

Role of cationic surfactants in palladium adsorption of commercial ion exchange resins using electroless plating solutions

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ABSTRACT

This work investigates the role of cationic surfactants in the adsorption of palladium ions from synthetic electroless plating solutions using a commercial resin, Lewatit TP-214. This would also help us in determining the batch adsorption experiments elaborated on the optimal parameters such as surfactant concentration, pH, dosage, initial metal ion concentration for the development of an ion-exchange resin with high metal removal efficiency. Critical micelle concentration (CMC) appears to be an important parameter in determining the adsorption behavior of ion-exchange resins with palladium ions. Equilibrium models were measured for their fitness with the obtained Pd (II) batch adsorption characteristics and Freundlich isotherm confirms the heterogeneous Pd (II) adsorption on Lewatit TP-214. FTIR analysis confirmed that the Pd (II) metal uptake of Lewatit TP-214 resin largely depends on amine groups ($-\text{NH}^{2+}$ and $-\text{NH}^+$) and the donor atoms attached to cationic surfactant. The optimized choice of adsorption parameters (pH of 8, dosage of 1 g/L, and contact time of 300 min) of Lewatit TP-214 adsorbent provided the highest metal uptake and removal efficiency as 201.7 mg/g and 90.16%, respectively, for the lowest Pd concentration of 300 mg/L.

Key words: adsorption, Lewatit TP-214, palladium (II) metal, synthetic electroless plating solution

HIGHLIGHT

- The highest metal uptake (201.7 mg/g) and removal efficiency (90.16%) are obtained at the lowest Pd concentration of 300 mg/L. The Pd (II) metal uptake of Lewatit TP-214 resin is highly dependent on stronger bonding of -NH and S groups in the resin with $[\text{Pd}(\text{NH}_3)_4]^{2+}$ and the donor atoms connected to cationic surfactant confirmed with FTIR characterization.

INTRODUCTION

Global populations and economy are continually showing rising tendencies as a result of the breakthroughs made possible by science and technology. In addition, there is an increase in demand for many different resources, such as heavy and noble metals. (Mack *et al.* 2007; Das 2010; Morf *et al.* 2013). Heavy metals (nickel, arsenic, copper, and cadmium) and precious metals (platinum, palladium, silver, and gold) are the two main types of metals and their compounds are found in industrial effluents. Mines, foundries, smelters, electroplating, tanneries, and coal-burning power plants are the main businesses that release wastewater containing metals. The biological cycle of metals has been dramatically accelerated by waste management ignorance, and the deposition of heavy metals in terrestrial and aquatic environments has increased, posing risks to human health (Grandjean *et al.* 1999; Wong *et al.* 1999; Eisler 2004).

Due to this, it is crucial to eliminate metal contamination from industrial waste streams. Palladium catalysts are particularly effective because they exhibit superior chemisorption, resistance to oxidation at high temperatures, and selective activity toward reactants. In addition, precious metals play a significant role in many fields of industry. According to the most recent market analysis of supply and demand for platinum metals, a comparison of the palladium supplies over the last 3 years from South Africa, Russia, and other nations shows rising tendencies (Fleming 1992; Schubert *et al.* 2015). The recovery

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of platinum group metals (PGM) is a matter of significant concern because platinum-rich natural resources are few and sources are depleting (Mishra & Rhee 2010; Morf *et al.* 2013).

The importance of speciation in affecting adsorption and desorption characteristics could be extrapolated from such systems. As a result, solutions with a moderate level of complexity must be sought as references when evaluating adsorbent effectiveness in the control of industrial and complex waste streams. Synthetic electroless plating (ELP) solutions, which contain ethylenediaminetetraacetic acid (EDTA) and ammonia (NH₄OH) in addition to Pd, can be considered complex (Nagireddi *et al.* 2020).

Because noble metal levels are typically fairly low, recovering PGM from the electroplating or ELP industries is restricted (Butewicz *et al.* 2010; Sharififard *et al.* 2013). Therefore, recovering noble metals by adding chemical reagents does not make economic sense when employing conventional ion exchange, solvent extraction, or reduction and precipitation methods. Surfactant effects on the removal characteristics of Pd (II) ions should also be explored. Surfactants are being used to minimize industrial sludge and disperse heavy metals. By reacting with hydrophilic oxygen-containing functional groups, disrupting the colloidal network, and releasing bound water, cetrimonium bromide (C-TAB, a cationic surfactant) can neutralize negative charge (Pujari *et al.* 2014). Therefore, it is vital to discover and apply low-cost, environmentally friendly techniques for recovering precious metals (Rajesh & Uppaluri. 2016).

