



Comparison of the adsorption by rice hulls and Lewatit TP 214 of platinum from chloroplatinic solution

MEHMET HAKAN MORCALI*, BIHTER ZEYTUNCU and ONURALP YUCEL

*Istanbul Technical University, Faculty of Chemical and Metallurgical Engineering,
Maslak, 34469, Istanbul, Turkey*

(Received 12 September, revised 1 December 2012)

Abstract: Rice hulls, a biomass waste product, and Lewatit TP 214, a thiosemicarbazide sorbent, were investigated as adsorbents for the adsorption of platinum(IV) ions from synthetically prepared dilute chloroplatinic acid solutions. The rice hulls were characterized by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR). The effects of the different adsorption parameters, sorbent dosage, contact time, temperature and pH of the solution on the percent adsorption were studied in detail for batch sorption. The adsorption equilibrium data were best fitted with the Langmuir isotherm model. The maximum monolayer adsorption capacities, Q_{\max} , at 25 °C were found to be 42.02 and 33.22 mg g⁻¹ for the rice hulls and Lewatit TP 214, respectively. Thermodynamic calculations using the measured ΔH° , ΔS° and ΔG° values indicated that the adsorption process was spontaneous and endothermic. The pseudo-first-order and pseudo-second-order rate equations were investigated; the adsorption of platinum ions for both sorbents was found to be described by the pseudo-second-order kinetic model. The kinetic rate, k_2 , using 30 mg sorbent at 25 °C was found to be 0.0289 and 0.0039 g min⁻¹ mg⁻¹ for the rice hulls and Lewatit TP 214, respectively. The results indicated that the rice hulls could be effectively used for the removal of platinum from aqueous solution.

Keywords: adsorption; platinum; rice hulls; kinetics; isotherm.

INTRODUCTION

Platinum is one of the most important precious metals as it is widely used worldwide in many industrial applications, such as in catalytic converters, thermocouples, the jewelry sector, platinum electroplating solutions, and laboratory equipments, *etc*. The diminishing availability of mineral sources and the increasing demand for platinum make its recovery from waste solutions and scrap materials important.¹ Platinum recovery from secondary sources, such as catalytic converters, thermocouples, waste electroplating solutions and leaching solutions

*Corresponding author. E-mail: hakanmorcali@gmail.com
doi: 10.2298/JSC120912150M

stemming from primary resources, is of paramount importance.¹ Recently, platinum adsorption from aqueous solutions via resins or waste materials has received considerable attention because platinum is appreciably present in electronic parts and plating materials due to its high resistance to oxidation.²

Worldwide, adsorption is commonly applied in waste treatment applications. Liquid–solid adsorption systems are based on the ability of certain solids to concentrate preferentially specific substances from solutions onto their surfaces. This ability can be used for the removal of pollutants, such as heavy metal ions and chemical compounds, from wastewater.^{3–6}

Over the past decade, significant research effort has been directed to find low cost, high capacity adsorbents for the removal of metal ions. A wide range of adsorbents have been developed and tested, including several activated carbons.^{7–10} In addition, a number of low cost agricultural wastes, such as peat coal, rice hulls, tree fern and chitosan, have been used for the removal of a range of metal ions. In particular, several natural resources have been studied for platinum recovery, including activated carbon,² chitosan¹¹ and ion exchange resins.¹²

Adsorption methods are widely used and are very effective at low metal concentrations. Among the different types of sorbents, synthetic ion-exchange resins offer substantial advantages, such as high selectivity, good kinetic properties, and the following convenient forms for use: granules, powders, fibers, and filters. The majority of these resins are based on organic matrices with chemically bound functional groups that coordinate to or chelate metal ions. Lewatit TP-214 is a chelating resin with thiourea groups that exhibit a high affinity for platinum and other precious metals, such as silver and gold. The resin possesses a matrix of cross-linked polystyrene. Lewatit TP 214 is one of the most commonly used resins that consist of polystyrene-containing thiourea groups.¹³

Rice hulls, the hard protective covering of rice grains, are an agricultural waste material. Recently, rice hulls have been employed as building materials, fertilizers, insulation materials and fuel. In the majority of rice-producing countries (*e.g.*, Japan, China, Turkey and India) most of the hulls generated from rice processing are either burned or discarded as waste.^{13,14}

In Turkey, agricultural by-products and waste materials that are available in large quantities may have the potential to be used as low-cost adsorbents. The conversion of agricultural waste materials into activated carbon would add considerable economic value, help to reduce the cost of waste disposal and, most importantly, provide a potentially inexpensive alternative to the existing commercial activated carbons.

