHODS

3.1. Preparation of the Solution

Palladium (II) chloride solution obtained from waste palladium plating solutions which contain ammonium ions was the source solution of the study. The palladium concentration was determined as 600 ppm using an atomic absorption spectrometer, and for the experimental studies, two stock solutions of 60 ppm Pd (II) of pH's of 4 and 7.5 were prepared as initial solutions. 1000 cc volumetric flask is used to prepare the solutions. A little amount of diluted HCl was poured to the solution to achieve pH 4. Lewatit TP 214 was chosen as the selective resin for Pd (II) ions for this study. Other analytical grade chemicals also used in this study.

3.2. Process Layout of Experiments

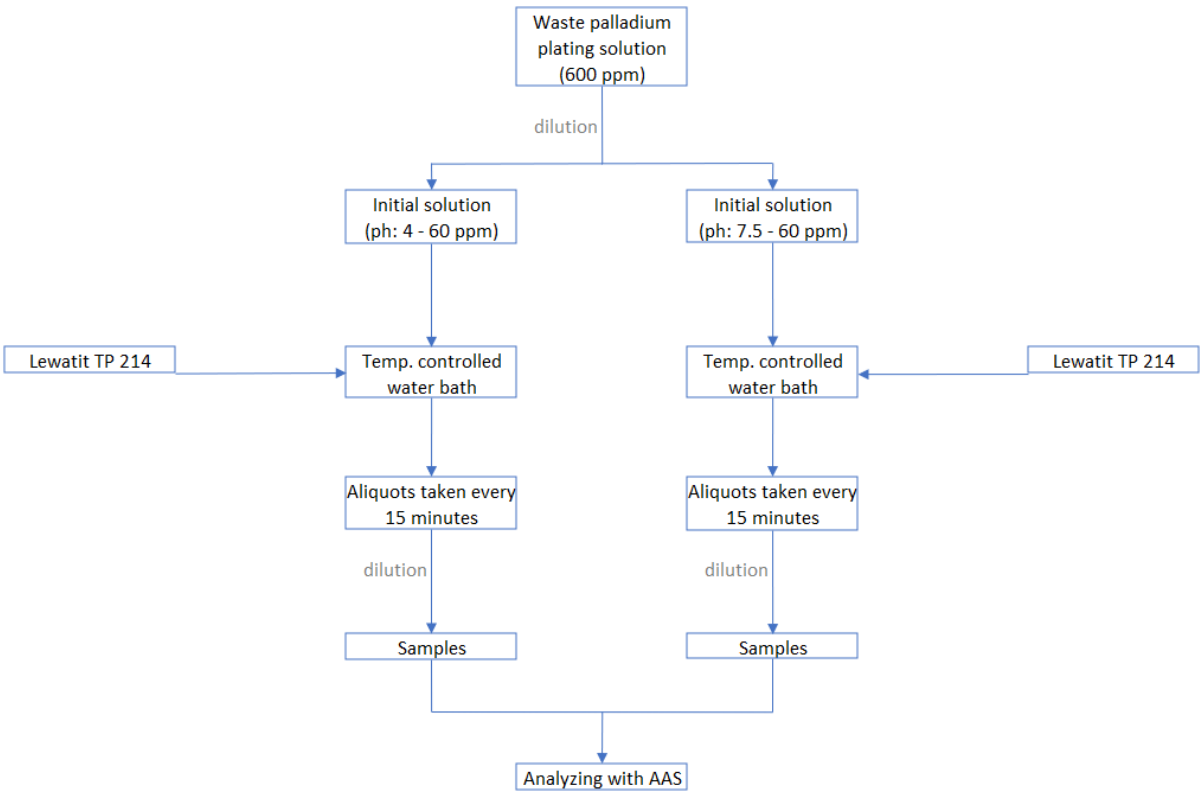


Figure 3.1: The flowsheet of the study

All stages of the study are shown in Figure 3.1 as a flowsheet. In order to ensure the accuracy and reliability of the results, all weighing operations were performed using precision scales.

3.3. Experimental Procedure

This study was performed in a shaking water bath to examine each of the four parameters at once; time, temperature, amount of resin, and solution pH using a 0.25-L glass boiling flask as a reactor. The glass boiling flask was immersed in a water bath to ensure the homogenous bath temperature at a constant temperature condition and the lid of the glass boiling flask was tightly closed and the stirring speed of 100 rpm was kept constant throughout the experiments. Figure 3.1 shows the layout of the experimental procedure. The reaction temperature was adjusted using a digitally controlled hot plate. The volume of the solution was 150 ml and for each experiment series, aliquots of 5 ml were sampled every 15 min for the kinetic study to measure the Pd concentration of the solution.

Some blank experiments were conducted and 100, 200, 300, and 400 mg Lewatit amounts were chosen according to the results, and added into the initial solutions at the beginning of the experiment. The temperature was kept constant at 25, 40, 50, and 60ºC for each experiment series, and the variable of this experiment was the amount of sorbent from 100 to 400 mg for each pH range 4, and 7.5. The experimental setup is given in Table 3.1. Analytical grade chemicals used during the experiments. Optimum adsorption parameters were determined by examining factors such as contact time, temperature, amount of Lewatit TP 214 used, pH. Heidolph MR3001 K was used as the thermostatic heater. Each experiment was repeated three times to ensure the accuracy of the results. HI2002-01edge® Dedicated pH/ORP Meter and wireless pH electrode were used to measure the pH. The yield of palladium ions' adsorption in the stock solution was determined by utilizing the atomic absorption spectrometer, Analytic Jena.

Figure 3.2: The pH meter and the volumetric flask

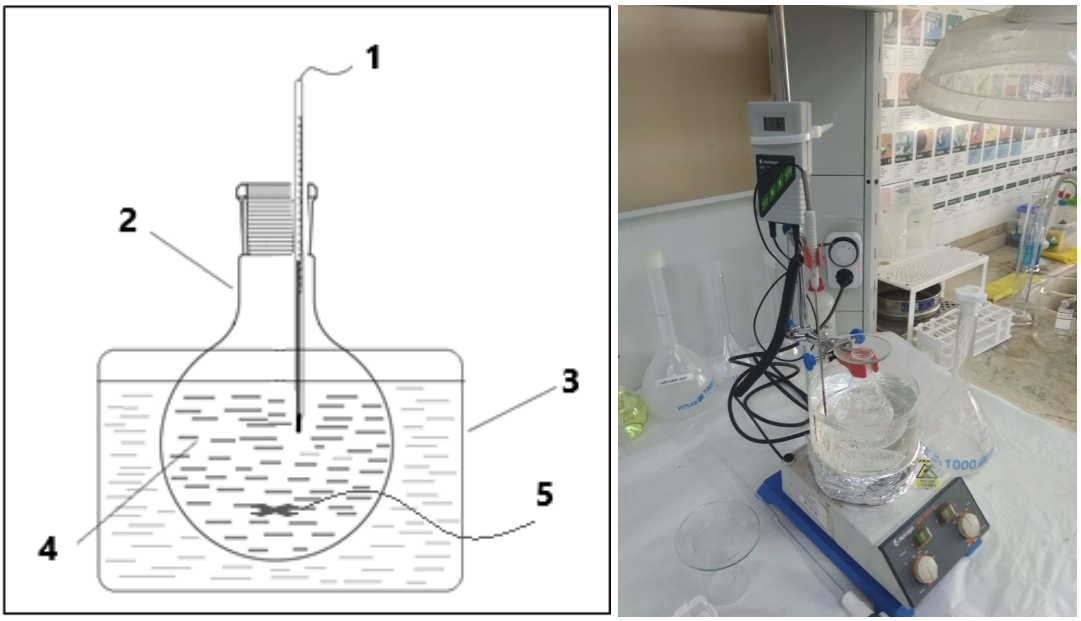


Figure 3.3: The temperature-controlled water bath

1: Electronic thermometer, 2: Glass boiling flask, 3: Water bath, 4: Solution, 5: magnetic stirring bar

Figure 3.4: The atomic absorption spectrometer (Analytic Jena)

After the experiments, the solutions in all tubes were filtered with filter paper (Blue band, Sartorius), to separate the resin from the solutions. Therefore, 2 ml of solution was obtained from each tube at the end of the experiments.

The equation mentioned below was used to calculate the recovery efficiency (%) of the process:

$$Adsorption\ (\%) = \left[\frac{(C_0 - C_t)}{C_0}\right] \times 100 \quad (1)$$

In this formula, C_0 indicates the amount of Pd in the solution initially and C_t indicates the amount of Pd remaining in the solution at the end of the t period. The measurement results of each sample were compared with the graphical method.

