Equilibrium, kinetics, and thermodynamics of Pd(II) adsorption onto poly(*m*-aminobenzoic acid) chelating polymer

Elif Mildan, Mustafa Gülfen

Department of Chemistry, Faculty of Arts and Sciences, Sakarya University, Serdivan 54187, Sakarya, Turkey
Correspondence to: M. Gülfen (E-mail: mgulfen@sakarya.edu.tr)

ABSTRACT: This study describes the equilibrium, kinetics, and thermodynamics of the palladium(II) (Pd(II)) adsorption onto poly(m-aminobenzoic acid) (p-mABA) chelating polymer. The p-mABA was synthesized by the oxidation reaction of m-aminobenzoic acid monomer with ammonium peroxydisulfate (APS). The synthesized p-mABA chelating polymer was characterized by FTIR spectroscopy, gel permeation chromatography (GPC), thermal analysis, potentiometric titration, and scanning electron microscopy (SEM) analysis methods. The effects of the acidity, temperature, and initial Pd(II) concentration on the adsorption were examined by using batch adsorption technique. The optimum acidity for the Pd(II) adsorption was determined as pH 2. In the equilibrium studies, it was found that the Pd(II) adsorption capacity of the polymer was to be 24.21 mg/g and the adsorption data fitted better to the Langmuir isotherm than the Freundlich isotherm. The kinetics of the adsorption fitted to pseudo-second-order kinetic model. In the thermodynamic evaluation of the adsorption, the $\Delta G°$ values were calculated as -16.98 and -22.26 kJ/mol at 25–55°C temperatures. The enthalpy ($\Delta H°$), entropy ($\Delta S°$), and the activation energy (E_a) were found as 35.40 kJ/mol, 176.05 J/mol K, and 61.71 kJ/mol, respectively. The adsorption of Pd(II) ions onto p-mABA was a spontaneous, endothermic, and chemical adsorption process which is governed by both ionic interaction and chelating mechanisms. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42533.

INTRODUCTION

Palladium, a platinum group metal (PGM), is used in many advanced industries such as automotive catalytic converters, dental/medical devices, jewelry, fuel cells, pharmaceuticals, telecommunication, petroleum, electronics, heat apparatus, corrosion resistance, and chemistry. It is an industrially important catalyst and utilized widely in automotive catalytic converters.[1] Palladium is an expensive metal and its demand has been increasing in recent years.[2] Catalysts are considered as a waste after a certain period of their active usage. The recovery of Pd(II) ions from both the leaching solutions of natural ores and industrial wastes are quite important because of full utilization of resources and expensive metal perspective of palladium[1]. Therefore, the analysis, separation, enrichment, and adsorption of Pd(II) ions are significant processes in the recycling of palladium.

In the adsorption of Pd(II) ions, ion exchange resins,[3,4] chelating polymers,[5–7] bioadsorbents,[8,9] and activate carbon[10] are used mostly. Chelating polymers are more preferable adsorbents in the adsorption of Pd(II) ions because of selectivity.[2] The

main problem in the adsorption with anion exchange resins and activate carbon is their low selectivity.[11] Chelating adsorbents are evaluated in the presence of functional groups on their surfaces for complexation reaction or ion exchange reactions with Pd(II) ions. Based on Pearson Hard–Soft Acid–Base (HSAB) theory, Pd(II) ion is among the soft acid metal ions such as gold(III) and Ag(I) ions and they show higher affinity to soft bases with N donor atom.[11,12] Chelating polymers containing N donor atoms exhibited a stable complex formation tendency with Pd(II) at specific pH area.[13] In other words, amine functional groups are known as good coordinating groups for Pd(II) ions.[5,6,14] The adsorption of Pd(II) ions has been studied by some researchers using the chelating polymers with amine functional groups. The some examples of these polymers are melamine–formaldehyde–thiourea,[5] thiourea/urea–formaldehyde,[6] aminated lignin derivatives,[15] amine functionalized ion exchanges,[3,16] imidazole containing resin,[17] and polyamine functionalized polystyrene.[18]

Poly(*m*-aminobenzoic acid) is a poly(aniline) derivative polymer, which is also named poly(aniline-3-carboxylic acid).

Therefore, poly(aminobenzoic acid)s can be synthesized by an oxidative reaction as similar to polyaniline. They are categorized in the functional polyanilines. Poly(m-aminobenzoic acid) is a chelating polymer which includes the seconder amine (C—NH—C) and carboxylic acid (—COOH) functional groups. The seconder amine group shows good chelating ability to Pd(II) ions. The secondary amine in poly(m-aminobenzoic acid) polymer can be protonated in acidic solutions and the amine group results in C—NH_2^+—C structure. So this protonated amine groups can adsorb $PdCl_n^{x-}$ anionic complexes via ionic interaction. As the other functional group, the carboxylic acid can also adsorb Pd(II) ions via ionic interaction and chelating mechanisms.[19]

In the present work, poly(m-aminobenzoic acid), (p-mABA) was synthesized by chemical oxidation of m-aminobenzoic acid by using ammonium peroxydisulfate. The synthesized p-mABA chelating polymer was characterized by fourier transform infrared spectroscopy (FTIR) spectroscopy, gel permeation chromatography (GPC), thermal analysis, and potentiometric titration methods. The adsorption of Pd(II) ions onto p-mABA polymer was studied by examining the influence of the initial acidity of the metal ion solution, contact time, initial concentration, and temperature. The equilibrium, kinetic, and thermodynamic behaviors of the Pd(II) adsorption were evaluated.

EXPERIMENTAL

Materials

All the chemicals were of analytical grade and used as purchased without further purification. The m-aminobenzoic acid (98%, Melting point: 178–180°C) which is used as a monomer and the ammonium peroxydisulfate (APS, $(NH_4)_2S_2O_8$) as the oxidant in the polymerization were supplied from Sigma-Aldrich Chemie GmbH, Steinheim. The palladium(II) chloride ($PdCl_2$, 99.9% Sigma-Aldrich Chemie GmbH, Steinheim) was dissolved in the ultra-pure water (18.2 megaohm, Milli-Q, United Kingdom) to prepare a stock solution at the concentration of 1000 mg/L. This obtained solution was diluted and used in the adsorption studies.