There are many studies in the literature on the preparation of activated carbons from agricultural wastes, such as sunflower seed hulls, peanut hulls, almond shells, wheat bran, coir pith, banana pith, date pits, cotton stalks, palm tree,

orange peel, corncob, barley husk, palm kernel shells, rice husk, pinewood and soy hulls.^{15–27}

In this work, rice hulls, an agricultural by-product, and Lewatit TP 214 were used to adsorb platinum from dilute platinum chloride solutions. The objective of the study was to describe an effective adsorption process using either Lewatit TP 214 or rice hulls and to compare the two sorbents by describing the optimal conditions and parameters for the adsorption of platinum, including the adsorption isotherms of platinum ions and the kinetics and thermodynamics of the adsorption process. For these reasons, the following parameters were studied to investigate their effect on the percentage of platinum adsorbed: amount of sorbent, contact time, temperature and solution pH.

EXPERIMENTAL

The Lewatit TP 214 (with a density of approximately 1.1 g ml⁻¹) was obtained from the Lanxess Company, Germany. The rice hulls were obtained from the Gokbayrak Company, Turkey. The rice hull material of ≈250 µm was used for all experiments.

The platinum-containing solutions for the experiments were prepared from chloroplatinic acid (H_2PtCl_6) standard solution (Merck, Germany). Distilled water was used for the wet chemical analyses.

This study was conducted using a batch system by varying one parameter at a time. For each experiment, 5 ml of a platinum solution was brought into contact with the sorbent (Lewatit TP 214 or rice hulls) in a Falcon tube to avoid exposure to air. The Falcon tubes were shaken in a temperature-controlled water bath at a manually adjusted shaking rate of 100 rpm. The initial platinum ion concentrations were 100, 150, 200 and 250 mg L⁻¹.

The first experimental series examined the effect of varying the sorbent dosage. The second experimental series investigated the effect of varying the contact time from 15 to 120 min. The third experimental series explored the influence of temperature, which ranged from 25 to 45 °C. In the fourth experimental series, the effect of solution pH was evaluated. For this purpose, hydrochloric acid and sodium hydroxide were employed to adjust the pH level of the solution. The final experimental series investigated the adsorption kinetics, isotherm and thermodynamics.

Solid–liquid separation was performed following each run. For the ICP-OES analysis, each filtered solution was introduced into the instrument following an appropriate dilution.

The adsorption percentage, A , was calculated using the following equation:^{28,29}

$$A = 100(c_0 - c_t)/c_0 \quad (1)$$

The adsorption capacity of the platinum ion was calculated using the following general equation:^{28,29}

$$q_e = (c_0 - c_t)V/m \quad (2)$$

in which q_e is the amount of metal ions adsorbed at equilibrium per unit weight of sorbent (mg g⁻¹), c_0 and c_t (mg L⁻¹) are the platinum ion concentrations present in the solution before and after adsorption, respectively, V is the volume of the solution (in L), and m is the amount of sorbent (in g) used in the adsorption experiment.



Preparation and characterization of the rice hulls

The dry rice hulls were crushed using a crushing mill. The resulting recovered product was washed several times with distilled water to eliminate water-soluble impurities and then dried in an oven at 105 °C. The sample was then removed from the oven and cooled in a desiccator. After cooling, the rice hull material was subsequently subjected to a homogenization treatment using a three-dimensional shaker for 1 h.