Table 3.1: The experimental parameters

Parameters	Value
Lewatit TP 214	100-400 mg
Temperature (°C)	25-40-50-60
pH	4.0 & 7.5

4. RESULTS AND DISCUSSION

The results of palladium adsorption via Lewatit TP 214, which emphasize primary factors and the optimal conditions of the maximum adsorption yields for each parameter studied; i.e., contact time, temperature, amount of Lewatit TP 214 used, and pH of the solution, are given below.

4.1. Effect of used amount of Lewatit TP 214

As the aliquots were taken every 15 min, the results are also a function of the time at 120 min. There are two experimental series conducted at 50°C at each solution pH 4, and 7.5. The results for the palladium adsorption with increasing Lewatit TP 214 amounts are presented in Fig. 4.1. for solution pH 4, and in Fig. 4.2 for solution pH 7.5.

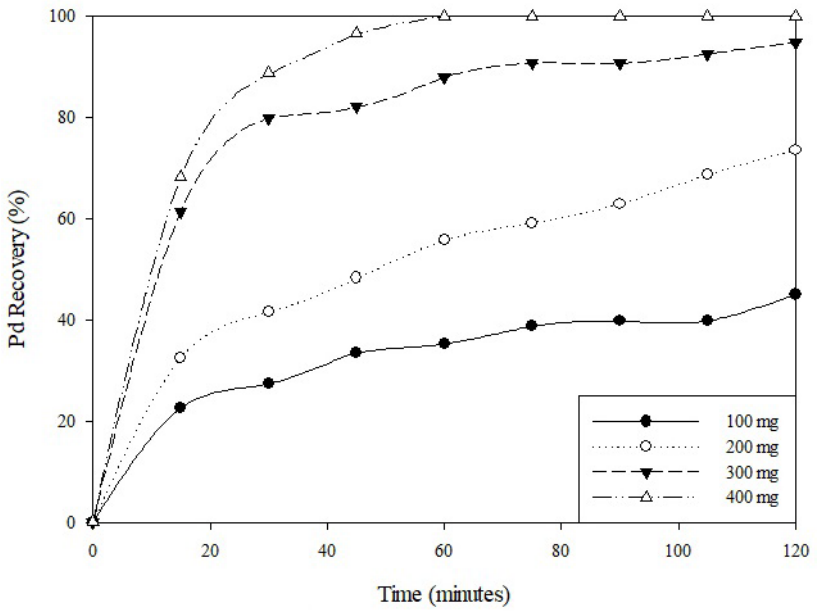


Figure 4.1: The effect of used Lewatit amount on Pd recovery (0-120 minutes, 100 mg, 200 mg, 300 mg, 400 mg, pH 4.0, 100 rpm)

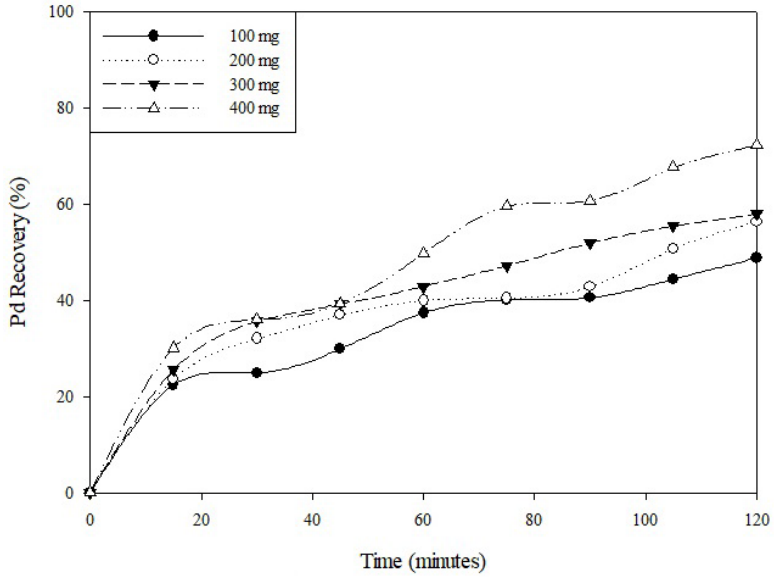
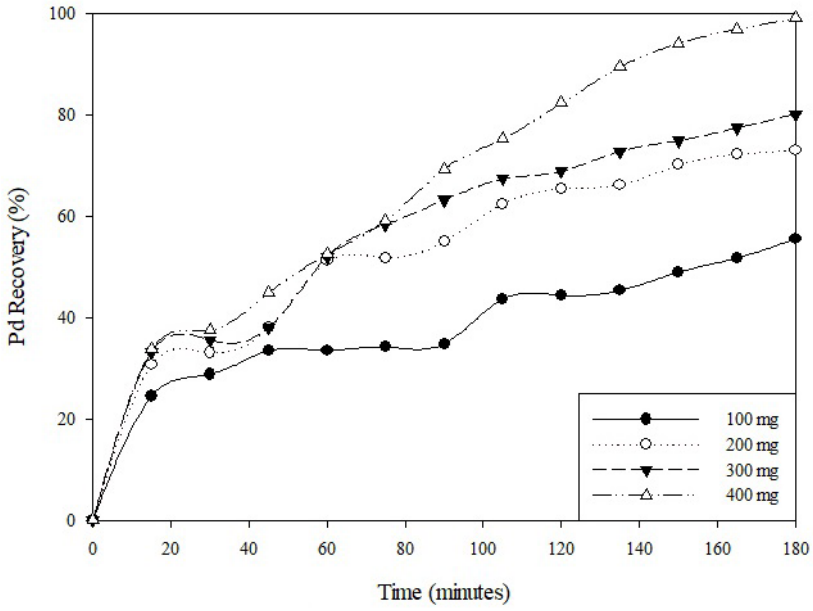


Figure 4.2: The effect of used Lewatit amount on Pd recovery (0-120 minutes, 100 mg, 200 mg, 300 mg, 400 mg, pH 7.5, 100 rpm)

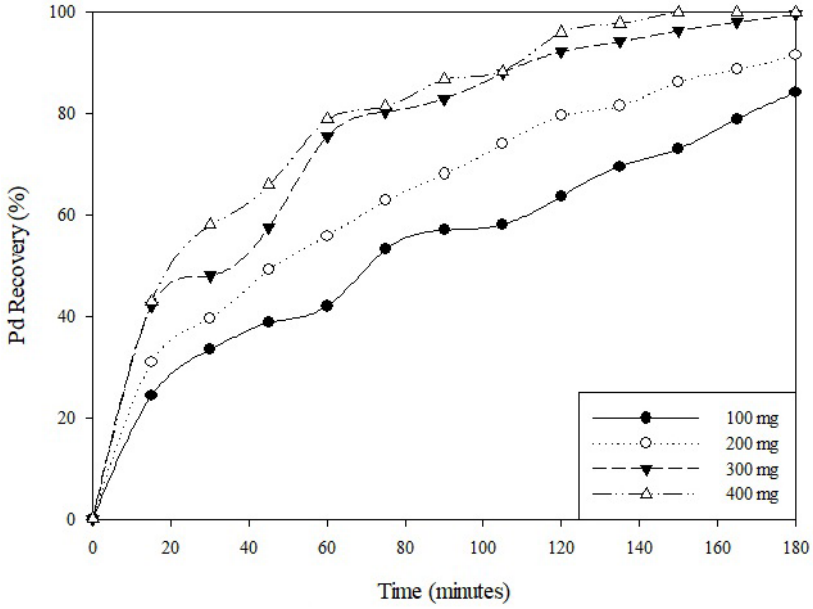
400 mg of the resin provided 100% Pd recovery from the pH 4 solution at 50ºC. The same amount of resin only provided 70% of Pd recovery from the pH 7.5 solution at the same temperature. On the other hand, 100 mg of the resin provided 40% recovery from the pH 4 solution at 50ºC, and the same amount of resin provided 50% recovery from the pH 7.5 solution at 50 ºC. It was found that the increasing amount of Lewatit TP 214 increased the palladium recovery as the resin/metal ratio was high, the total of effective sites on the surface was enhanced, and this state was thermodynamically more convenient, as stated in similar studies [15].