According to Nagireddi *et al.* (2018), this might be accomplished by using ion-exchange resins (Chitosan, Lewatit TP-214, Purolite S920, Chelite S, and Duolite GT 73) on used ELP solutions (Kanai *et al.* 2008; Baba *et al.* 2011; Bratskaya *et al.* 2011; Sopena *et al.* 2011). The majority of the metal removal work has focused on aqueous and acidic solutions. The author chose Lewatit TP-214 as an effective resin after researching the majority of ion-exchange resins in the literature because of its inexpensive cost and excellent metal removal efficiency. Surfactants also make surfaces more wettable and reduce surface tension in solutions, which activates adsorbents and increases the effectiveness of metal removal. To increase plating rates and achieve acceptable surface finishes, cationic surfactants like C-TAB are added to the electroplating solutions. This study works on commercial ion-exchange resins (LewatitTP-214) from ELP solutions to examine the role of cationic surfactant (C-TAB) and its effects on palladium adsorption.

MATERIALS AND METHODS

Selection of an ion-exchange resin

The affinity series of palladium (II) complexes for the chelating and cationic ion exchangers is as follows based on the calculated values of working ion-exchange capacity: Purolite S 920 > Chelite S > Lewatit TP 214 > Duolite GT 73. Table 1 displays a summary of ion-exchange resins. The Pd (II) complexes in aqueous solutions can be exchanged with Lewatit TP 214 most effectively, according to Table 1. TP-214 Lewatit, a monospherical, macroporous chelating resin containing thiourea

Table 1 | Summary of adsorption capacity (mg/g), cost (Rs.), and ion-exchange resins used in various applications

Name of adsorbent	Type of solution	Cost of the resin/100 g (Rs.) ^a	Adsorption capacity (mg/g)
Duolite GT 73	Aqueous solution	–	78.8
Lewatit TP 214	Acidic solution	3,653	10.57
Amberlyst A 21	Acidic solution	1,550	9.81
Poly-4 vinyl pyridine	Electroless solution	11,833	3.6
Lewatit M500	Acidic solution	2,631	9.3
Dowex MSA 1	Acidic solution	2,552	8.8–9.7
Varion	Acidic solution	–	9.44
Amberlite IRA 458	Acidic solution	5,800	7.8
Amberlite IRA 958	Acidic solution	6,600	4.81
Lewatitmonoplus TP-220	Acidic solution	4,800	9.95
MFT chelating resin	Aqueous solution	9,587	15.29

^aCost has been taken from Sigma Aldrich Corporation.

groups, Lewatit MonoPlus TP 214 has a high selectivity for PGM metals like platinum, gold, and silver. Polystyrene makes up the resin's matrix.

Materials

Lewatit TP-214, used as an adsorbent, was purchased from Sigma- Aldrich Corporation and physical properties and structure of Lewatit TP-214 are mentioned in [Table 2](#) and [Figure 1](#). Synthetic ELP solutions were prepared by dissolving PdCl₂, Na₂EDTA, and liquid NH₃ with Millipore water. The pH of the synthetic ELP solutions was controlled with 1 M HCl and NaOH solutions. All the chemicals used were of analytical reagent grade.

Preparation of ELP solution composition

Palladium chloride (PdCl₂) was used as a source of palladium ions with ethylenediaminetetraacetic acid (Na₂EDTA) as a stabilizer and cetrimonium bromide (C-TAB) as a surfactant. The experiment was conducted using Millipore water. [Table 3](#) provides a detailed breakdown of the composition of the ELP solution ([Pujari et al. 2014](#); [Rajesh & Uppaluri 2016](#)).

Adsorbent characterization

The commercial ion-exchange resin (Lewatit TP-214) was characterized with Fourier Transform Infrared Spectroscopy (PerkinElmer, PE-RXI, range: 500–4,000 cm⁻¹) for the identification of existing functional groups over the surface of the resin. BET analysis is to conduct a nitrogen adsorption isotherm, and measurements of surface area and pore volumes were made using a surface area analyzer (Beckman Coulter, SA-3100).