The identification of some characteristic functional groups was performed using FTIR spectroscopy. The IR spectrum of the rice hulls is displayed in Fig. 1.

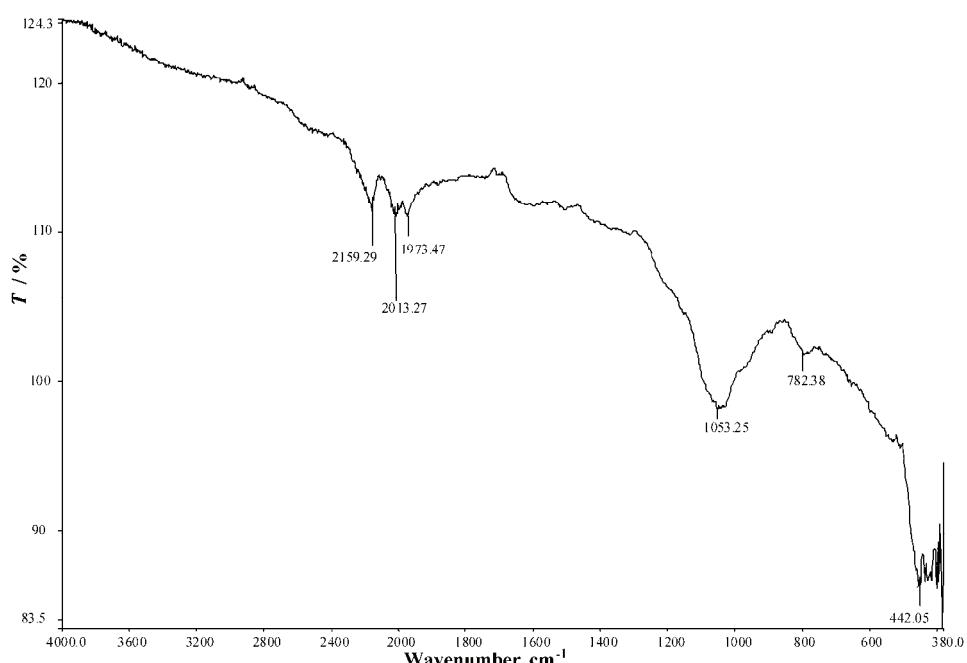


Fig. 1. FTIR absorption spectrum of rice hulls.

The IR bands of rice hulls in the region 1200–1000 cm⁻¹ were considered to result from the superposition of vibrations of the C–OH bonds and Si–O bonds in the siloxane (Si–O–Si) groups. The intense band at 1053 cm⁻¹ corresponds to the stretching vibrations of silicon–oxygen tetrahedrons (SiO₄). The high intensity of this peak was probably due to the superposition of the stretching vibrations of the C–OH bonds in the interval 1200–1000 cm⁻¹ and the stretching vibrations of the Si–O bonds. The absorbance peak at 442 cm⁻¹ was due to the bending vibration of siloxane bonds.¹³

RESULTS AND DISCUSSION

The following results outline the factors that play a role in platinum adsorption and the conditions for attaining maximum adsorption percentage of platinum.

Effect of sorbent dosage on platinum adsorption

The dosages of the rice hulls and Lewatit TP 214 material were varied, ranging from 10 to 100 mg in the first experimental series. The adsorptions of platinum with increasing sorbent dosages are presented in Fig. 2.