Synthesis of Poly(m-Aminobenzoic Acid)

Poly(m-aminobenzoic acid) (p-mABA) chelating polymer was synthesized by the chemical oxidative polymerization reaction of m-aminobenzoic acid as the monomer and ammonium peroxydisulfate (APS) as the oxidant. The oxidative polymerization of the p-mABA was performed similarly to poly(aniline). The reduction and oxidation reactions in the polymerization are shown with eqs. (1) and (3). In addition, the mechanism of the polymerization was also given in Figure 1.[19,20] In this study, the molar ratio of the monomer to oxidant in the polymerization of the p-mABA was taken as 1 : 2. For the synthesis, 40 mmol (5.48 g) m-aminobenzoic acid was dissolved in 50 mL water in a beaker and 80 mmol $(NH_4)_2S_2O_8$ (18.24 g) was dissolved in 100 mL water in a different beaker. The $(NH_4)_2S_2O_8$ solution is acidified with 2 mL HCl solution (d=1.18 g/mL, 36.5%). After heating up to 50°C, the acidic solution of $(NH_4)_2S_2O_8$ was added into the m-aminobenzoic acid solution by droping. At same time, the mixture was stirred strongly. Five minutes later, black color polymer began to precipitate. The precipitated polymeric suspension was stirred at 50°C for 24 h.

The obtained polymer was filtered and washed thoroughly with 0.1 M HCl solution and then ultra-pure water to remove the residual oxidant and water-soluble oligomers. It was dried under vacuum at 40°C for 3 h. The polymeric yield was calculated as 54.1%. This synthesized polymer was used in all the experimental studies.[21–27]

$$S_2O_8^{2-} + 2H^+ + 2e^- => 2HSO_4^- \quad \text{(Reduction reaction) (1)}$$

$$\text{(Oxidation reaction) (2)}$$
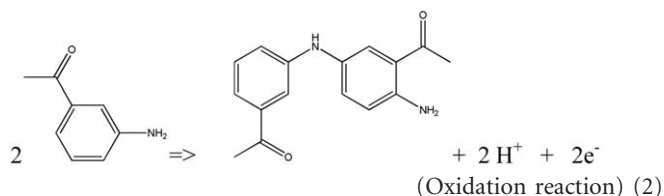
FTIR Spectroscopy

The FTIR spectra of the m-aminobenzoic acid, HCl doped p-mABA, undoped p-mABA, and Pd(II) adsorbed p-mABA samples were recorded on a Spectrum Two model spectrometer (Perkin Elmer) equipped with ATR. The spectra of the samples were measured in the range of 450 and 4000 cm^{-1} with 2 cm^{-1} resolution. The m-aminobenzoic acid monomer was used as received without any processing. The undoped p-mABA sample was prepared by equilibrating in the solution at pH 9–10. The HCl doped polymer was obtained by washing the p-mABA with 1 M HCl solution and then ultra-pure water. It was dried under vacuum condition at 40°C. The Pd(II) adsorbed polymer sample was prepared by stirring 0.3 g polymer in 100 mL 45 mg/L Pd(II) solution at 25°C. The Pd(II) adsorbed polymer was also washed with ultra-pure water and dried under vacuum condition at 40°C.

Thermal Analysis

In the examination of the thermal stability of the p-mABA polymer, the TG, and DTA analyses were performed on a Netzsch STA 449F1 model (Geratebau, GmbH) thermal analyzer. In the measurement, the HCl doped form of the polymer was used. About 50 mg of the HCl doped p-mABA sample was filled into an alumina crucible, and then the thermal analysis measurements were carried out from 25 to 750°C with a heating rate of 10°C/min in the air atmosphere.

Potentiometric Titration

To examine the H^+ ion adsorption capacity or the protonation capability of the synthesized p-mABA polymer, a 2.00 g amount of the p-mABA was equilibrated in 100 mL of 1 M HCl solution and it was filtered and dried at 40°C. The H^+ ion adsorption capacity of the p-mABA was measured by the potentiometric titration method using 0.1 M NaOH solution as the titrant. In the potentiometric titration, the pH change vs. mL titrant was measured by using a pH meter and a titration curve has been drawn from the obtained data.

Molecular Weight

A gel permeation chromatography (GPC, Shimadzu) instrument was used in the measurements of the molecular weights of the p-mABA polymer. The number average molecular weight (Mn) and weight average molecular weight (Mw) values of the p-mABA were obtained. Standard polystyrene solutions were used in calibration
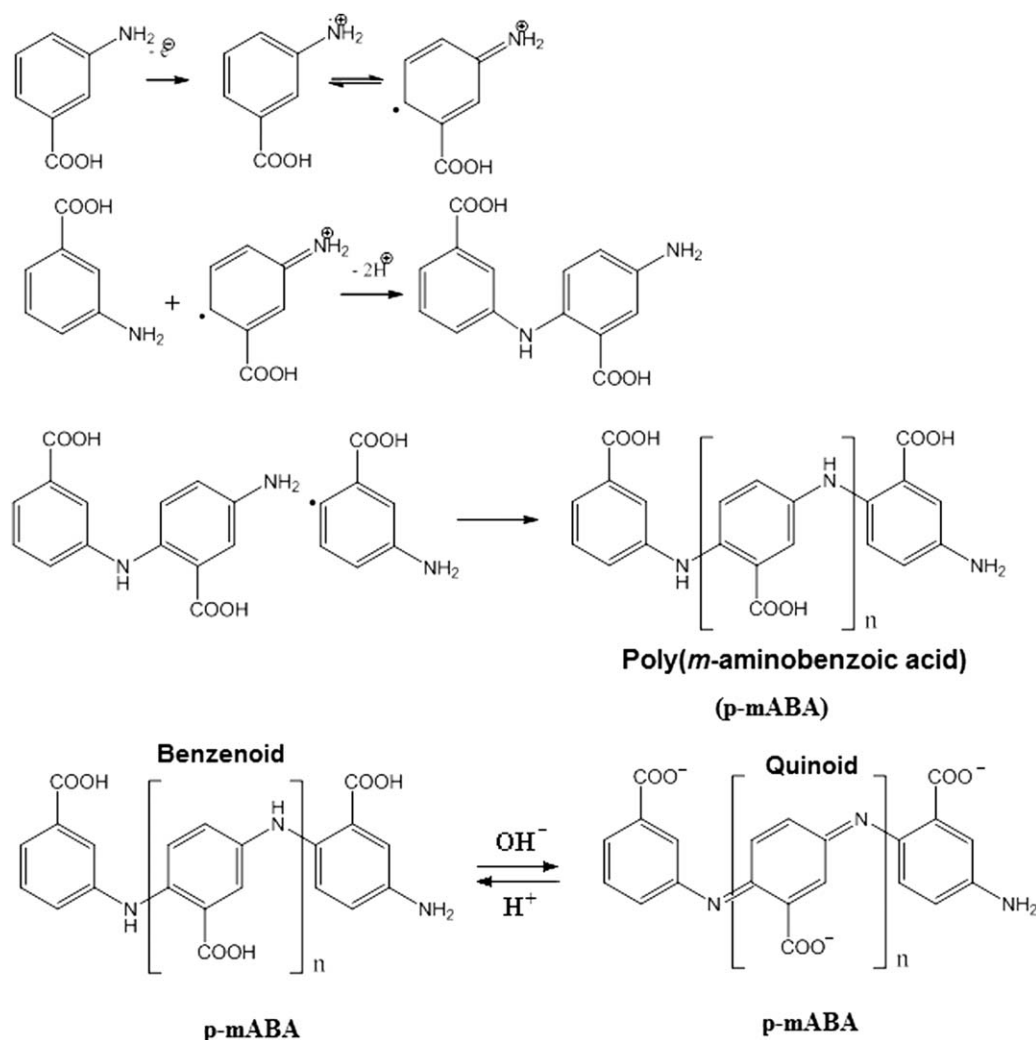
Figure 1. The synthesis mechanism, benzenoid, and quinoid forms of poly(*m*-aminobenzoic acid).[19,20]