Adsorption studies

Based on the adsorption characteristics of metal uptake and removal efficiency, the optimal conditions were reported by [Nagireddi et al. \(2018\)](#) as pH of solution 8, contact time 300 min, and dosage of adsorbent of 100 mg. Batch adsorption studies were carried out at these optimal conditions on 50 mL of synthetic ELP solutions with varying palladium concentrations for each critical micelle concentration (CMC); details are mentioned in [Table 3](#). The studies were conducted using 250 mL flasks holding 50 mL solutions of specified Pd (II) concentrations (50–500 mg/L) at room temperature for a duration of 5 h at 200 rpm in a wrist action shaker (Make: Lab Tech., India). To achieve mass transfer equilibrium, continuous mixing was offered throughout the experimental time with a constant agitation speed of 200 rpm through a shaker. Using an atomic absorption spectrophotometer (AAS; Varian Spectra, FS240, India, equipped with an air-acetylene flame detector) operating at a wavelength of 247.6 nm, the concentration of Pd (II) in the filtrate was determined ([Rajesh et al. 2017](#)).

Table 2 | Physical, mechanical, and surface properties of Lewatit TP-214

Property	Lewatit TP-214
Producer Bayer	Germany
Functional group	Thiourea
Matrix cross	Linked p
Structure	Macro porous
Specific surface area (m ² /g)	15
Pore volume (cc/g)	0.013
Physical form and appearance	Mat beige spheres
pH range	0–10
Thermal stability	80 °C
Bead size	0.55 (± 0,05) mm
Water retention	Water retention 50–56
Total exchange capacity	1.2 meq/cm
Additional information	High mechanical and osmotic resistance

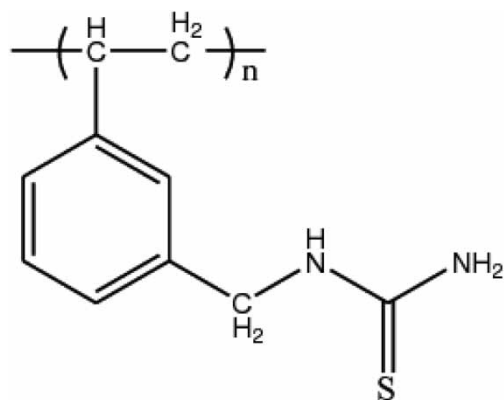


Figure 1 | Structure of Lewatit TP 214 resin.

Table 3 | Compositions of synthetic ELP solutions

Concentration (mg/L)	Amount of PdCl ₂ (mg)	Amount of Na ₂ EDTA(g/L)	Amount of NH ₃ (mL/L)	Critical Micelle concentration (CMC)	Amount of C-TAB required (mg)
50	83.31	1.3997	10.337	1	1.57
100	166.8	1.3997	10.337	2	3.15
200	333.6	1.3997	10.337	3	4.72
300	500.4	1.3997	10.337	4	6.30
400	667.2	1.3997	10.337	5	7.87
500	834.1	1.3997	10.337	-	-

Using the measured Pd (II) solution concentrations, various adsorption parameters, namely, metal uptake mg/g and metal removal % were calculated using the following equations:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

$$\text{Removal \%} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

where C_o is the initial concentration of the Pd metal ions in synthetic ELP solution; C_e is the final concentration of the Pd metal ions in synthetic ELP solution; V is the volume of the solution (mL), 50 mL; W is the weight of the adsorbent (g), 0.1 g; q_e is the adsorption capacity (mg/g).

RESULTS AND DISCUSSIONS

Adsorbent characterization

Fourier transform infrared spectral analysis was carried out on pure Lewatit and palladium adsorbed Lewatit in Figure 2. The FTIR analysis revealed that the Lewatit TP-214's peaks at frequencies of 3,362 and 3,380 cm^{-1} (-NH stretching), 2,924 and 2,913 cm^{-1} (stretching vibrations of C-H groups), 1,671 and 1,691 cm^{-1} (CO stretching), 1,580 and 1,602 cm^{-1} (NH bending), 1,478 and 1,482 cm^{-1} (CN-asymmetric stretching), 1,093 and 1,100 cm^{-1} (CN stretching), 732 and 735 cm^{-1} (C = S rocking), whereas Na₂EDTA stabilizer, present in the artificial ELP solution, prevented these vibrations from occurring in Pd adsorbed Lewatit TP-214. The stretching vibrations of amine groups (-NH²⁺ and -NH⁺), which shifted to 2,364 and 2,330 cm^{-1} after interacting with liquid ammonia contained in synthetic ELP solution, are also responsible for the peak at 2,374 cm^{-1} in Lewatit TP-214 (Nagireddi *et al.* 2017a).