4.2 The effect of contact time

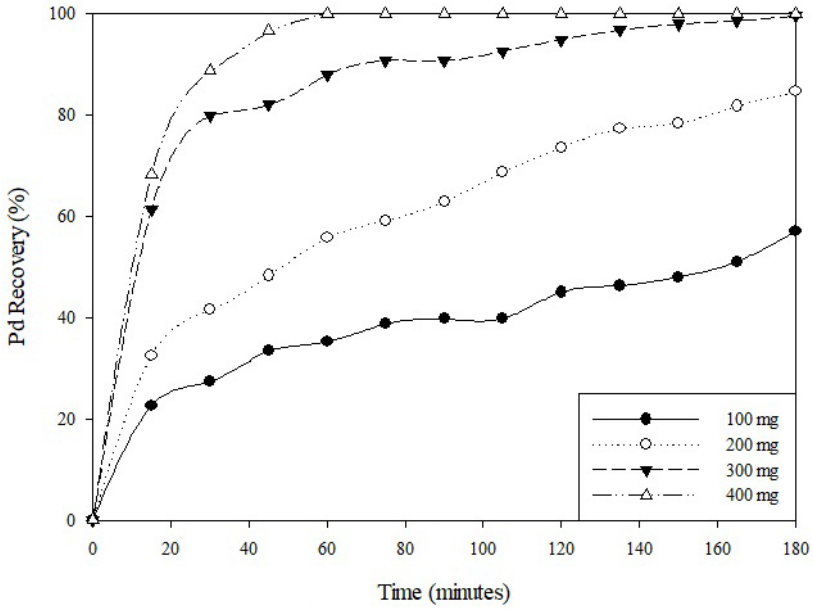
In order to examine the effect of contact time on Pd adsorption, 180 minutes long experiments were conducted at both pH 4.0 and 7.5. Four different amounts of Lewatit TP 214 (100 mg, 200 mg, 300 mg, and 400 mg) were used at four different temperatures (25°C, 40°C, 50°C, and 60°C). The shaking speed was 100 rpm. Fig. 4.3 and 4.4 demonstrate that Pd adsorption percentage was positively affected at different solution pH's, sorbent dosage, and even temperatures. Depending on these other three parameters, i.e., solution pH's, sorbent dosage, and temperatures, the required time to reach the maximum efficiency percentage changed.


Pd Recovery (%)
Time (minutes)
100 mg
200 mg
300 mg
400 mg

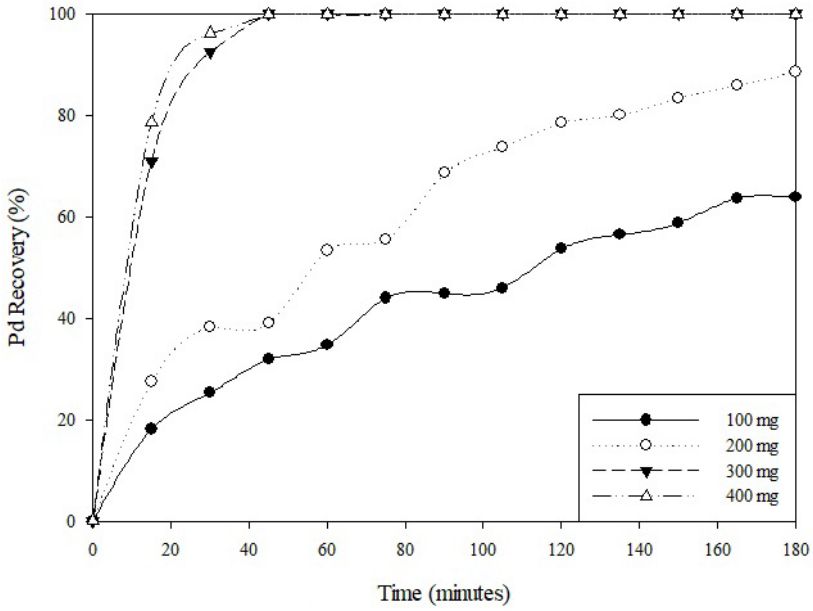
(a)


Pd Recovery (%)
Time (minutes)
100 mg
200 mg
300 mg
400 mg

(b)

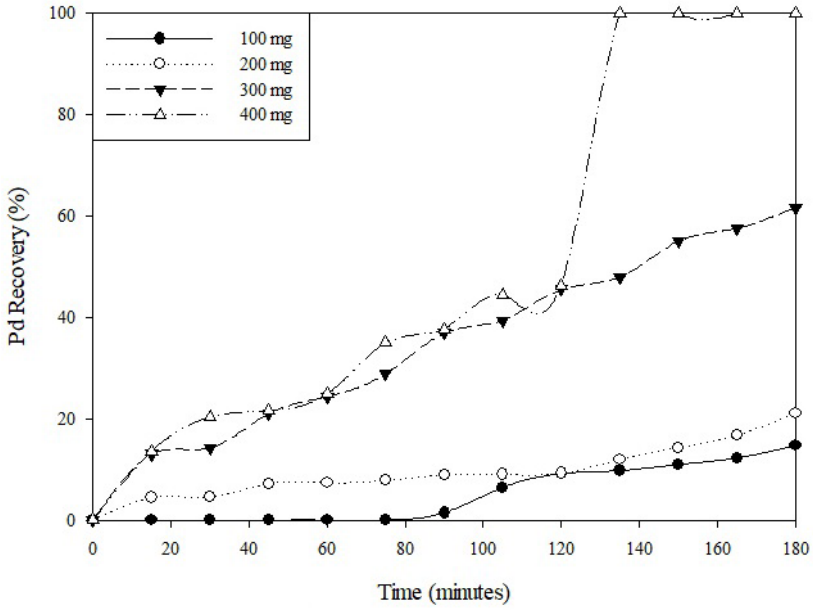


(c)

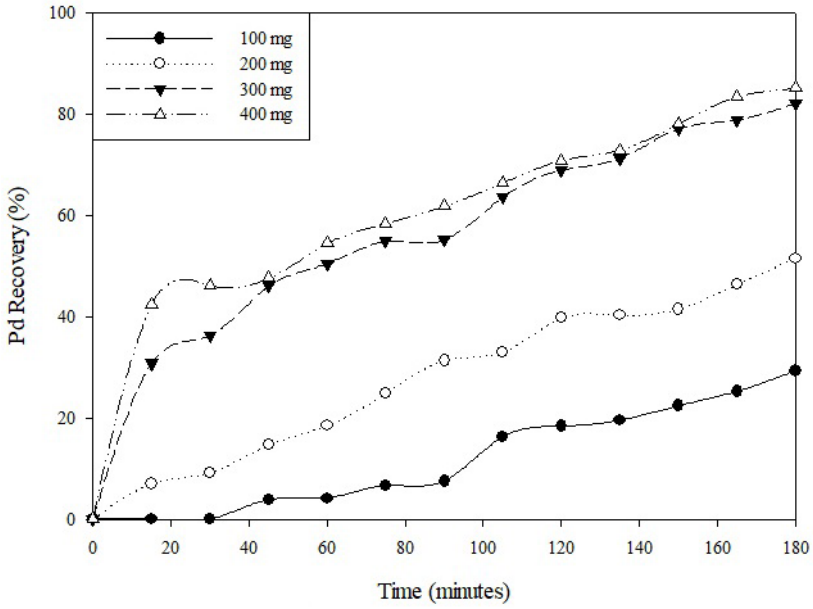


(d)

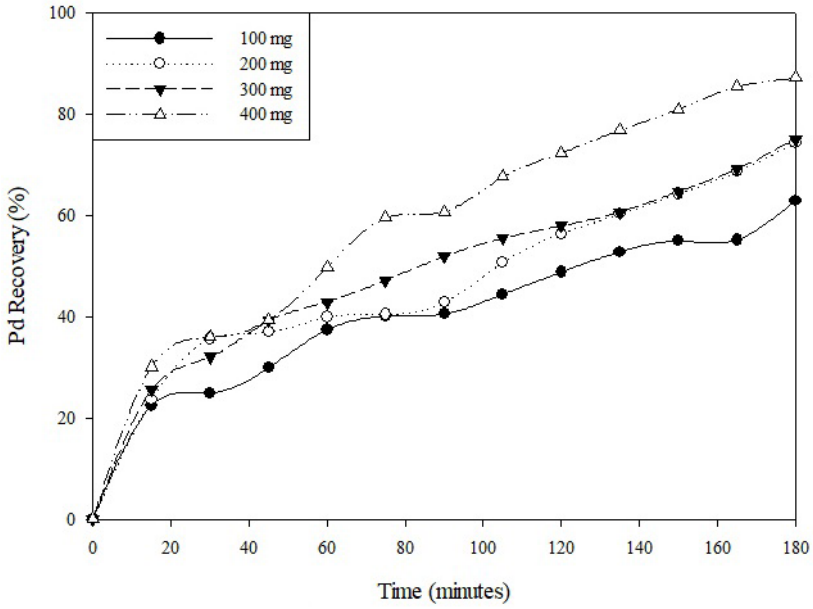
Figure 4.3: The effect of contact time on Pd recovery
(0-180 min, a) 25°C, b) 40°C, c) 50°C, d) 60°C, pH 4.0, 100 rpm)