of the GPC instrument. The measurements of the p-mABA polymer were performed after it was dissolved in THF solvent.

Scanning Electron Microscopy (SEM) Analysis

To observe the surface morphology of the p-mABA polymer, scanning electron microscopy (SEM) was used. The acid, base, and Pd(II) adsorbed forms of the p-mABA polymer were examined with SEM analysis. The p-mABA-acid and p-mABA-base samples were prepared by equilibrating in 0.1 *M* HCl acid solution and NaOH base solution at pH 10, respectively. The Pd(II) adsorbed p-mABA sample was prepared by equilibrating the polymer in 75 mg/L Pd(II) solution and then washing with distilled water. In the measurements, a JEOL 6060LV model scanning electron microscope (SEM) was used to image the surface morphology of the prepared polymer samples.

Pd(II) Adsorption Studies

Effect of Acidity. The effect of acidity on the Pd(II) adsorption was examined by the batch equilibrium technique. A series of 100 mL Pd(II) solutions at the concentration of 45 mg/L were prepared. The initial acidities of the solutions were adjusted to

3, 2, and 1 *M* HCl, and pH 1, 2, 4, and 6 by using HCl or NaOH solutions. The 0.3 g of the polymer samples were added into each prepared solution and the obtained mixtures were stirred on a magnetic stirrer at room temperature for 120 min. The sample solutions were taken in time intervals of 0, 15, 30, 60, and 120 min and the Pd(II) concentrations in these sample solutions were determined on Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The adsorbed Pd(II) amounts on the polymer surface were calculated and the optimum acidity in the Pd(II) adsorption was determined.

Effect of Initial Pd(II) Concentration. The effect of initial Pd(II) concentration on the adsorption was examined. The 0.3 g portions of polymer samples were added into the each of 100 mL Pd(II) solutions at the concentrations of 30, 45, 60, and 75 mg/L. The acidities of the Pd(II) solutions were adjusted to pH 2 which is determined previously as the optimum pH value. They were equilibrated for 120 min. During the adsorption, the sample solutions were taken in the different time intervals. The Pd(II) concentrations in these sample solutions were
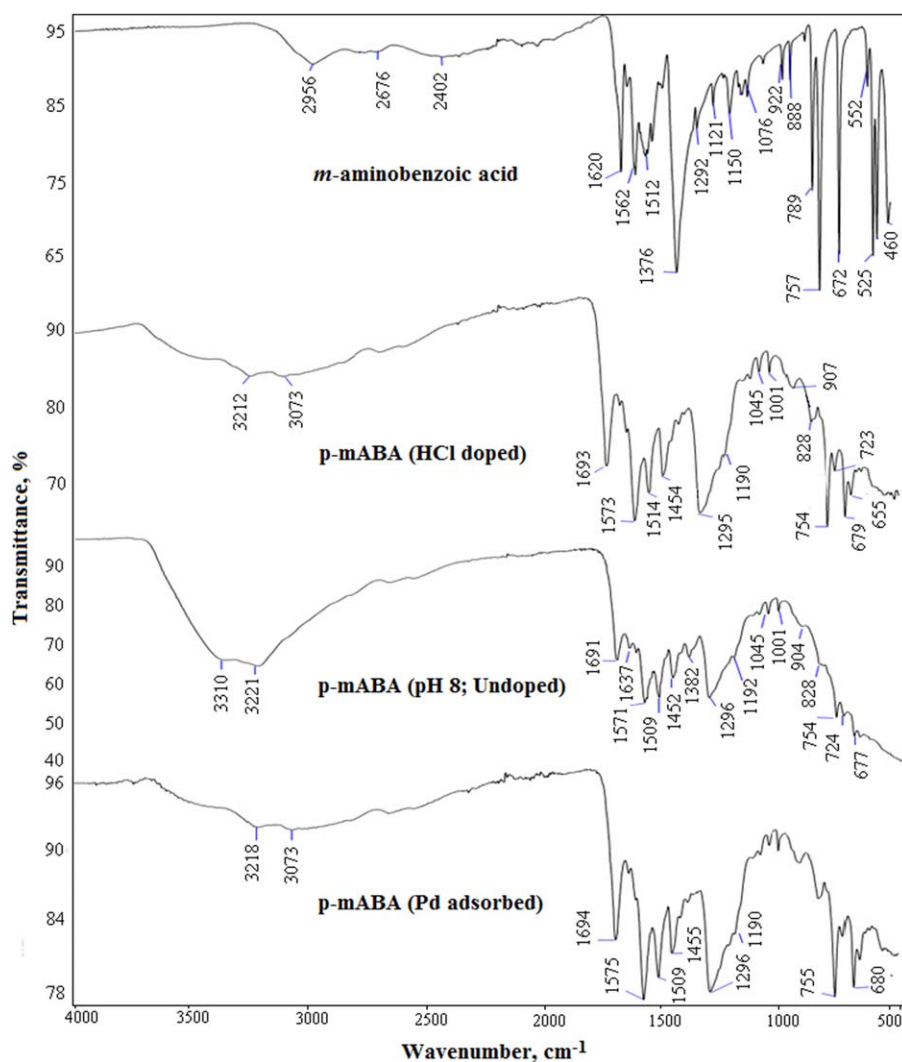
Figure 2. FTIR spectra of *m*-aminobenzoic acid, p-mABA, and Pd(II) adsorbed p-mABA polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

determined by using ICP-OES instrument. The obtained adsorption data were applied to the Langmuir and the Freundlich isotherms to calculate the maximum adsorption capacity (q_m) and to investigate the adsorption equilibrium.