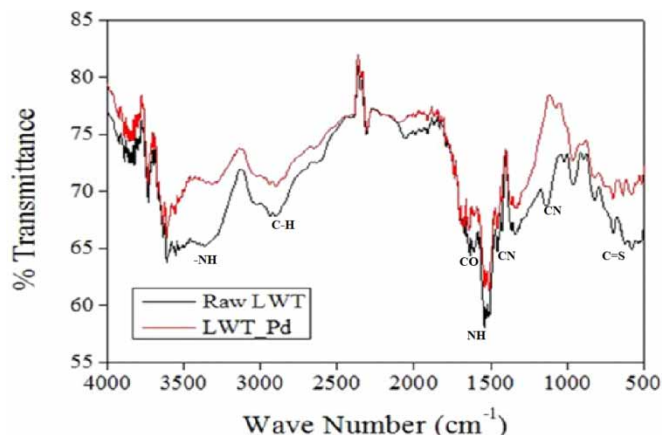
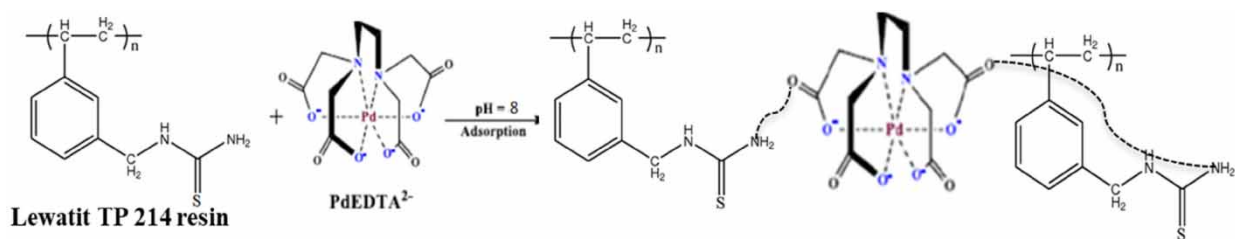


Figure 2 | FTIR analysis of raw LWT (Lewatit TP 214 Resin) and LWT-Pd (II).

Based on the adsorbent properties mentioned in Table 2 and available functional groups on Lewatit TP-214, resin provided an ideal removal efficiency and adsorption capacity of 86.7% and 137.8 mg/g at pH 8, respectively.

Mechanism of palladium's adsorption to the industrial resin Lewatit TP-214

The mechanism of Lewatit TP-214 is a chelating resin with thiourea groups that exhibit a high affinity for Pd (II) recovery from model ELP solution adsorbate system, considering the efficacy of sulfur containing functional groups with respect to nitrogen- and oxygen-containing functional groups. Pd (II) can exist in a variety of forms in synthetic ELP solutions, including $[\text{Pd}(\text{edta})]^{2-}$, $[\text{PdCl}_4]^{2-}$, $[\text{PdCl}_3]^-$, $\text{PdCl}_2(\text{aq})$, $[\text{PdCl}]^+$, $[\text{Pd}(\text{NH}_3)_4]^{2+}$, and $[\text{Pd}(\text{NH}_3)_5]^{2+}$. In lower pH ranges (1–6) and higher chloride concentrations, only $[\text{Pd}(\text{edta})]^{2-}$ is present. On the other hand, Pd (II) occurs as $[\text{Pd}(\text{NH}_3)_4]^{2+}$ at higher pH (basic medium). Given Pd (II) adsorptive capacity being maximum at optimal pH of 8 for the Lewatit TP-214 resin, at lower pH, it is hypothesized that stronger bonding of -NH and S groups in the resin with $[\text{Pd}(\text{NH}_3)_4]^{2+}$ but not $[\text{Pd}(\text{edta})]^{2-}$ is responsible for non-optimal adsorption capacity (Nagireddi *et al.* 2018). However, for Pd (II) recovery, the optimal performance of N- and N-O-containing functional groups needs to be affirmed along with cost competitiveness to ensure the sustainability of commercial resins. Therefore, considering the ease of availability, promising Pd (II) uptake/selectivity values, and lower cost of alternate resins containing nitrogen and nitrogen–oxygen functional groups.