100 mg
200 mg
300 mg
400 mg
Pd Recovery (%)
Time (minutes)
0
20
40
60
80
100
120
140
160
180

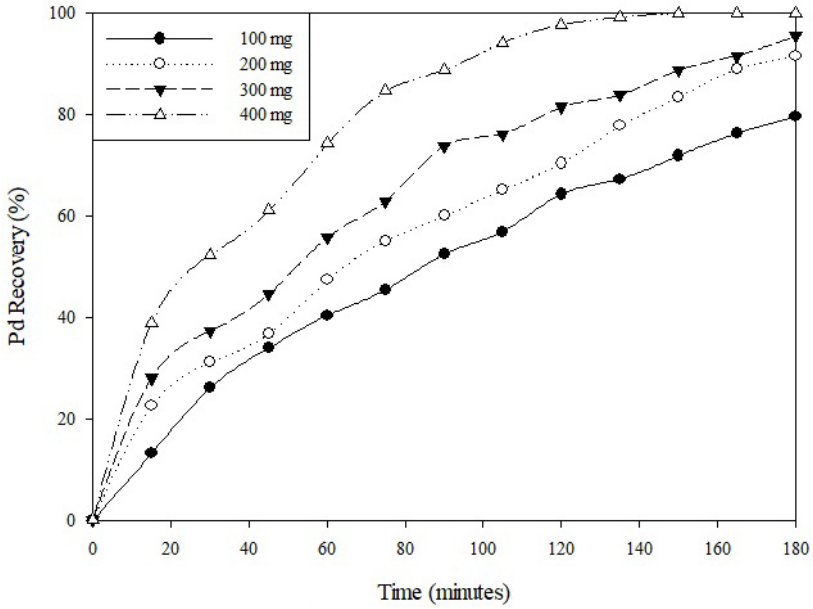
(a)


100 mg
200 mg
300 mg
400 mg
Pd Recovery (%)
Time (minutes)
0
20
40
60
80
100
120
140
160
180

(b)



(c)

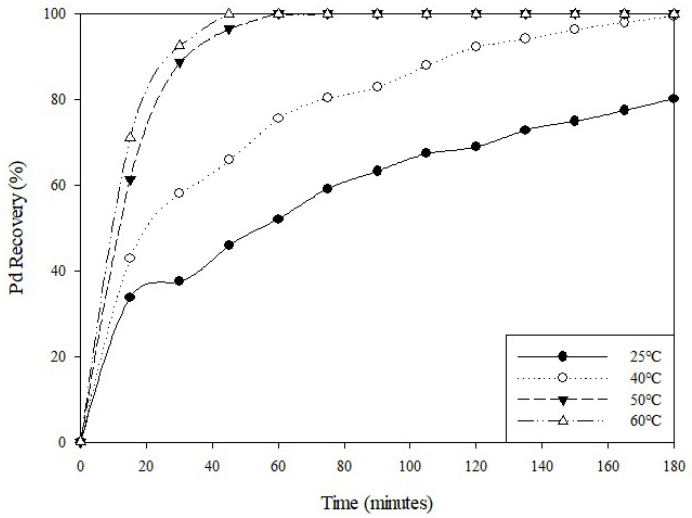


(d)

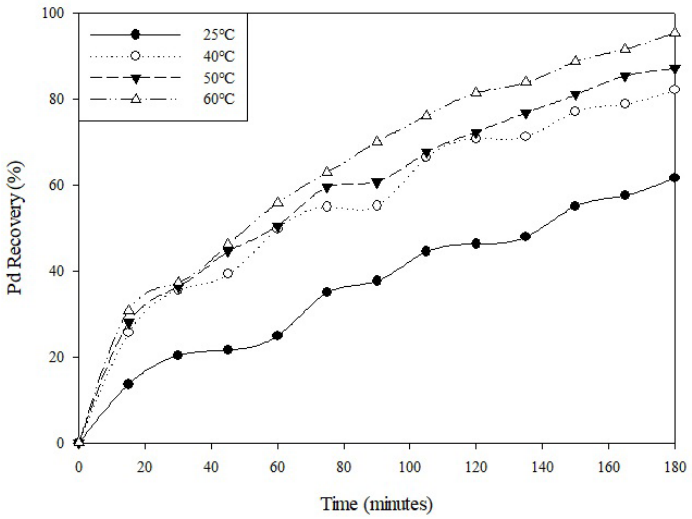
Figure 4.4: The effect of contact time on Pd recovery
(0-180 min, a) 25°C, b) 40°C, c) 50°C, d) 60°C, pH 7.5, 100 rpm)

4.2. The effect of time and temperature

Many experiments have been conducted to examine the effect of time and temperature on Pd adsorption kinetics. The experiments were carried out using aliquots of 2 mL taken every 15 min for 180 min at 25°C, 40°C, 50°C, and 60°C, of solutions at pH 4.0 and 7.5 using Lewatit TP 214 of 400 mg. The shaking bath speed was 100 rpm.



(a)



(b)

Figure 4.5: The effect of time and temperature on Pd recovery % (0-180 min)
a) pH 4.0, b) pH 7.5, Lewatit TP 214 of 400 mg, 100 rpm, 2 mL of 60 ppm solution for each aliquot)

As seen in Fig. 4.5, Lewatit TP 214 showed its optimal performance at pH 4.0 compared to pH 7.5. At about 40 min at 60ºC, it reached Pd adsorption of 100% at pH 4.0; meanwhile, at 7.5, the maximum performance was attained at 180 min at 60ºC. A similar performance was shown at 40ºC, at pH 4.0 at 180 min. The examples may be numbered by examining Fig. 4.5. Thus, the temperature has a significant effect on Pd adsorption.

4.3. The Adsorption Kinetics

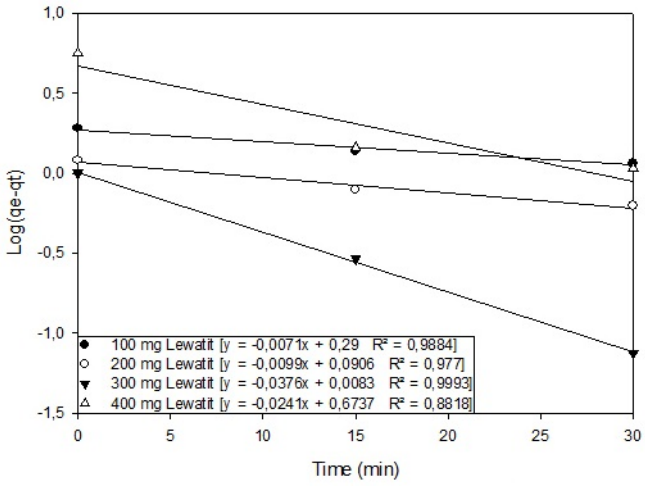
Adsorption kinetics and mechanisms were investigated using three different models. These three models used are shown in Table 4.1.

Table 4.1: The studied kinetic models [36-39]

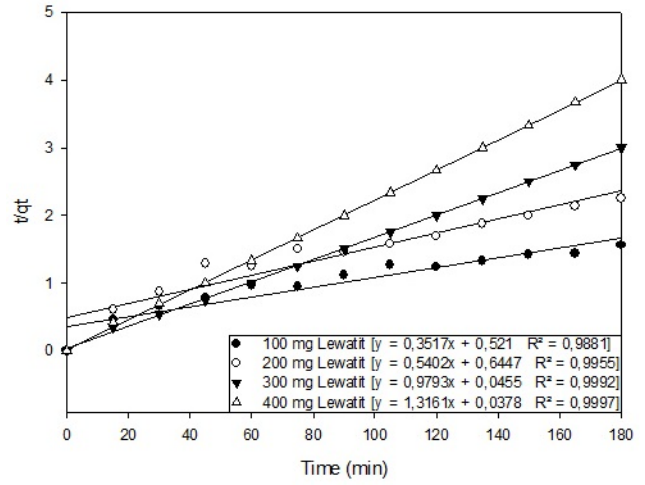
Adsorption model	Kinetic equation
Pseudo-first-order model (PFO) - Lagergren model-	$\frac{dq_t}{dt} = k_1(q_e - q_t)$
Pseudo-second-order (PSO) model	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$
Intra-particle diffusion (IP) model	$q_t = k_p\sqrt{t} + C$

This research, conducted with three different kinetic models, provided interesting results of the adsorption process mechanism.