Effect of Temperature. The effect of temperature on the Pd(II) adsorption was studied at 25, 35, 45, and 55°C. In these adsorption studies, 0.3 g polymer samples were equilibrated in 100 mL Pd(II) solutions at pH 2 for 120 min. The sample solutions were taken at pre-determined time intervals for the residual Pd(II) ion concentrations in the solutions. The Pd(II) ion concentrations in the solution phase were measured by ICP-OES. The amounts of adsorbed Pd(II) ions on the p-mABA polymer were calculated for each temperature. The obtained data were used in the calculations of the thermodynamic parameters ($\Delta G°$, $\Delta H°$, $\Delta S°$, and E_a) of the Pd(II) adsorption.

Chemical Analysis of Pd(II) Ions
All the Pd(II) concentrations in the adsorption studies have been determined by using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). A Spectro Arcos model

ICP–OES instrument (SPECTRO Analytical Instruments GmbH, Germany) was used. The ICP-OES spectrophotometer equipped with horizontal torch and an auto sampler. It was operated at a plasma argon flow-rate of 12.0 L/min, auxiliary argon flow-rate of 1.0 L/min, and integration time of 45 s. The polychromator of the ICP-OES was thermostated at 15°C and purged with argon gas. Pd(II) concentrations were measured at the emission wavelength of 340.458 nm. The standard solutions at the concentrations of 250, 500, 1000, 5000, 10,000, and 15,000 μg/L were used in the calibration of the ICP-OES. In the measurements, the limit of detection (LOD = $X_{bl} \pm 3s$) was calculated as 200 μg/L from the blank standard solutions.

RESULTS AND DISCUSSION

FTIR Spectroscopy
FTIR spectroscopy was used for controlling the polymeric structure of the p-mABA and the binding of the Pd(II) ions on the p-mABA. The FTIR spectra of the monomer, HCl doped p-mABA, undoped p-mABA, and Pd(II) adsorbed p-mABA are given in Figure 2. On the spectra, the absorption peaks between
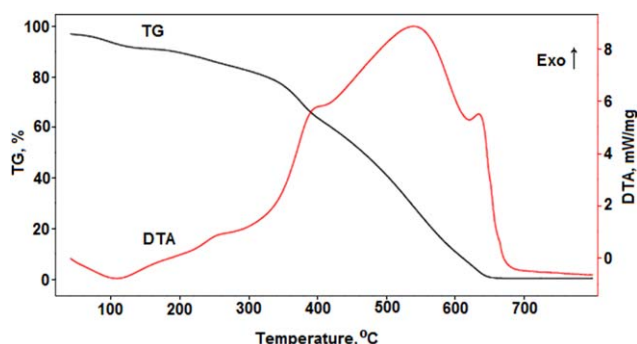
Figure 3. Thermal analysis of p-mABA polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

3000 and 3400 cm^{-1} were assigned as the primary and secondary amines (N—H stretching). The peak at around 1690 cm^{-1} corresponds the C=O bond due to the presence of —COOH groups in the polymer. For the monomer, this peak appeared at 1620 cm^{-1} wavenumber.[23,28] The peaks at around 1573 and 1514 cm^{-1} were noted for the quinoid ring C=C stretching and benzenoid ring C=C stretching, respectively.[19,29] The intensities of these peaks have changed after the polymer was deprotonated with NaOH solution. The protonation equilibrium is effective in the formation of the benzenoid and quinoid rings of the polymer. The peak at around 828 cm^{-1} shows the new substitution to benzene ring. This confirms the C—NH—C bounding in polymerization. Also, NaOH addition has changed the aromatic C—H peaks at around 754 cm^{-1} due to the quinoid form.[28] As a result, the obtained FT-IR spectra confirm the polymeric structure of p-mABA. In addition, the Pd(II) adsorption on the p-mABA chelating polymer was also examined by FT-IR spectroscopy. It was found that the spectrum of the Pd(II) adsorbed p-mABA polymer are similar to the spectrum of the HCl doped polymer. This may be due to the exchange of H-bonding with Pd(II) coordination on the N donor atom. It means that the chelating mechanism in the Pd(II) adsorption is also possible.

Thermal Analysis

The thermal stability of the p-mABA polymer was performed on a thermal analyzer. The TG and DTA curves of the polymer obtained from the thermal analysis are given in Figure 3.
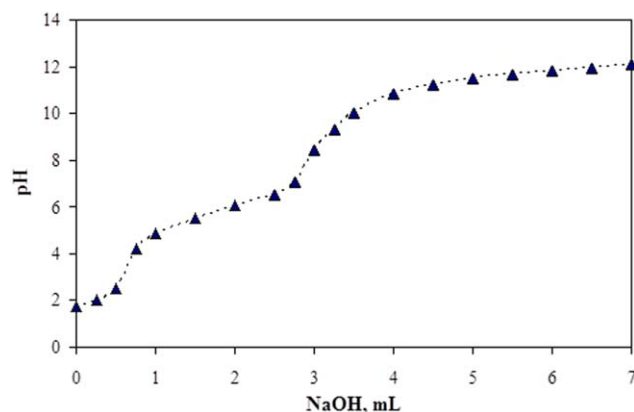

Figure 4. Potentiometric titration of p-mABA polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

According to the TG curve, it was found that the p-mABA polymer showed high thermal stability from room temperature to about 300°C. The polymer has relatively small weight loss at the temperatures below 300°C due to probably water and HCl release. The polymer started to decompose above 300°C. The exothermic peak of DTA curve above 300°C also confirms the decomposition of the polymer. Also, the DTA curve of the polymer did not show any glassy transition or melting point. The melting point of m-aminobenzoic acid monomer is 180°C. The fact that there is no endothermic peak at around 180°C is that the residual monomer molecules could be washed at the end of the polymerization. The all thermal analysis results reveal that the p-mABA polymer can be used as an adsorbent at high temperatures.

Potentiometric Titration

Poly(aminocarboxylic) acid polymers include secondary amine and carboxylic acid groups which can be protonated and form equilibrium with H$^+$ ions in solutions. Therefore, the Pd(II) adsorption on the p-mABA polymer can be affected from the acidity of the solution. In this study, the p-mABA polymer was characterized by potentiometric titration method to examine the H$^+$ ion equilibrium between the p-mABA and the solution phase. The obtained titration curve is given in Figure 4. The p-mABA polymer showed two different end points at pH 3.33 and 8.47. Below these pH values, the p-mABA polymer is protonated and the Pd(II) adsorption is affected from the protonation. Additionally, the hydrogen ion capacity of the p-mABA polymer was calculated from the potentiometric titration curve. It was found that the hydrogen ion capacity of the p-mABA was 0.16 meq H$^+$/g polymer. The H$^+$ ion capacity shows the possible Pd(II) ion adsorption capability of the polymer.