Role of cationic surfactant in Pd (II) adsorption

The effect of surfactant was investigated by varying the Pd (II) concentration from 50 to 500 mg/L for each surfactant CMC ranging from 0 to 5. As seen in Figure 3, adding the surfactant to the synthetic ELP solution causes an increase in the amount of metal absorption (from 112.9 to 137.8 mg/g) and removal efficiency (from 75 to 86.7%) of palladium ions (Fujiwara *et al.* 2007; Rajesh & Uppaluri. 2016). This could be explained by the surfactant concentration changing the interface's charge density and boosting activity at the resin's surface as well as its functional groups (Hubicki & Wolowicz 2009a, 2009b).

The cationic and anionic surfactants in synthetic solutions form micelles, which are roughly spherical, dynamic aggregates with a highly anisotropic interface between their hydrocarbon cores and the surrounding bulk aqueous phase (Nagireddi *et al.* 2018). This interface is made up of head groups, counter ions, solubilizates, and water. Plotting of the fluctuation in surfactant concentration was done at a fixed palladium ion concentration of 300 mg/L. The graph showed that from 0 to 5 CMC,

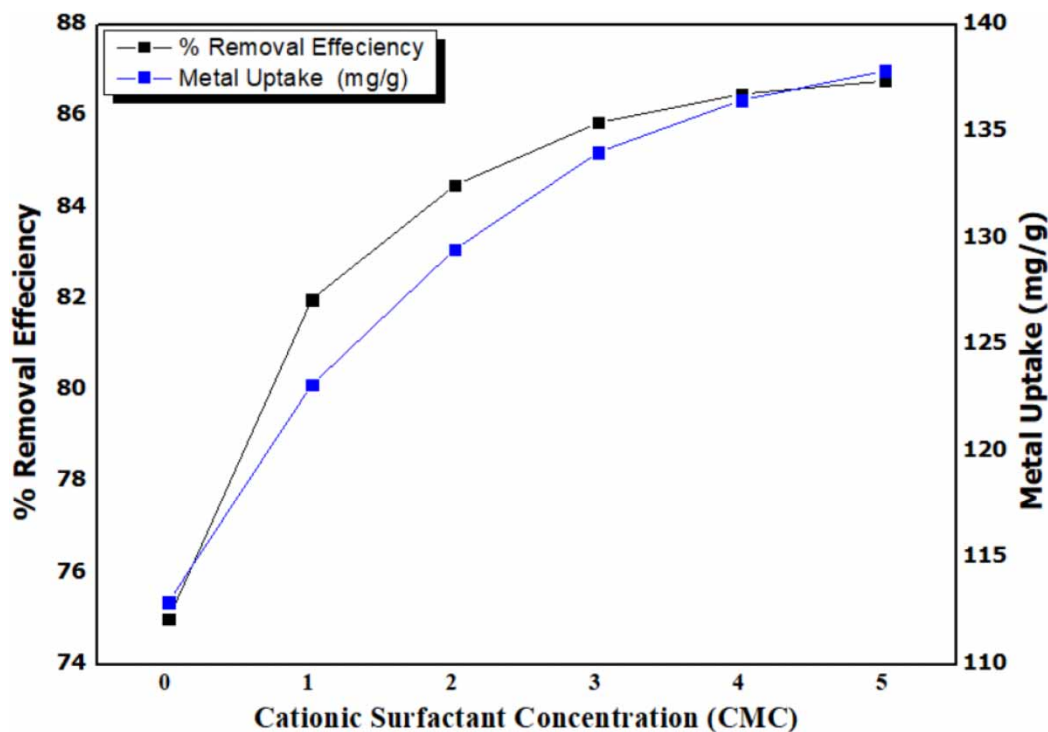


Figure 3 | Role of cationic surfactant in Pd (II) adsorption on Lewatit TP 214 resin.

increasing the surfactant concentration increased both the metal uptake from 112.9 to 137.8 mg/g and removal efficiencies from 75 to 86.7%, respectively.