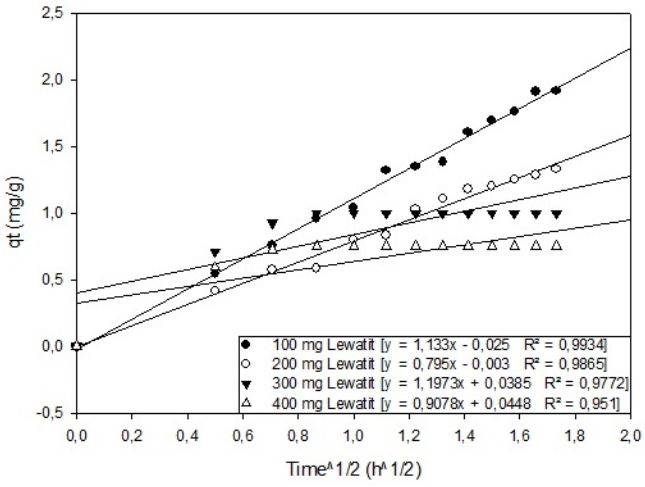
According to the kinetic calculations, the most suitable model for Pd adsorption with Lewatit TP 214 is the pseudo-second-order model. Figures 4.6 and 4.7 show equation plots of Pd adsorption with Lewatit TP 214 for both pH 4.0 and pH 7.5. Besides, all the constants' values calculated for Pd ion adsorption onto Lewatit TP 214 at pH 4.0 and 7.5 are given in tables 4.2 and 4.3. When the correlation coefficients were calculated, it was understood that the correlation coefficients of pseudo-second-order were closer to one than the correlation coefficients of pseudo-first-order, so the pseudo-second-order model explains this adsorption process better. Intra-particle diffusion correlation coefficients are lower than pseudo-second-order. Therefore, intra-particle diffusion may be an alternative model for the current system [36-39].



(a)



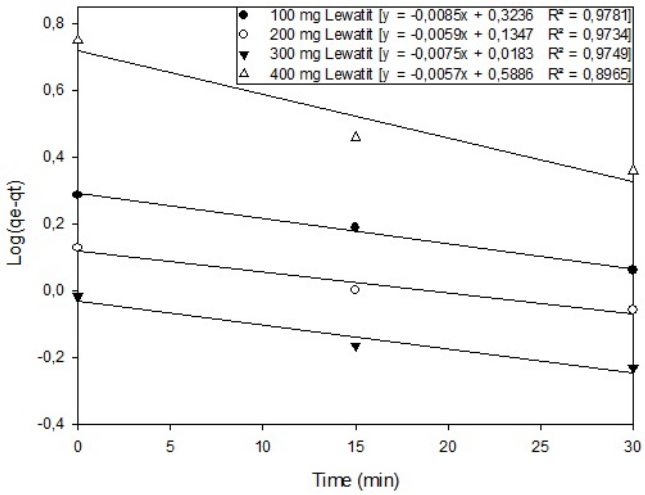
(b)



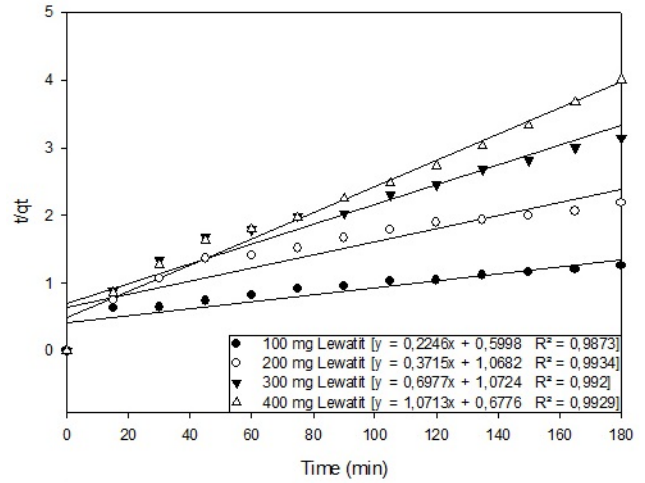
(c)

Figure 4.6: All the equation plots for pH 4.0

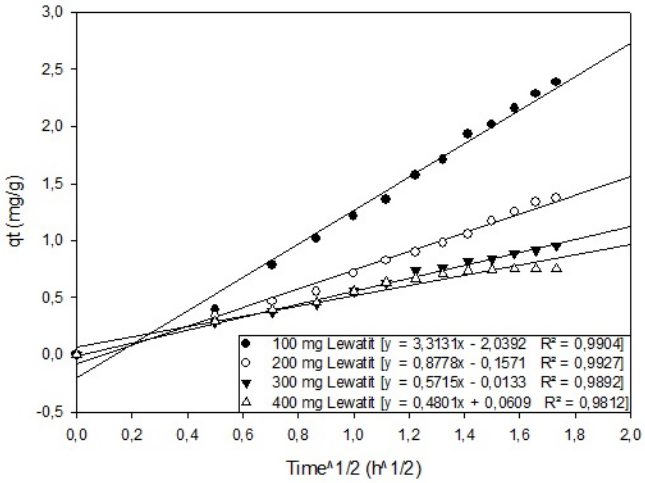
a) PFO b) PSO c) IP (60°C, Lewatit TP 214, 100 rpm, and 2 mL of 60 ppm solution)



(a)



(b)



(c)

Figure 4.7: All the equation plots for pH 7.5

a) PFO b) PSO c) IP (60°C, Lewatit TP 214, 100 rpm, and 2 mL of 60 ppm solution)

Table 4.2: Constants for all the equations calculated for Pd ion adsorption onto Lewatit TP 214 at pH 4.0

The pseudo-first-order constants			
Lewatit, mg	k_1 / min^{-1}	q_e / mg g^{-1} (experimental)	R^2
100 mg	0.0071	1.91	0.9884
200 mg	0.0099	1.20	0.9501
300 mg	0.0376	1.00	0.9976
400 mg	0.0241	0.75	0.8818
The pseudo-second-order constants			
Lewatit, mg	k_2 / min^{-1}	q_e / mg g^{-1} (experimental)	R^2
100 mg	0.3517	1.91	0.9881
200 mg	0.5402	1.20	0.9955
300 mg	0.9793	1.00	0.9992
400 mg	1.3161	0.75	0.9997
The intra-particle diffusion constants			
Lewatit, mg	k_p / min^{-1}	R^2	
100 mg	1.133	0.9934	
200 mg	0.795	0.9865	
300 mg	1.1973	0.9772	
400 mg	0.9078	0.9510	

Table 4.3: Constants for all the equations calculated for Pd ion adsorption onto Lewatit TP 214 at pH 7.5

The pseudo-first-order constants			
Lewatit, mg	k_1 / min^{-1}	q_e / mg g^{-1}	R^2
100 mg	0.0085	1.93	0.9781
200 mg	0.0059	1.34	0.9734
300 mg	0.0075	0.96	0.9749
400 mg	0.0083	0.75	0.9587
The pseudo-second-order constants			
Lewatit, mg	k_2 / min^{-1}	q_e / mg g^{-1}	R^2
100 mg	0.2246	1.93	0.9873
200 mg	0.3715	1.34	0.9934
300 mg	0.6977	0.96	0.992
400 mg	1.0713	0.75	0.9929
The intra-particle diffusion constants			
Lewatit, mg	k_p / min^{-1}	R^2	
100 mg	3.3131	0.9904	
200 mg	0.8778	0.9927	
300 mg	0.5715	0.9892	
400 mg	0.4801	0.9812	

4.4. The effect of pH

It has been observed through the experiments that pH has a very important effect on the adsorption of Pd by Lewatit resin. This effect is shown in Fig. 4.5. The Pd adsorption percentage increased dynamically and aggressively, then reached 100% at 40 min at pH 4.0; meanwhile, this behavior was extended over time and more stable at pH 7.5. It may conclude that the Lewatit TP 214 performed better at lower pH levels.

4.5. The study of the adsorption isotherms

The Adsorption isotherms were examined at four different temperatures (25, 40, 50, and 60°C) by using four different resin amounts (100, 200, 300, and 400 mg). The other parameters were constant. By using Equation (2), the amount of adsorbed Pd at equilibrium (qe, mg Pd/g) was calculated:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

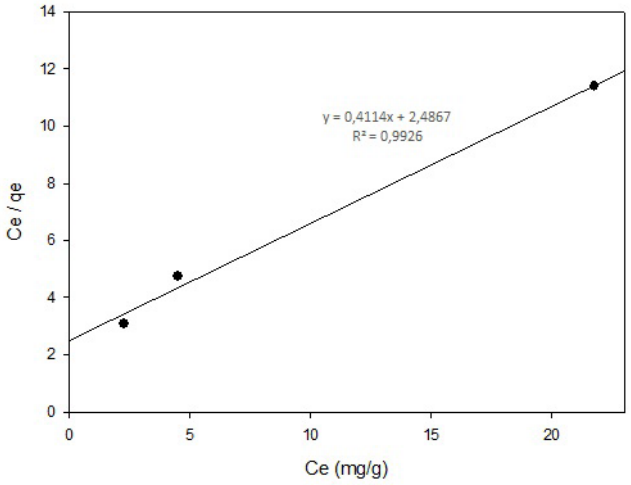
C_0 (mg Pd/L) is the initial concentration, C_e (mg Pd/L) is the equilibrium concentration, V (L) is the volume of the solution, and m (g) is the mass of the Lewatit resin.