Molecular Weight

Molecular weight measurement gives a general idea about polymeric structures. In this study, the synthesized p-mABA polymer was also examined by measuring its average molecular weights (Mn and Mw) with GPC method. According to the results, the number average molecular weight (Mn) and the weight average molecular weight (Mw) values for the major fractions of the p-mABA were found as 1444 and 1474 g/mol, respectively. The empirical formula of the p-mABA polymer can be written as $(C_7H_4O_2N)_{n=7-11}$. As a polymeric material, the obtained molecular weights are low values. However, a polymer which is not dissoluble in aqueous solutions is enough for the Pd(II) adsorption.

SEM Analysis

The acid, base, and Pd(II) adsorbed forms of the p-mABA polymer were examined by using SEM analysis. The obtained SEM micrographs are given in Figure 5. It was found that the acid and base forms of the polymer showed different particle sizes. The acid form of the polymer has been flocculated in about 5–20 μm particle sizes. The base form of the polymer has low flocculated particles as about 1–5 μm. The flocculation morphology of the Pd(II) adsorbed p-mABA is similar to the p-mABA-acid sample. The flocculation of the p-mABA-acid and p-mABA-Pd samples may be due to ionic interactions on the surfaces of the particles. In case of the p-mABA-base, the
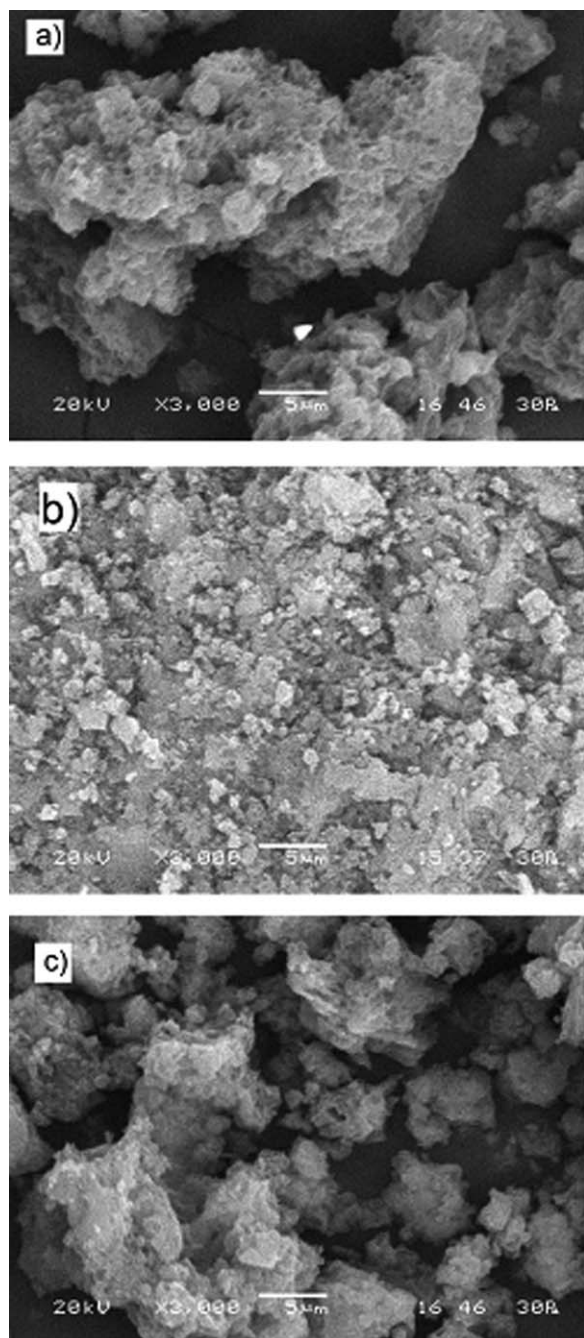
Figure 6. Effect of acidity on Pd(II) adsorption (0.3 g polymer; 45 mg/L Pd(II); 100 mL solution; 25°C).

$$\text{Adsorption } (\%) \ = \frac{(C_0 - C_e).100}{C_0} \qquad (3)$$

where, C_o is the initial concentration (mg/L) and C_e is the equilibrium concentration (mg/L) of Pd(II) ions in the solutions.

The experimental results from the examining the effect of acidity are given in Figure 6. The maximum adsorption values for Pd(II) ions were obtained in the pH range of 2–4. So, the optimum acidity was selected as pH 2 and the further Pd(II) adsorption studies were carried out according to that pH value.

The pH of the solution in the adsorption process affects both the species of Pd(II) ions as the adsorbate and the surface of the polymeric adsorbent. The speciation of Pd(II) ions in aqueous solutions depends on pH and total Cl^- ion concentration. Pd(II) ions can form a variety of mostly anionic chloride ($PdCl^+$, $PdCl_2$, $PdCl_3^-$, $PdCl_4^{2-}$), hydroxide ($Pd(OH)_2$, $Pd(OH)_4^{2-}$), and hydroxychloride ($PdCl_3(OH)^{2-}$, $PdCl_2(OH)_2^{2-}$, $PdCl(OH)_3^{2-}$) species, related to pH and total Cl^- ion concentration. In the solutions containing higher Cl^- ion concentrations than 0.1 M, the dominant Pd(II) ion is $PdCl_4^{2-}$. The hydroxychloride complexes of Pd(II) begin to occur at pH 8 and over. The cationic Pd(II) species, such as $[PdCl(H_2O)_3]^+$, Pd^{2+}, $Pd(OH)^+$ are predominant only when the concentration of Cl^- ions is lower than 0.001 M.[14,30–33] As a result, the cationic, anionic, hydroxo, chloro, and hydroxychloro complexes of Pd(II) ions are determinative species in the amount and mechanism of the Pd(II) adsorption.

On the other hand, the chemical structure of p-mABA polymer is also affected by the acidity of the solution. p-mABA chelating polymer has got the secondary amine (C—NH—C) and carboxylic acid (—COOH) groups which are responsible for the Pd(II) adsorption. These groups are protonated in acidic solutions [eqs. (4) and (5)]. Hence, the Pd(II) adsorption onto the p-mABA polymer is assumed to occur through single or mixed mechanisms including: (a) ionic interaction (ion exchange with protonated groups) [eqs. (6) and (7)] and (b) chelating with amino and carbonyl groups [eqs. (8) and (9)]. The nature of the Pd(II) adsorption depends on the parameters related to the species of Pd(II) ions and the protonation of the polymer, which can be adjusted by the pH of the solution. The

Figure 5. SEM micrographs of p-mABA-acid (a), p-mABA-base (b), and p-mABA-Pd(II) (c).

protonated groups on the polymer surfaces were neutralized by NaOH solution and the polymer has resulted in dispersed particles with low particle sizes.