Role of metal ion concentration in Pd(II) adsorption

Lewatit TP-214's removal effectiveness was investigated with metal ion concentrations rising from 50 to 500 mg/L as shown in Figure 4. The author found that the efficacy of removing ions constantly declines as ion concentration rises at low surfactant concentrations. This outcome can be attributed to the cationic surfactant's counter-ion influence and inhibitory effect, which block more active sites as the surfactant increases, as reported by Nagireddi *et al.* (2017a).

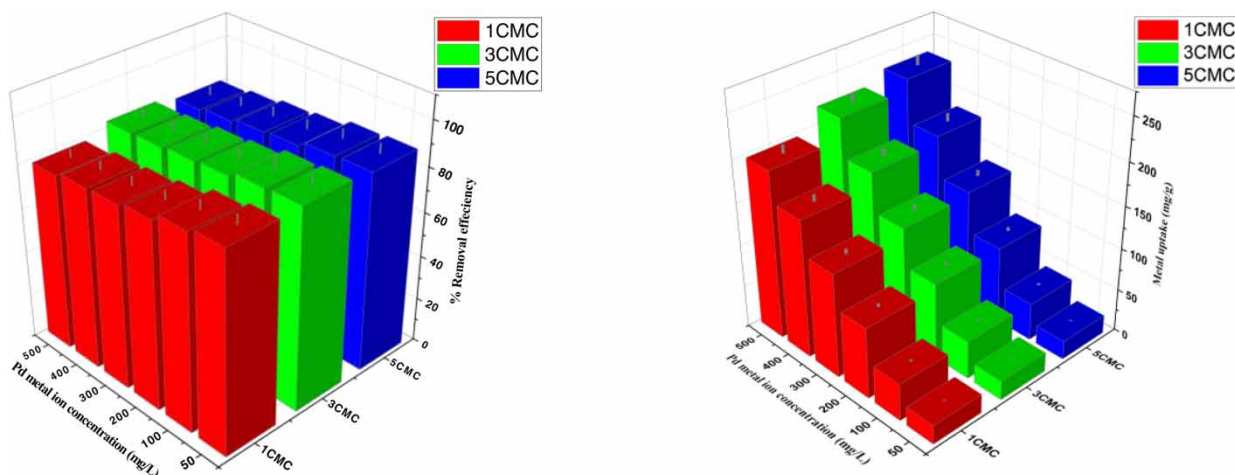


Figure 4 | Role of metal ion concentration in Pd (II) adsorption.

Lewatit TP-214's ability to absorb metal has been investigated with increasing metal ion concentrations ranging from 50 to 500 mg/L. The author notices that at both low and high concentrations of C-TAB, the efficiency of resin in absorbing metal ions increases continuously. At high surfactant concentrations, no change in the trend in removal efficiency patterns has been seen in Figure 4 and similar information reported (Nagireddi *et al.* 2019).

Adsorption isotherm modeling

For the purposes of designing sorption systems as efficiently as possible, equilibrium sorption data analysis is crucial. The interaction between the adsorbed species and the adsorbent surface determines the adsorption process. Van der Waals forces, hydrophobic forces, chemical bonds, and hydrogen bonds could all be involved in the interaction (Ramesh *et al.* 2008). The adsorption isotherms show the relationship between the amount of solute absorbed by a unit weight of solid adsorbent and the amount remaining in the solution at equilibrium. The Langmuir and Freundlich isotherms models are frequently used to explain the adsorption of palladium metal ions on Lewatit TP-214 adsorbents. Both the Langmuir and Freundlich isotherms are applied to depict the equilibrium data of adsorbents and indicate that either monolayer or multilayer adsorption may occur depending on the type of adsorbent surface (Nagireddi *et al.* 2017b).

The Freundlich isotherm posits that the metal ion adsorption happens as a heterogeneous process on the adsorbent surface, in contrast to the Langmuir model, which predicts that sorption occurs on the homogenous surface of the adsorbent and a saturation monolayer is created. The Temkin and Redlich models are two further reliable representations of adsorption equilibrium. In this study, the suitability of each of the four models to accurately depict the experimentally observed adsorption properties of Lewatit TP-214 adsorbents was evaluated. As evidenced by experimental data, the Temkin and Redlich-Peterson models displayed poor fitness toward isothermal fitness. Because of this, the author has included the data from the Langmuir and Freundlich models in the following sections.