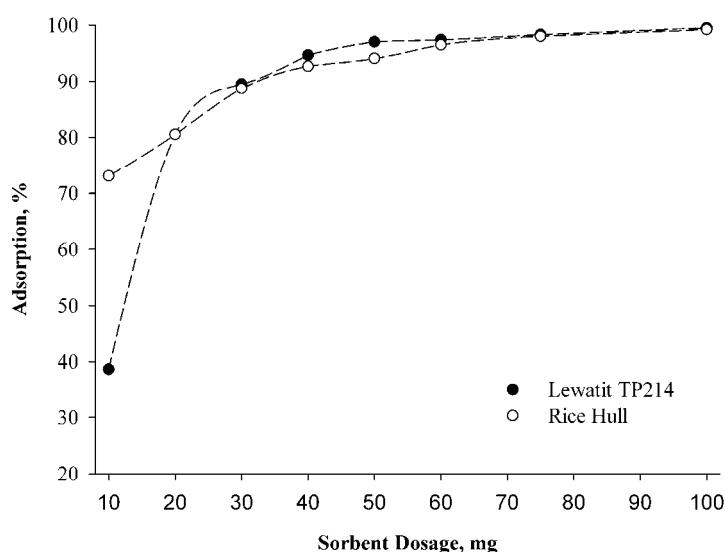


Fig. 2. The effect of increasing sorbent dosage on platinum adsorption (60 min, 25 °C, 100 rpm, pH 1.5 and 5 mL of 100 ppm solution).

The platinum adsorption was found to increase with increasing sorbent dosage because adsorption reactions are thermodynamically more favorable when the sorbent-to-metal ion ratio is high.^{13,30} This is an expected result because as the amount of adsorbent increased, the available surface area increased, thereby exposing more active sites for the binding of metal ions. A similar trend for the effect of adsorbent concentration was observed in a study by Aktas and Morcali.¹³

The rice hull material was equally successful as Lewatit TP 214 at adsorbing platinum ions. For a 60 min contact time with the platinum-containing solution, Lewatit TP 214 (20 mg) exhibited a platinum adsorption of 80 %; with 50 mg of the Lewatit TP 214, 95 % of the platinum was adsorbed. Similarly, for a 60 min contact time, 95 % of the platinum was adsorbed using 60 mg of the rice hull material.

Effect of time on the platinum adsorption

In this experimental series, the effect of contact time on the percent platinum adsorption was studied in the range of 15 to 120 min. The platinum adsorption as a function of contact time is presented in Fig. 3.

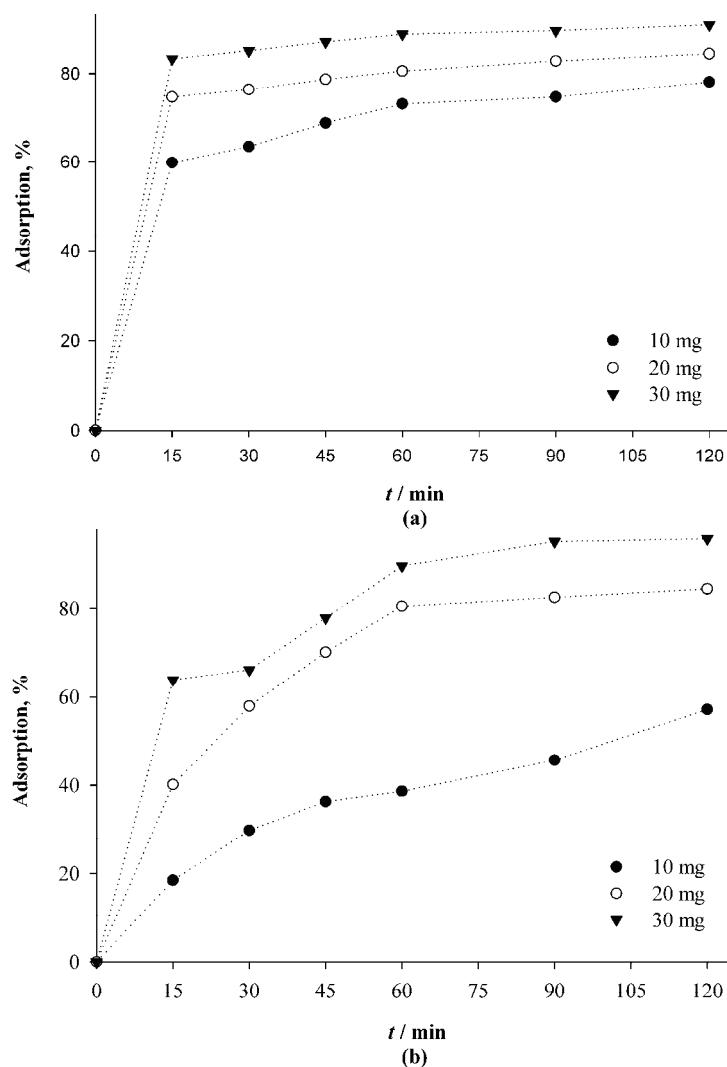


Fig. 3. Platinum adsorption as a function of contact time by a) rice hulls and b) Lewatit TP 214 (25 °C, 100 rpm, pH 1.5 and 5 mL of 100 ppm solution).