Pd(II) Adsorption Studies

Effect of Acidity. In adsorption processes, the acidity of aqueous solutions is an important control parameter. Therefore, firstly, the effect of acidity on the Pd(II) adsorption has been investigated in the range of 3 M HCl and pH 6. In the adsorption studies, the percent amounts of the adsorbed Pd(II) ions were calculated with following equation:
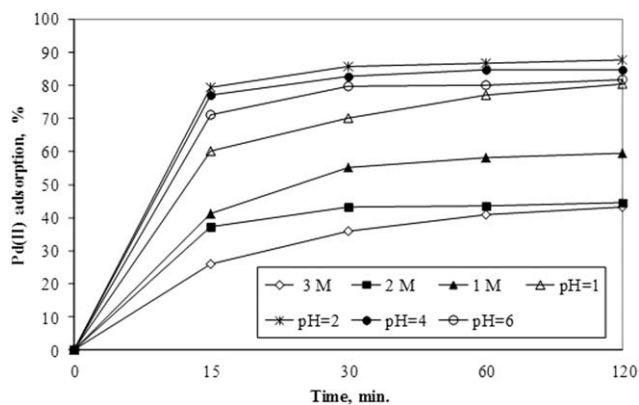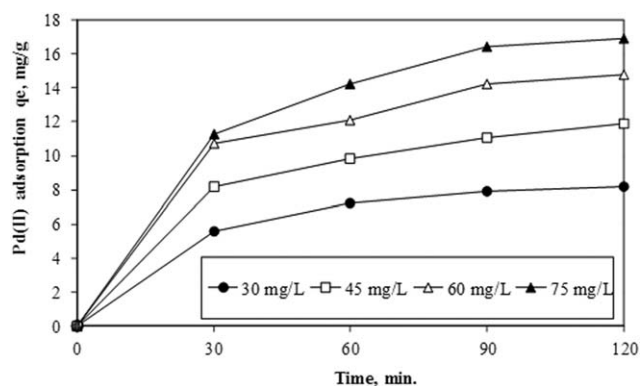
Figure 7. Effect of initial Pd(II) concentration (0.3 g polymer; 100 mL Pd(II) solution; 25°C; pH 2).

$$(R)(OH)C{=}O \;+\; PdCl_4^- \;\rightarrow\; (R)(OH)C{=}O$$
$$PdCl_3^- + H^+ + \; Cl^- \quad (Chelating) \tag{9}$$

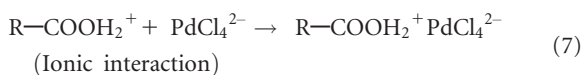If the Pd(II) adsorption studies with 3 and 1 M HCl in Figure 6 are examined, it can be seen that the adsorption values decreased according to the results at pH 2. This decrease is due to the competition of chloride ions with the anionic species of Pd(II) ion. The Pd(II) adsorption was found as about 70% at pH 6. This high adsorption value confirms the contribution of chelating mechanism in the adsorption. At pH 6, the chelating mechanism governs the Pd(II) adsorption because the polymer include less protonated amine or carbonyl groups.[34] At the end of the acidity effect studies, it can be concluded that both ionic interaction and chelating mechanisms are possible in the adsorption. The chelating mechanism is favorable at high pH values and the ionic interaction is favorable in high acidic conditions. The ionic interaction is more effective at around pH 2 and the chelating is effective pH 6 and over.

protonation of the polymer can be examined by a potentiometric titration. It gives a good idea about the pH values in which the polymer is protonated. The titration curve exhibited two end points as pH 3.33 and 8.47 (Figure 4). At pH 2 and 4, $PdCl_4^{2-}$ and $PdCl_3^-$ anionic complexes are the predominant species and high Pd(II) adsorption values were obtained (Figure 6).[5,6,32]

$$R{-}NH{-}R \;+\; H^+ + \; Cl^- \rightarrow \; R{-}NH_2^+{-}R \;+\; Cl^- \quad (Protonation) \tag{4}$$

$$R{-}COOH \;+\; H^+ + \; Cl^- \rightarrow \; R{-}COOH_2^+ + \; Cl^- \quad (Protonation) \tag{5}$$

$$(R_2)NH_2^+ + \; PdCl_4^{2-} \rightarrow \; (R_2)NH_2^+PdCl_4^{2-} \quad (Ionic\ interaction) \tag{6}$$

$$R{-}COOH_2^+ + \; PdCl_4^{2-} \rightarrow \; R{-}COOH_2^+PdCl_4^{2-}$$
$$(Ionic\ interaction) \tag{7}$$

$$(R_2)NH_2^+ + \; PdCl_4^- \;\rightarrow\; (R_2)NHPdCl_3^- + H^+ + \; Cl^-$$
$$(Chelating) \tag{8}$$

Effect of Initial Pd(II) Concentration. For examining the effect of initial Pd(II) concentration on the adsorption, the experimental studies were performed at the different initial Pd(II) concentrations of 30, 45, 60, and 75 mg/L. The amounts of the adsorbed Pd(II) ions were calculated according to eq. (10).

$$q_e = \frac{(C_i - C_e).V}{m} \tag{10}$$

where, q_e is the adsorbed amount (mg/g), V is the solution volume (L), m is the mass of the polymer (g), C_i and C_e are the initial and equilibrium concentrations of Pd(II) ions (mg/L), respectively. The obtained adsorption values with the different initial Pd(II) concentrations are given in Figure 7.

Adsorption isotherms are mathematical models that describe the equilibrium of the adsorbate species among liquid and adsorbent.[2,35] For the adsorption equilibrium of Pd(II) ions, the Langmuir and Freundlich isotherm models were applied to the adsorption data. The linear forms of the Langmuir [eq. (11)] and Freundlich [eq. (12)] isotherms are represented with the following equations;[2,35–37]
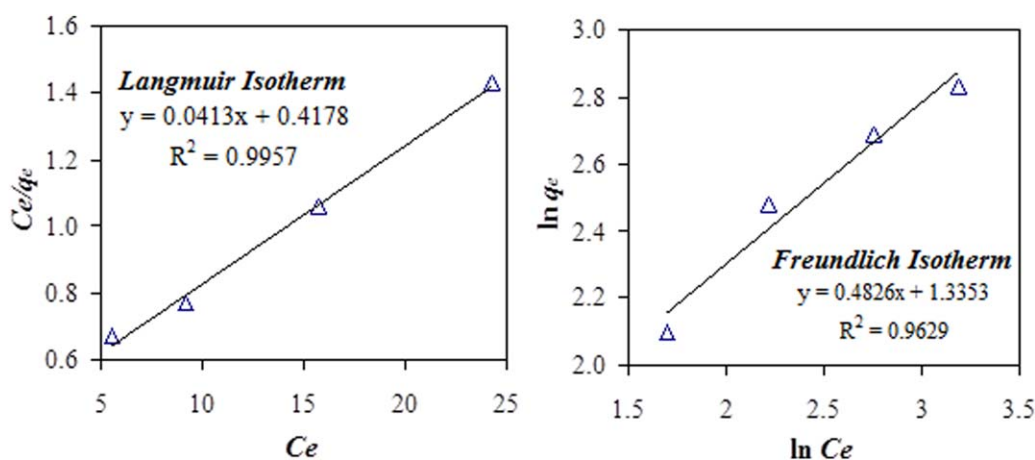