Assuming complete monolayer coverage on a homogenous adsorbent surface without any interaction between the adsorbed ions, the Langmuir equilibrium isotherm model is represented as (Langmuir 1908):

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{1}{q_{\max}} C_e \quad (3)$$

where C_e is the equilibrium adsorption concentration of Pd (II), mg/L; q_e is the mass of solute adsorbed per mass of adsorbent at equilibrium, mg/g; q_{\max} is the Langmuir monolayer capacity, mg/g; b is the Langmuir equilibrium constant; and C_o is the initial concentration of Pd (II) in aqueous solution, mg/L.

The Freundlich isotherm model is defined as follows, assuming the exponential distribution of active centers, heterogeneous surface, and infinite surface coverage (Freundlich 1906):

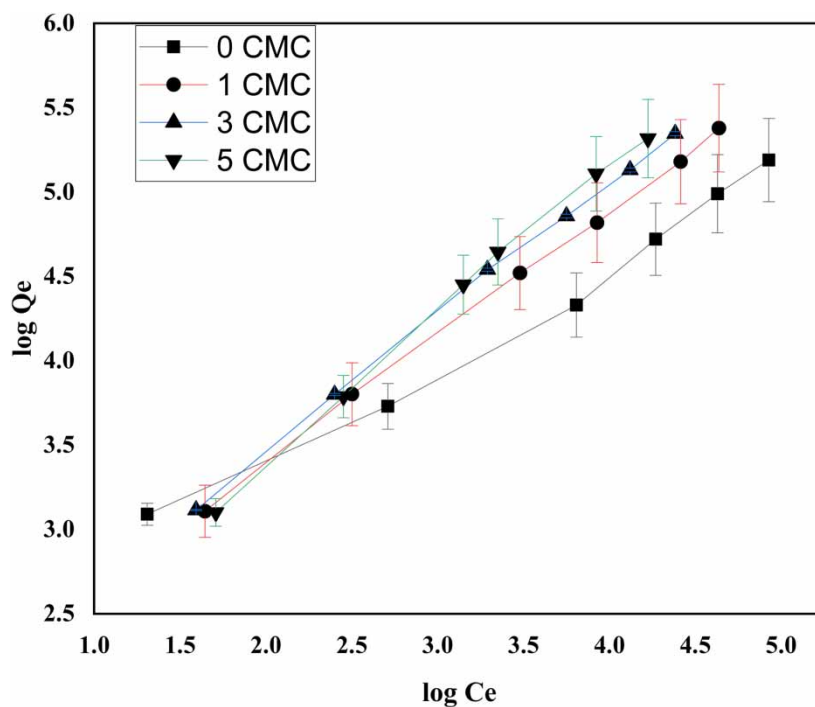
$$\log q_e = \log K_f + m \log C_e \quad (4)$$

where k_f is the Freundlich isotherm coefficient; m is the amount of adsorbent taken, mg/L.

The concentration and surfactant studies were finished before isotherm modeling was done using the Langmuir and Freundlich isotherm models, respectively. The suitability of Langmuir and Freundlich isotherm palladium ion adsorption on Lewatit TP-214 using synthetic ELP solutions containing the cationic surfactant, C-TAB (Rajesh & Uppaluri 2016), is shown in Table 4 and Figure 5. The Freundlich and Langmuir isotherm models both offered good fitting to the measured equilibrium adsorption data in all situations, it can be seen. However, for both low and high CMC concentrations, the Freundlich isotherm showed the greatest fitness ($R^2 = 0.99$) for Pd (II) adsorption characteristics. It indicates that heterogeneous adsorption is the most likely mechanism during Pd (II) adsorption with functional groups containing N and N-O. As the author goes toward high CMC concentration, the fit improves ($R^2 = 0.97$), whereas the Langmuir isotherm fails at low CMC concentration with a low regression coefficient $R^2 = 0.88$). Table 4 also confirms that the $1/n$ value always lies between 0 and 1, indicating that the chosen adsorbent-adsorbate system is favorable for Pd (II) recovery.