Experimental adsorption equilibrium parameters can be examined with more than one isotherm equation. The most used models for this purpose are Langmuir and Freundlich. The Langmuir isotherm is used for monolayer adsorption. In this case, the surface of the adsorbent is the limit for the adsorption process. However, the Freundlich isoterm is suitable for multilayer adsorption. Table 4.4 shows these two isotherm models.

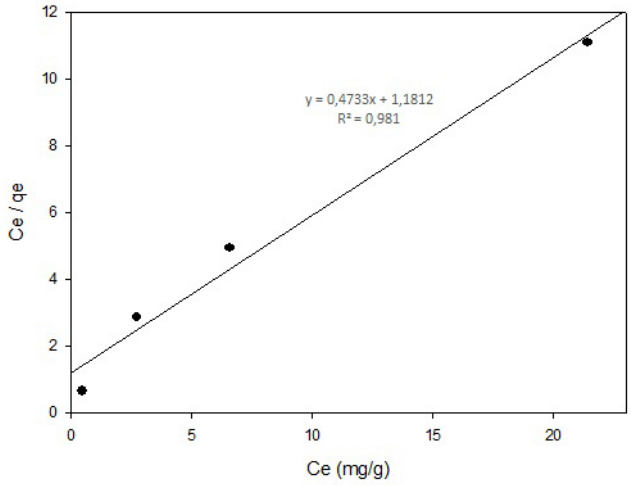
Table 4.4: Linear forms of the isotherm models [36-40]

Isotherm Models	Linear form equation
Freundlich	$q_e = K_F C_e^{1/n}$
Langmuir	$q_e = Q_{max} \frac{K_L C_e}{1 + K_L C_e}$

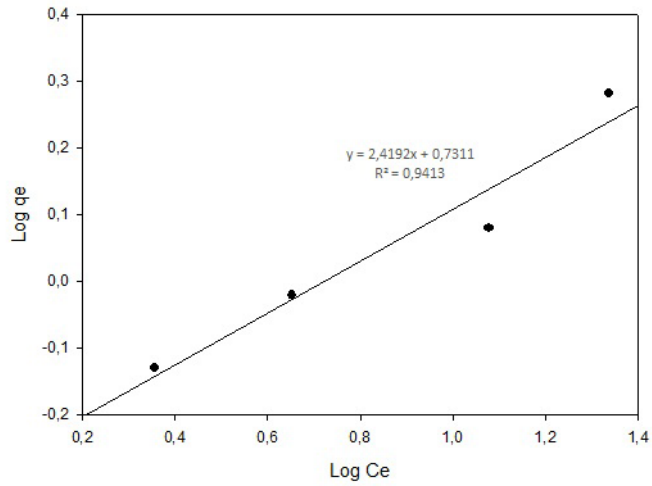
The isotherms of Langmuir and Freundlich at 60ºC are given in Fig. 4.8. K_F, K_L, Q_{max}, and n are computed by using the slope and the lines' intercepts in Fig. 4.8.


y = 0,4114x + 2,4867
R² = 0,9926
Ce / qe
Ce (mg/g)
0
2
4
6
8
10
12
14
0
5
10
15
20

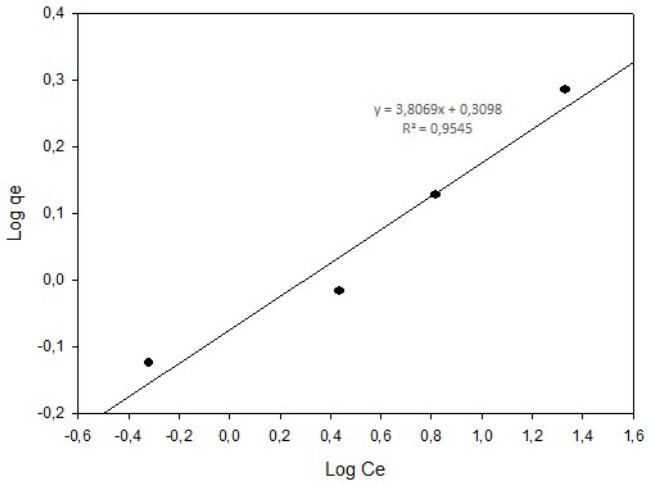
(a)


y = 0,4733x + 1,1812
R² = 0,981
Ce / qe
Ce (mg/g)
0
2
4
6
8
10
12
0
5
10
15
20

(b)


y = 2,4192x + 0,7311
R² = 0,9413
Log qe
Log Ce
-0,2
-0,1
0,0
0,1
0,2
0,3
0,4
0,2
0,4
0,6
0,8
1,0
1,2
1,4

(c)



(d)

Figure 4.8: The isotherms of Langmuir and Freundlich at 60°C
a) Langmuir - pH: 4.0 b) Langmuir - pH: 7.5
c) Freundlich - pH: 4.0 d) Freundlich - pH: 7.5

Table 4.5: The isotherm constants of Langmuir and Freundlich at 60°C

Langmuir			
pH	**Q_{max} (mg/g)**	**K_L (L/g)**	**R^2**
4.0	2.431	0.165	0.9926
7.5	2.113	0.401	0.9810
Freundlich			
pH	**n**	**K_F (mg/g)**	**R^2**
4.0	0.413	5.384	0.9413
7.5	0.263	2.041	0.9545

K_F is the Freundlich constant and an indicator for the adsorption capability of the resin. Thus, n is the divergence magnitude from the adsorption linearity. The Freundlich isotherm is generally used for the heterogeneous systems [37-39].

The Langmuir constant K_L is an indicator for the free energy of adsorption. According to the Langmuir model, adsorbed molecules cannot bind other molecules by lateral interaction. Therefore, the adsorption process is limited to the surface of the adsorbent. However, since Q_{max} (the maximum capacity of the adsorbent) is computed by the Langmuir isotherm, the total capacity must also be computed by the Langmuir [37, 38, 40].

When the correlation coefficients were investigated, it was determined that the Langmuir isotherm ($R^2 \geq 0.98$) is more suitable for both pH 4.0 and pH 7.5 than the Freundlich isotherm ($R2 \leq 0.96$). Therefore, it can be said that the Pd adsorption with Lewatit TP 214 is a monolayer adsorption at both pH values [37-39].

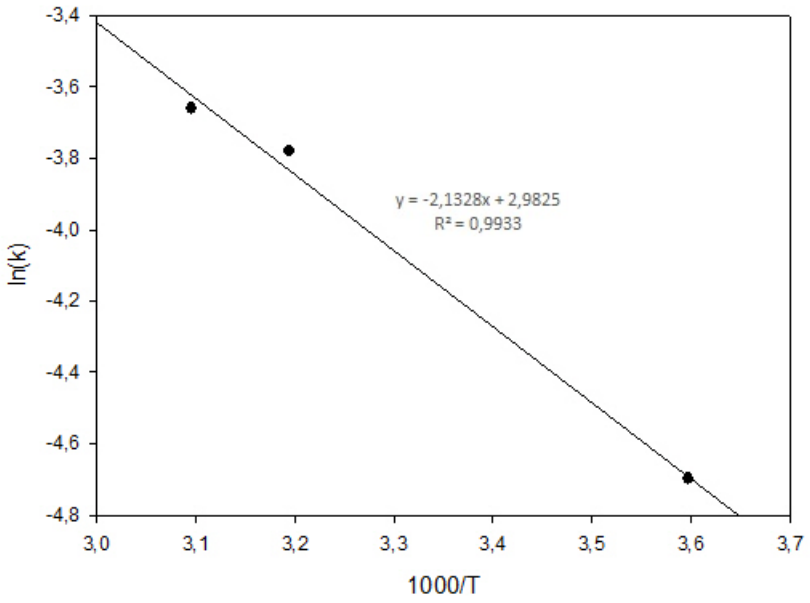
4.6. The investigation of adsorption thermodynamics