Figure 8. The Langmuir and the Freundlich adsorption isotherms. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. The Parameters of the Langmuir and Freundlich Isotherms

Temperature (°C)	The Langmuir			The Freundlich		
	q_m (mg/g)	K_L(L/mg)	R^2	K_F(L/g)	$1/n$	R^2
25	24.21	0.0982	0.9962	3.816	0.4826	0.9629

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (11)$$

$$\ln q_e = \ln K_F + \frac{1}{n}(\ln C_e) \qquad (12)$$

where, C_e is the equilibrium concentration of adsorbate (mg/L); q_e is the amount of Pd(II) ions adsorbed per gram of the adsorbent at equilibrium (mg/g); q_m is the maximum monolayer coverage capacity (mg/g); K_L is the Langmuir isotherm constant (L/mg); K_F is the Freundlich isotherm constant (mg/g); and n is adsorption intensity.

The adsorption data were used in the plotting of the Langmuir [eq. (11)] and Freundlich [eq. (12)] isotherms[2,35–37] and the obtained plots of the isotherms were demonstrated in Figure 8. The parameters of the Langmuir and the Freundlich isotherms were calculated from the linear plots in Figure 8. They are given separately together with the regression coefficients (R^2) in Table I.

Based on the regression coefficients (R^2) criteria, it was found that the adsorption of Pd(II) onto p-mABA polymer fitted better to the Langmuir model than the Freundlich model. The maximum adsorption capacity (q_m) was calculated as 24.21 mg Pd(II)/g polymer. The Langmuir adsorption isotherm describes a monolayer adsorption on the surface of the adsorbent, and after that no further adsorption takes place. The model assumes uniform energies of adsorption onto the surface. This means that Pd(II) ions were adsorbed by homogeneous sites on the surface of the p-mABA polymer. These sites are probably protonated secondary amine and carboxylic acid groups.

One of the essential characteristics of the Langmuir isotherm model could be expressed by dimensionless constant called the equilibrium parameter (R_L). The R_L value indicates the shape of the isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$),

favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). R_L can be calculated using following equation:[22,38]

$$R_L = \frac{1}{1 + K_L C_i} \qquad (13)$$

where, C_i is the initial concentration (mg/L) and K_L is the Langmuir constant related to the energy of adsorption (L/mg).[22,38] The R_L values were calculated between 0.120 and 0.253 for the different initial Pd(II) concentrations. These R_L values show that the adsorption of Pd(II) ions on the p-mABA polymer is a favorable adsorption.

Effect of Temperature. The effect of temperature on the adsorption of Pd(II) ions was studied at 25, 35, 45, and 55°C temperatures for 120 min contact time. The obtained experimental results are given in Figure 9. With respect to the contact time, it was found that the Pd(II) adsorption increased rapidly within first 30 min contact time and then the adsorption rate slowed. The equilibrium state of the adsorption was obtained in 120 min time. If the effect of temperature on the adsorption of the Pd(II) ions in Figure 9 is examined, it can be seen that higher temperatures favor in the adsorption. So, it can be concluded that the Pd(II) adsorption is a temperature-dependent and endothermic process. This attributes a chemical interaction between Pd(II) ions and the p-mABA polymer.

Adsorption Kinetics. In order to examine the rate controlling mechanism in the adsorption, the kinetic data obtained from the adsorption studies at different temperatures were applied to pseudo-first-order and pseudo-second-order kinetic models. The linear forms of pseudo-first-order [eq. (14)] and pseudo-second-order [eq. (15)] kinetic models are given with the following equations;

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (14)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (15)$$

where, q_t and q_e (mg/g) are the amounts of Pd(II) ions adsorbed at equilibrium (mg/g) and t (min), respectively. k_1 (1/min) and k_2 (g/mg min) are the rate constants.[39,40]

The plots of the pseudo-first-order and the pseudo-second-order kinetic equations are given in Figure 10. The regression coefficient (R^2) values and the rate constants (k_1 and k_2) were calculated and they are given in Table II. The R^2 values of the plots showed that the adsorption kinetic data fitted better the pseudo-second-order kinetic model. The pseudo-second-order kinetic equation agrees with chemisorption (chemical reaction) as the rate-controlling mechanism.[39,40]

Figure 9. Effect of temperature on the adsorption (0.3 g polymer, 100 mL Pd(II) solution, 45 mg/L Pd(II), pH 2).

Adsorption Thermodynamics. Thermodynamic behaviors of the adsorption of Pd(II) ions on the p-mABA chelating polymer

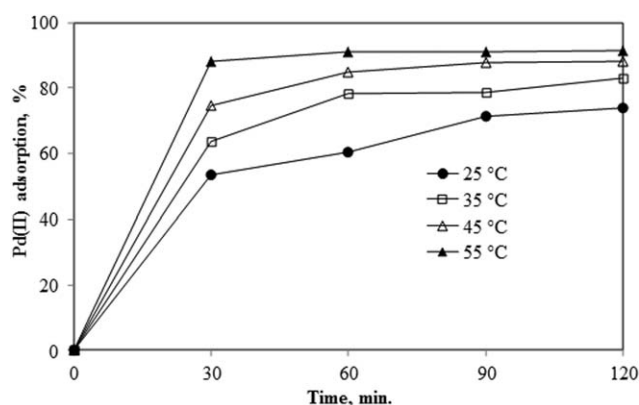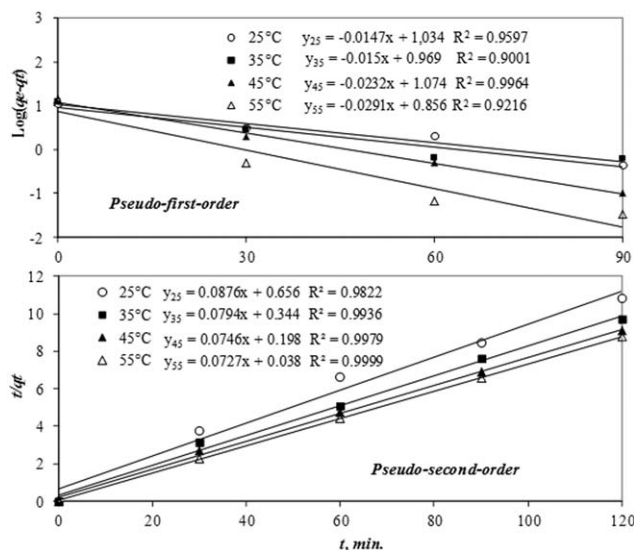**Figure 10.** The plots of pseudo-first-order and pseudo-second-order kinetic models.