Table 4 | Langmuir and Freundlich isotherm fitness and model parameters for Pd (II) adsorption from synthetic ELP solutions with surfactant

Surfactant concentration	Model	R^2	% Error				Adsorption capacity (mg/g)	Model parameters
			RMS	Avg	Max	Min		
1 CMC	Langmuir	0.9264	7.8	7.78	15.4	3.25	180	$b = 0.001$
	Freundlich	0.9973	1.14	1.1	1.4	0.002	–	$K_F = 6.747$ $n = 1.367$
3 CMC	Langmuir	0.9423	3.5	3.26	4.87	1.23	201.7	$b = 0.0099$
	Freundlich	0.9989	1.4	1.39	1.9	0.004	–	$K_F = 6.64$ $n = 1.267$
5 CMC	Langmuir	0.9760	2.2	2.24	4.59	0.97	220.3	$b = 0.009$
	Freundlich	0.9976	1.35	1.35	1.8	0.003	–	$K_F = 6.162$ $n = 1.2789$

**Figure 5** | Fitness of Freundlich isotherm towards Pd (II) adsorption on Lewatit TP-214.**Table 5** | Comparison of the adsorption capacity of the Pd (II) with various ion-exchange resins

Adsorbent name	Pd (II) concentration (mg/L)	Adsorption capacity (mg/g)	Reference
Lewatit TP-214	50–300	201	Present study
Amberlyst A21	50–300	100	Hubicki & Wolowicz (2009a, 2009b)
Amberlyst A21	50–300	172.41	Nagireddi <i>et al.</i> (2018)
3-amino-1,2,4 triazole, 5-thiol cross-linked chitosan	50–300	175.44	Nagireddi <i>et al.</i> (2019)
Glutaraldehyde cross-linked chitosan	50–500	166.7	Nagireddi <i>et al.</i> (2017a)
Chitosan	50–300	90.91	Nagireddi <i>et al.</i> (2017b)

The following equations are used to evaluate the inaccuracies in the isothermal equilibrium models related to the compatibility of experimental data with the models:

$$Er_i = \frac{|C_i^{\text{exp}} - C_i^{\text{model}}|}{C_i^{\text{exp}}} \times 100 \quad (5)$$

$$Er_{\text{max}} = \text{Max}(Er_i) \quad (6)$$

$$Er_{\text{min}} = \text{Min}(Er_i) \quad (7)$$

$$Er_{\text{avg}} = \frac{\sum_{i=1}^n Er_i}{n} \quad (8)$$

$$\text{RMSE} = \frac{\sqrt{\sum_{i=1}^n Er_i^2}}{n} \quad (9)$$

where E_r is the Error function; i is the index for batch adsorption experiment corresponding to specific initial solution concentration of Pd (II); n is the total number of batch adsorption experiments carried out with variant concentration; Er_{max} is the error maximum; Er_{min} is the error minimum; Er_{average} is the average error; Er_{rms} is the root mean square error.

The experimental results (Table 5) have been compared to the most relevant systems (ELP solutions) and adsorbent systems in the finest literature that is currently available (chitosan, chitosan-derivatives, and commercial resins). The findings from our research group are solely pertinent for the direct comparison of resin performance with ELP adsorbate systems because other pertinent literature focuses mostly on aqueous solutions.

CONCLUSIONS

In this work, the author has used commercial ion-exchange resin Lewatit TP-214 as an adsorbent and to investigate the impact of cationic surfactants on the adsorption of palladium ions from synthetic ELP solutions. The highest metal uptake (201.7 mg/g) and removal efficiency (90.16%) are obtained at the lowest Pd concentration of 300 mg/L. The Pd (II) metal uptake of Lewatit TP-214 resin is highly dependent on stronger bonding of -NH and S groups in the resin with $[\text{Pd}(\text{NH}_3)_4]^{2+}$ and the donor atoms connected to cationic surfactant confirmed with FTIR characterization. Freundlich isotherms indicate that heterogeneous adsorption is the most likely mechanism during Pd (II) adsorption with functional groups containing N and N-O. This is because the surfactant molecules alter the interface's charge density and increase activity at the resin's surface. Therefore, both %removal efficiency and metal absorption are raised with increasing cationic surfactant concentration. Additionally, as the initial concentration of palladium ions increases, the adsorbent's removal efficiency keeps decreasing while Lewatit TP-214's metal-absorption capacity increases. In the near future, cross-linking and impregnation techniques will be used to synthesize hybrid resins from the reaction between Lewatit TP-214 and chitosan.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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