Figure 3 demonstrates that increasing the contact time had a positive effect on the platinum adsorption (*i.e.*, the platinum adsorption increased with increasing time). Figure 3a shows that the adsorption of platinum reached equilibrium after 15 min, *i.e.*, there was no significant increase in adsorption percentage after 15 min. Initially, the rate of adsorption was higher because all the adsorption sites on the rice hull material were vacant and the concentration was high, but after 15 min, all the adsorption sites were filled with platinum ions, resulting in unchanged adsorption percentages. Figure 3b indicates that the adsorption of pla-

tinum by Lewatit TP 214 reached equilibrium after 90 min. This is an expected result because the adsorption rate of Lewatit TP 214 was stable. Thus, the adsorption rate of the rice hull material is faster than that of Lewatit TP 214.

To analyze the adsorption rates of platinum ions onto the rice hull material and Lewatit TP 214, two different kinetic models were applied.

Adsorption kinetics

To investigate the controlling mechanism of the adsorption process, *i.e.*, mass transfer or chemical reaction, the pseudo-first-order and pseudo-second-order rate equations were studied for the adsorption of platinum ions by the rice hull material and Lewatit TP 214.

Pseudo-first-order rate equation. The pseudo-first-order rate expression, popularly known as the Lagergren Equation, is generally described by the following equation:^{31,32}

$$\frac{dq}{dt} = k_{ad}(q_e - q_t) \quad (3)$$

where q_e is the amount of metal ions adsorbed at equilibrium per unit weight of sorbent (mg g^{-1}), q_t is the amount of metal ions adsorbed at any time t (mg g^{-1}), and k_{ad} is the rate constant (min^{-1}). Integrating and applying the boundary conditions from $t = 0$ and $q = 0$ to $t = t$ and $q = q_t$, Eq. (3) takes the form:

$$\ln(q_e - q_t) = \ln q_e - k_{ad}t \quad (4)$$

To determine the rate constants, plots of $\ln(q_e - q_t)$ vs. t (time) were made (not presented). These plots exhibited straight lines for the rice hull material and for Lewatit TP 214. The intercept of these plots results in $\ln q_e$.

Pseudo-second-order rate equation. The adsorption data were also analyzed in terms of a pseudo-second-order mechanism given by:³³

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where k_2 is the rate constant ($\text{g min}^{-1} \text{ mg}^{-1}$). Integrating the above equation and applying the boundary conditions, *i.e.*, $t = 0$ for $q = 0$ and $t = t$ for $q = q_t$, gives:

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

The plots of t/q_t vs. t yielded straight lines, as shown in Fig. 4, which enabled the calculation of k_2 . The linear model exhibited a good fit for the two sorbents.

The application of the different kinetic models revealed interesting features regarding the mechanism and the rate-controlling step in the overall sorption process. The kinetic parameters of both the rice hulls and Lewatit TP 214 under different conditions were calculated and the results are given in Table I. To quantify the applicability of each model, the correlation coefficient (R^2) was calculated from these plots. The fits showed that the pseudo-second-order rate equation, an indication of a chemisorptions mechanism, is a better fit ($R^2 \geq 0.99$) than the pseudo-first-order rate equation ($R^2 \ll 0.99$) (Table I).