Another approach was also studied in the range of 25, 40, and 50°C to calculate the activation energy of the Pd adsorption; several kinetic models –i.e., one-dimensional, two-dimensional, and three-dimensional diffusion models, first-order kinetics, Jander equation, two-dimensional phase boundary reaction, three-dimensional phase boundary reaction, Erofeev and Avrami equation were investigated. Amongst them, the best fitting kinetic model was the first-order kinetics at pH 4.0 and one-dimensional diffusion at pH 7.5 by checking the results, using the following Equation 3 [38]:

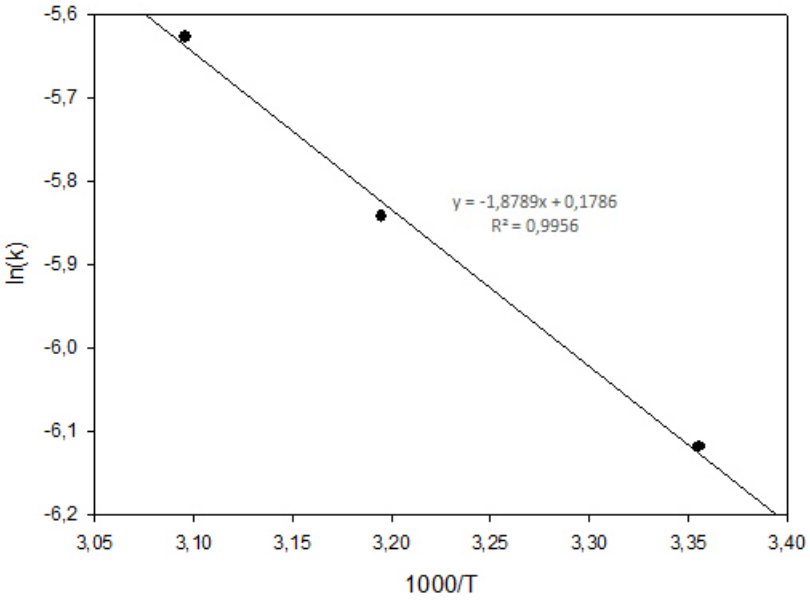
$$k_t = \left(\frac{C_o - C_t}{C_o}\right) \quad (3)$$

Table 4.6: The Pd adsorption rate constants at pH 4.0 and 7.5
(300 mg resin, 180 min, 100 rpm, pH 4.0 and 7.5, 2 mL of 60 ppm solution)

pH	T (°K)	k (min^{-1})	lnk	E_a	R^2
4.0	298	0.0091	-4.700	17.73	0.9933
	313	0.0228	-3.781		
	323	0.0257	-3.61		
pH	**T (°K)**	**k (min^{-1})**	**lnk**	**E_a**	**R^2**
7.5	298	0.0022	-6.119	15.62	0.9956
	313	0.0029	-5.843		
	323	0.0036	-5.627		



(a)



(b)

Figure 4.9: The Arrhenius plot of the Pd adsorption on the resin (ln(k) versus 1000/T) (300 mg Lewatit, 180 min, pH 4.0 and 7.5, 2 mL of 60 ppm solution, 100 rpm)

a) Arhenius – pH: 4.0 b) Arhenius – pH: 7.5

The activation energy (E_a) was computed by using the Equation 4 which is the Arrhenius equation [38]:

$$k = A\, e^{-Ea/RT} = RT \text{ or } \ln k = \ln A - E_a/RT \quad (4)$$

E_a is the activation energy, k is the rate constant, T is the temperature (K), and R is the gas constant. The Arrhenius plot for the Pd adsorption at both pHs are shown in Fig. 4.9. For the temperatures 25°C (298K), 40° (313K), and 50°C (323K), k and ln(k) values are shown in Table 4.6. At pH 4.0, the activation energy is 17.73 kJ/mol and at pH 7.5, the activation energy is 15,62 kJ/mol. Therefore, according to these results, a mixed mechanism controls the Pd adsorption process [38].

4.7. Characterization of Lewatit TP 214

4.7.1. XRF Analysis

As seen in Figures 4.10 and 4.11, unused Lewatit TP 214 has no significant peaks. As a result of the analysis made after the experiment, it was determined that Lewatit TP 214 retained Pd. Since the XRF method does not give as sharp results as XRD, some false peaks are seen. It is known that both Lewatit TP 214 and the waste solution do not contain elements such as Nb, Mo, Ag.

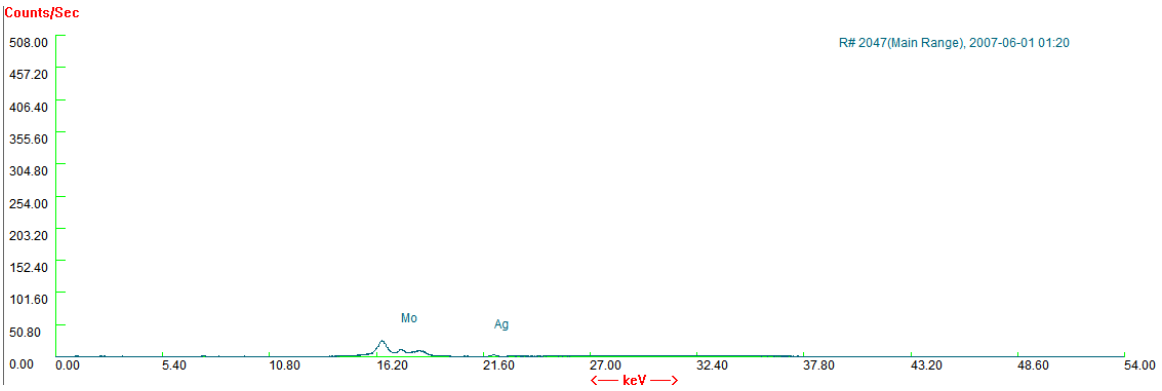


Figure 4.10: XRF result of unused Lewatit TP 214

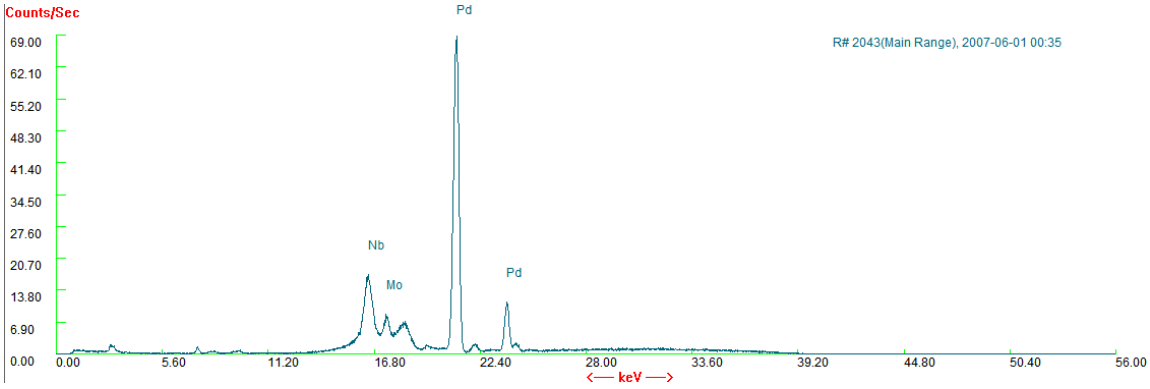


Figure 4.11: XRF pattern of Lewatit TP 214 after Pd recovery

4.7.2. SEM Images

The SEM images of the unused Lewatit TP 214 is shown in figure 4.12. In Figure 4.13, the SEM result of Lewatit TP 214 obtained after the experiment is given. The reason for the color change is that Lewatit has retained Pd.