Table II. The Regression Coefficients (R^2) and the Rate Constants (k_1 and k_2)

Temperature (°C)	Pseudo-first-order kinetic model		Pseudo-second-order kinetic model	
	k_1 (1/min)	R^2	k_2 (g/mg min)	R^2
25	0.0339	0.9597	0.0117	0.9822
35	0.0345	0.9001	0.0183	0.9636
45	0.0534	0.9964	0.0281	0.9979
55	0.0670	0.9216	0.1391	0.9999

were examined. Gibb's free energy ($\Delta G°$), enthalpy ($\Delta H°$), entropy ($\Delta S°$), and activation energy (E_a) parameters were calculated from eqs. (17) and (18).[8,22,41–43]

$$Kc = \frac{C_a}{C_e} \qquad (16)$$

$$\Delta G° = -RT \ \ln Kc \qquad (17)$$

$$\ln Kc = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (18)$$

where, C_a is the adsorbed Pd(II) concentration on the polymer (mg/g); C_e is the equilibrium concentration in the solution; R is the universal gas constant (8.314 J/mol K); and T is temperature (K). From the adsorption data at different temperatures, the Kc equilibrium constants were obtained by using eq. (16). The Gibbs free energy change ($\Delta G°$) values of the adsorption process were calculated from the obtained Kc values as -16.98, -18.92, -20.68, and -22.26 kJ/mol for 25, 35, 45, and 55°C temperatures, respectively [eq. (17)]. The negative $\Delta G°$ values indicate that the adsorption of Pd(II) ions onto p-mABA is thermodynamically feasible and spontaneous in the temperatures range of 25–55°C.[42] By considering eq. (18), the enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of the adsorption were calculated from the slope and intercept of the plot of ln Kc vs. 1/T, respectively (Figure
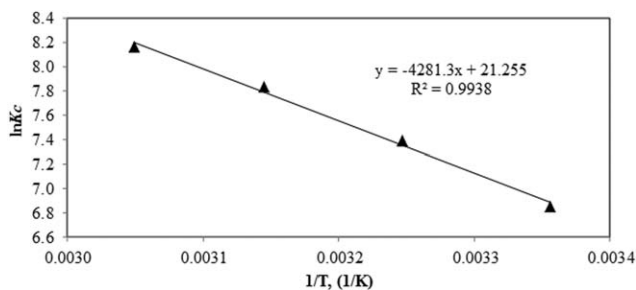
11). The $\Delta H°$ was found as 35.40 kJ/mol, which indicates the endothermic nature of the adsorption. The $\Delta S°$ parameter was calculated as 176.05 J/mol K. The positive $\Delta S°$ value reflects the affinity of the p-mABA for Pd(II) ions and suggests some structural changes in polymer and Pd(II) complexes.[8,42,43]

Furthermore, the activation energy (E_a) for the Pd(II) adsorption was calculated by drawing the plot of ln k_2 versus 1/T according to the Arrhenius equation [eq. (19)].

$$\ln k_2 = \ln A - \frac{E_a}{RT} \qquad (19)$$

where, k_2 value is the rate constant at temperature of T (K) which is calculated in pseudo-second-order kinetic, A is the frequency factor, R is the universal gas constant (8.314 J/mol K), and E_a (J/mol) is the activation energy for the adsorption process. The magnitude of activation energy may give an idea about the type of the adsorption. In physisorption, the equilibrium is usually rapidly attained and easily reversible, because the energy requirements are small. The activation energy for physisorption is usually no more than 4.2 kJ/mol since the forces involved in physisorption are weak. It was found from the plot in Figure 12 that the activation energy in the Pd(II) adsorption is 61.71 kJ/mol. It shows that the Pd(II) adsorption on the p-mABA chelating polymer is a chemisorption process.

CONCLUSIONS

This study investigated the adsorption of Pd(II) ions onto poly(m-aminobenzoic acid) chelating polymer. The characterization studies showed that the p-mABA is thermal stable polymer up to 300°C. The potentiometric titration of the polymer resulted in two end-points at pH 8.7 and pH 3.33 in which the polymer can be protonated gradually. In the adsorption studies,
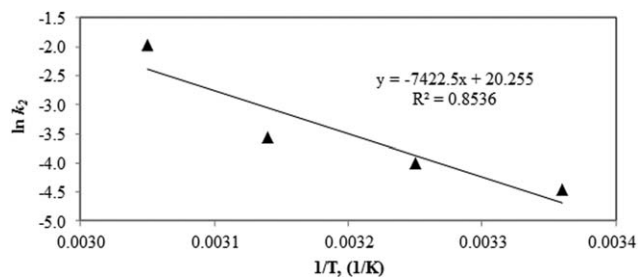

Figure 11. ln Kc−1/T graph.

Figure 12. lnk_2−1/T Arrhenius plot.

the optimum acidity was determined as pH 2. The Pd(II) adsorption equilibrium was better described by the Langmuir isotherm model than the Freundlich model. The monolayer adsorption capacity of the p-mABA polymer was found to be 24.21 mg Pd(II) /g polymer. The kinetic data of the adsorption fitted to the pseudo-second-order kinetic model. The Gibbs free energy changes ($\Delta G°$) of the adsorption process were calculated between -16.98 and -22.26 kJ/mol at 25–55°C temperatures. These values show that a spontaneous adsorption occurs at higher temperatures. The enthalpy change ($\Delta H°$), the entropy change ($\Delta S°$), and the activation energy (E_a) of the adsorption were 35.40 kJ/mol, 176.05 J/ mol K, and 61.71 kJ/mol, respectively. It is concluded that the adsorption of Pd(II) ions onto the p-mABA chelating polymer is an endothermic chemical adsorption process and it is governed by both the ionic interaction and the chelation mechanisms.

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