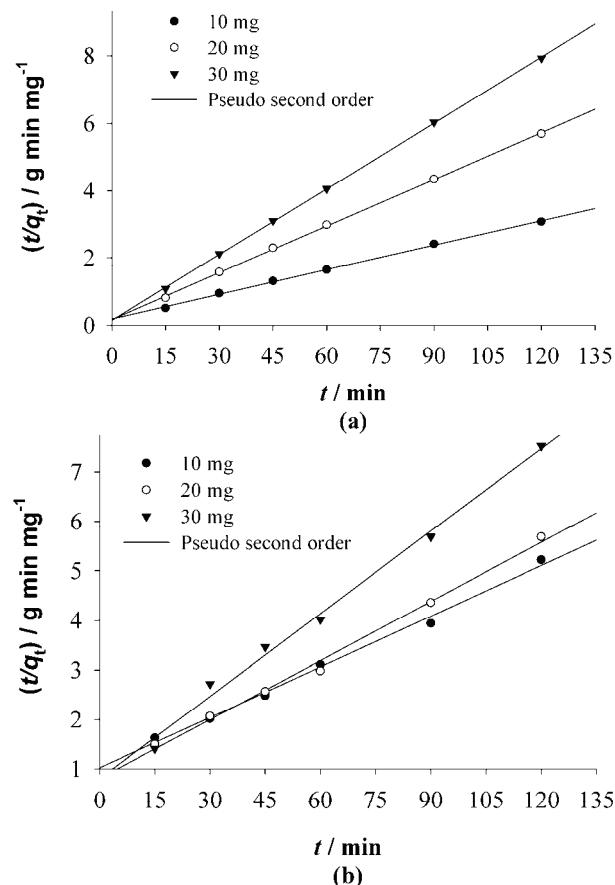


Fig. 4. a) The pseudo-second-order equation plots for platinum adsorbed onto rice hulls and b) the pseudo-second-order equation plots for platinum adsorbed onto Lewatit TP 214 (25 °C, 100 rpm, pH 1.5 and 5 mL of 100 ppm solution).

TABLE I. Constants for the pseudo-first-order and pseudo-second-order rate equations for platinum ion adsorption onto rice hulls and Lewatit TP 214

Rice hulls			Lewatit TP 214			
Constants for the pseudo first-order rate equation (Lagergren rate constants)						
Sorbent, mg	$k_{\text{ad}} / \text{min}^{-1}$	$q_e / \text{mg g}^{-1}$	R^2	$k_{\text{ad}} / \text{min}^{-1}$	$q_e / \text{mg g}^{-1}$	R^2
10	0.0438	29.02	0.8562	0.0436	32.08	0.9574
20	0.0291	5.09	0.9549	0.0451	23.63	0.9796
30	0.0268	2.23	0.9632	0.0462	16.10	0.9685
Constants for the pseudo second-order rate equation						
Sorbent, mg	$k_2 / \text{g min}^{-1} \text{mg}^{-1}$	$q_e / \text{mg g}^{-1}$	R^2	$k_2 / \text{g min}^{-1} \text{mg}^{-1}$	$q_e / \text{mg g}^{-1}$	R^2
10	0.0032	41.15	0.9986	0.0011	29.41	0.9944
20	0.0127	21.60	0.9995	0.0020	25.19	0.9941
30	0.0289	15.36	0.9999	0.0039	17.99	0.9927

Effect of temperature on platinum adsorption

In this experimental series, the effect of temperature on platinum adsorption was studied in the range of 25 to 45 °C. The percentage adsorption of platinum as a function of temperature is presented in Fig. 5.