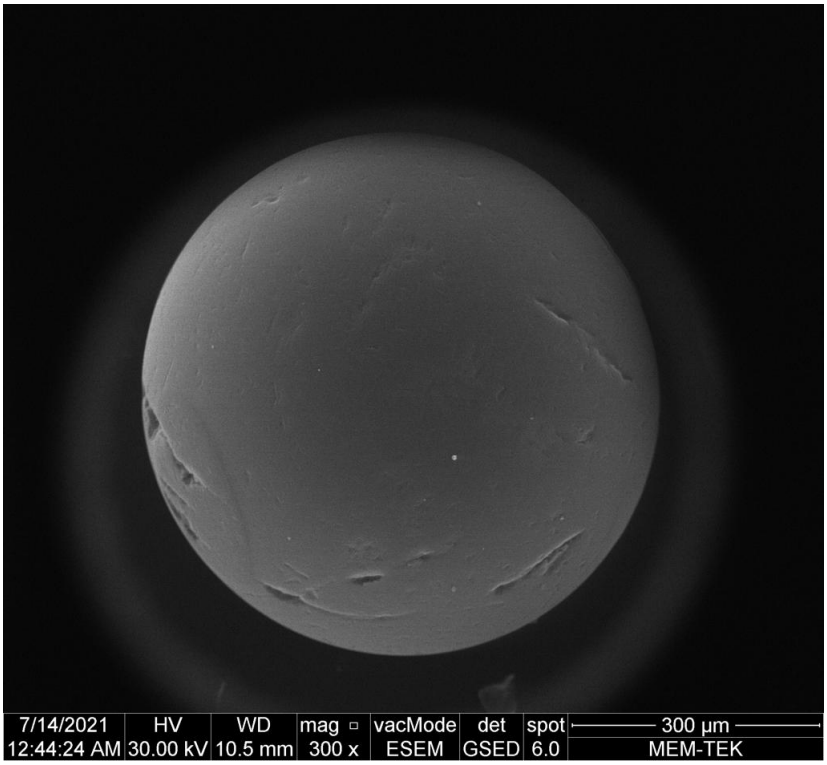


Figure 4.12: SEM result of unused Lewatit TP 214

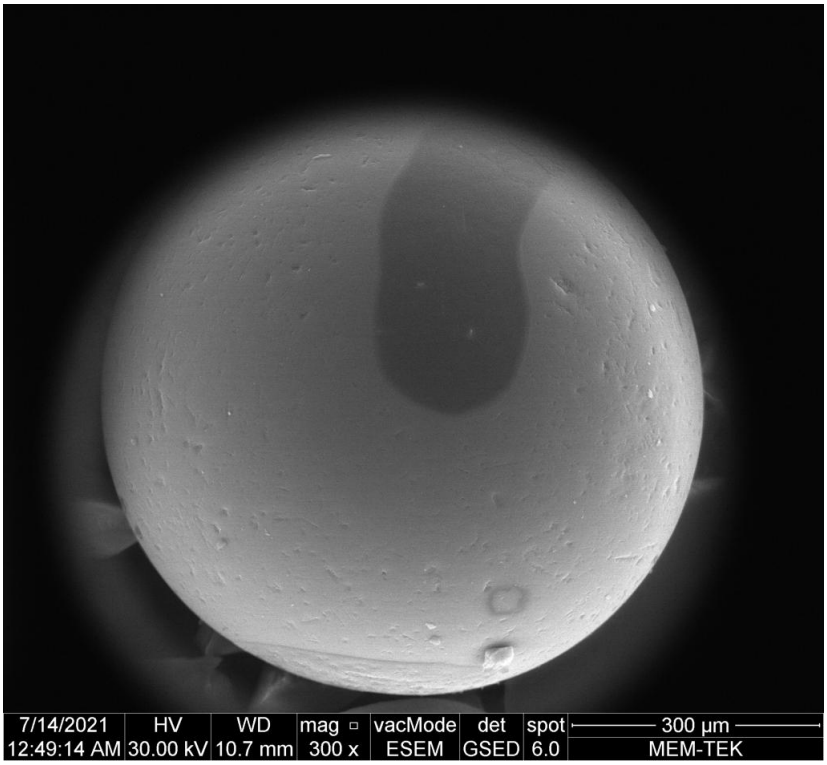


Figure 4.13: SEM result of Lewatit TP 214 after Pd recovery

4.7.3. FTIR Analysis

The FTIR spectral analyses of TP 214 resins before and after the adsorption have been carried out between 400 and 4000 cm^{-1} on an IFS Brukker 66v spectrometer.

As a result of the FTIR analysis, the asymmetric and symmetrical stretching bonds of -NH2 groups of thiouronium in the wavelength band 3200-3400 cm^{-1} (3358.44 cm^{-1} and 3266.33 cm^{-1}, respectively) were observed before and after adsorption on Lewatit TP 214 resin with thiouronium functional groups containing sulfur and nitrogen atoms. Beside the asymmetric stretching bonds of –CH2 (C-H) groups at 2922.22 cm^{-1} were present. N–H stretching of the unused Lewatit TP 214 were also observed in the wave range of 1620 cm^{-1}. The bands related to the functional group of Lewatit TP 214 were additionally present at 1530-1560 cm^{-1} indicating the stretch vibrations of C=C, the combination of C-N and C-S bonds in the range of 1427 cm^{-1}, finally the wavelength of the deformation bands of –NH2 groups between 1200-1080 cm^{-1}. The FTIR patterns prove that palladium was adsorbed by Lewatit TP 214.

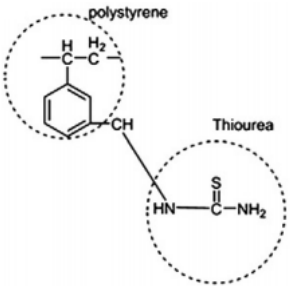


Fig 4.14: The molecular structure combined with PS and Thiourea of the Lewatit TP 214

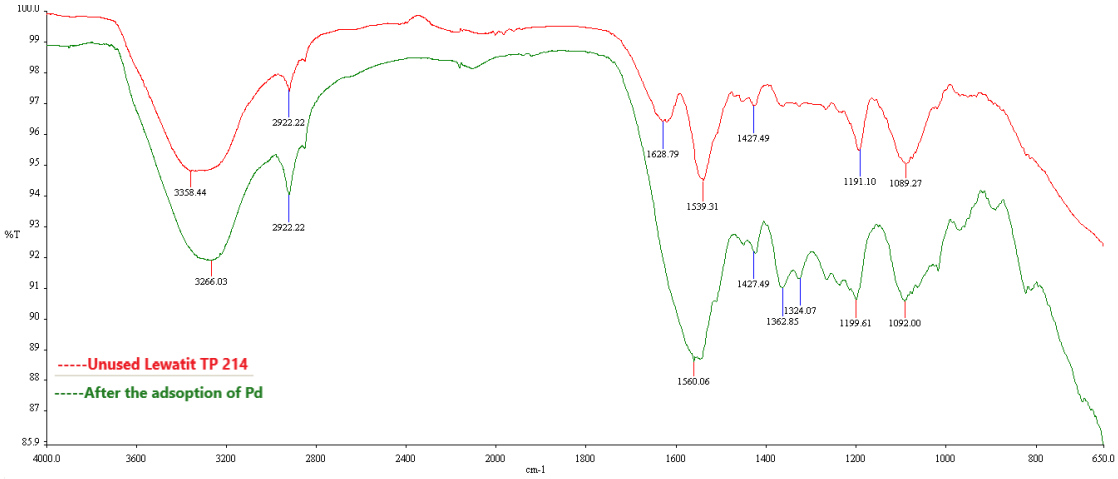


Fig 4.15: FTIR pattern of unused and used Lewatit TP 214

5. CONCLUSIONS

As a result of this detailed research on Pd adsorption behavior on Lewatit TP 214;

i. It was found that the increasing amount of Lewatit TP 214 increased the palladium adsorption as the sorbent/metal ratio was high, the amount of the active sites on the surface was enhanced, this state was thermodynamically more convenient, as stated in similar studies. The effect of the contact time on the Pd recovery was investigated between 0-180 min at pH 4.0 and 7.5 at the temperatures of 25°C, 40°C, 50°C, 60°C at 100 rpm by adding different amount of Lewatit TP 214 (100, 200, 300 and 400 mg). Depending on these other three parameters, i.e., solution pH's, sorbent dosage, and temperatures, the required time to reach the maximum efficiency percentage changed.

ii. The Pd adsorption percentage increased dynamically and aggressively, then reached 100 % at 40 min at pH 4.0; meanwhile, this behavior was extended over time and more stable at pH 7.5. It may conclude that the Lewatit TP 214 performed better at lower pH levels.

iii. When the correlation coefficients were investigated, it was determined that the Langmuir isotherm ($R2 \geq 0.98$) is more suitable for both pH 4.0 and pH 7.5 than the Freundlich isotherm ($R2 \leq 0.96$). Therefore, it can be said that the Pd adsorption with Lewatit TP 214 is a monolayer adsorption at both pH values.

iv. When the correlation coefficients were calculated, it was understood that the correlation coefficients of pseudo-second-order were closer to one than the correlation coefficients of pseudo-first-order, so the pseudo-second-order model explains this adsorption process better. Intra-particle diffusion correlation coefficients are lower than pseudo-second-order. Therefore, intra-particle diffusion may be an alternative model for the current system.

v. Several kinetic models were investigated. Amongst them; the best fitting kinetic model was the first-order kinetics at pH 4.0 and one-dimensional diffusion at pH 7.5. At pH 4.0, the activation energy is 17.73 kJ/mol and at pH 7.5, the activation energy is 15.62 kJ/mol. Therefore, according to these results, a mixed mechanism controls the Pd adsorption process.

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