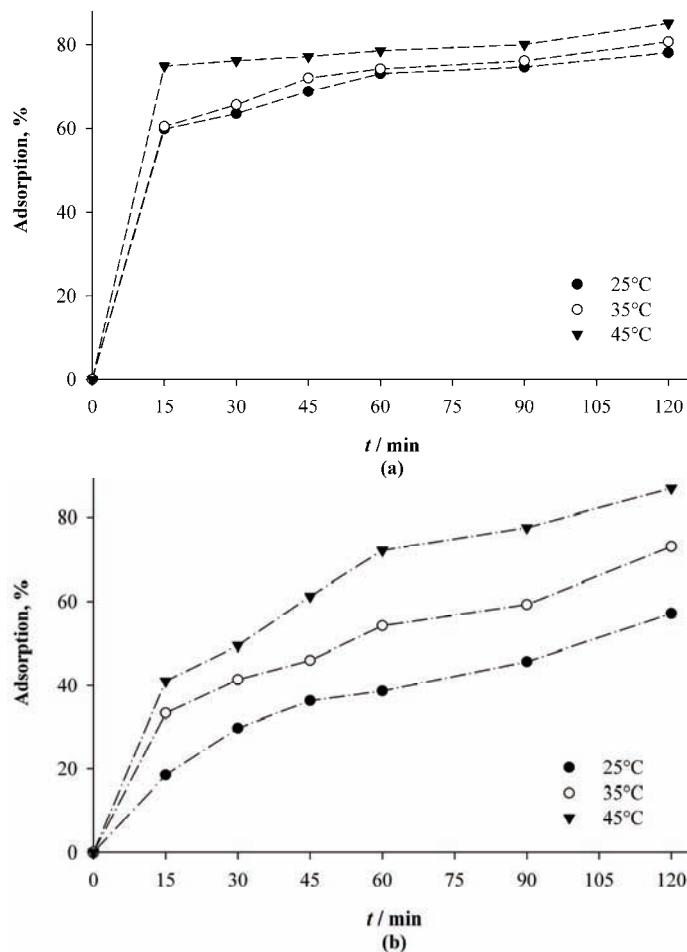


Fig. 5. Platinum adsorption as a function of temperature by a) rice hulls; b) Lewatit TP 214 (10 mg, 100 ppm, 100 rpm, pH 1.5 and 5 mL of 100 ppm solution).

Figure 5a shows that the temperature had little influence on the adsorption percentage for the rice hulls. After 120 min, only an approximately 10 % increment was obtained when the temperature was increased from 25 °C to 45 °C. The platinum adsorption *vs.* time curves at different temperatures were smooth and continuous, gradually leading to saturation, which indicates a monolayer coverage of metal ions on the surface of the adsorbent.³⁴ However, as evident from

Fig. 5b, increasing the temperature had a noticeable effect on platinum adsorption onto Lewatit TP214. After 120 min, an approximately 35 % increment was obtained when the temperature was increased from 25 to 45 °C. Thus, the temperature clearly had a greater effect for Lewatit TP 214 than for the rice hulls.

Effect of solution pH on platinum adsorption

In this experimental series, the effect of solution pH on platinum adsorption was studied using sorbent dosage of 20 and 30 mg at room temperature for 1 h. The influences of solution pH on platinum adsorption are presented in Fig. 6.

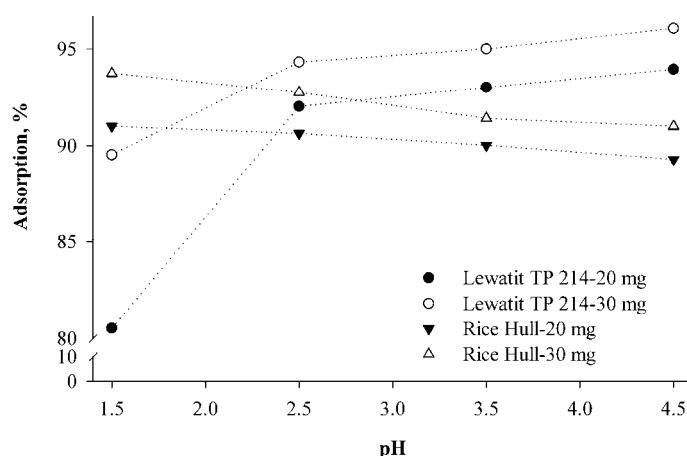


Fig. 6. Platinum adsorption as a function of solution pH by rice hulls and Lewatit TP 214 (25 °C, 60 min, 100 rpm, 5 mL of 100 ppm solution).

From Fig. 6, it can be seen that increasing the solution pH resulted in higher platinum adsorption by Lewatit TP 214. However, on increasing the solution pH, slightly lower adsorption percentages were obtained with the rice hulls. It could be concluded that platinum adsorption should be performed using acidic media of pH ≈ 2.5 .³⁵

Investigation of the adsorption isotherms

The adsorption isotherms of platinum ions on these sorbents were studied at three different temperatures, specifically 25, 35 and 45 °C, by varying the initial concentrations of the solutions from 100 to 250 ppm while keeping all other parameters constant.

The equilibrium data obtained were analyzed with respect to the Langmuir and Freundlich isotherms.

Freundlich isotherms. The data obtained for the adsorption of platinum ions onto the sorbents at equilibrium concentration, c_e , ranging from 100 to 250 ppm,

were fitted to the Freundlich Equation. The following linearized form was used:^{36,37}

$$\log q_e = \log K_F + (1/n)\log c_e \quad (7)$$

in which, q_e is the amount of metal ions adsorbed at equilibrium per unit weight of sorbent (mg g^{-1}), c_e is the equilibrium ion concentration present in the solution after adsorption, K_F is the empirical Freundlich constant or the capacity factor (mg g^{-1}), and $1/n$ is the Freundlich isotherm constant. The constants K_F and n are empirical constants that are characteristic of the system and depend on the nature of the sorbent, the nature of the sorbate, the temperature and the pressure.

Plots of $\log q_e$ vs. $\log c_e$ for the adsorption of platinum ions onto the rice hulls and the Lewatit TP 214 yielded straight lines with positive slopes, given by $1/n$, and intercepts at $\log K_F$ (not shown).

Langmuir isotherms. The following linearized form of the Langmuir Equation was used to analyze the adsorption data for the adsorption of platinum ion on the rice hulls and the Lewatit TP 214, respectively.^{37,38}

$$c_e/q_e = 1/(Q_{\max}K_L) + (1/Q_{\max})c_e \quad (8)$$

where q_e is the amount of metal ions adsorbed at equilibrium per unit weight of sorbent (mg g^{-1}), c_e is the equilibrium concentration of the sorbate in solution following adsorption, Q_{\max} is the maximum adsorption capacity (mg g^{-1}) (which is generally called the monolayer capacity), and K_L is the Langmuir equilibrium constant (L mg^{-1}). Figure 7 shows the Langmuir adsorption isotherm plot of c_e/q_e versus c_e .

The adsorption isotherms of both rice hulls and Lewatit TP 214 under different conditions were calculated and the results are given in Table II. The values of each model and the correlation coefficient, R^2 , were calculated from these plots. The linearity of these plots indicates the applicability of the two models. The correlation coefficients, R^2 , showed that the Langmuir isotherm ($R^2 \geq 0.99$) fits the data better than the Freundlich isotherm ($R^2 < 0.99$). This result indicates that the adsorption process of platinum ions onto the surfaces of Lewatit TP 214 and rice hulls is a monolayer adsorption process.

Investigation of adsorption thermodynamics

The temperature range chosen in this study was 298 to 318 K. The adsorption percentage increases with increasing temperature. The thermodynamic parameters for these adsorption processes, such as enthalpy change, ΔH° , entropy change, ΔS° , and the free energy of specific adsorption, ΔG° , were calculated using the following equations:^{34,39,40}

$$K_C = c_{Ac}/c_e \quad (9)$$

where K_C is the equilibrium constant, c_{Ac} and c_e are the equilibrium concentrations (in mg L^{-1}) of the platinum ion adsorbed and remaining in solution,

respectively. The free energy of adsorption, ΔG° , was calculated from the following relationship:

$$\Delta G = \Delta G^\circ + RT \ln K_c \quad (10)$$

At equilibrium, $\Delta G = 0$, thus:

$$\Delta G^\circ = -RT \ln K_c \quad (11)$$

where T is absolute temperature in Kelvin and R is the gas constant.

ΔH° was calculated from the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

$$\ln K_c = \Delta S^\circ / R - \Delta H^\circ / RT \quad (13)$$

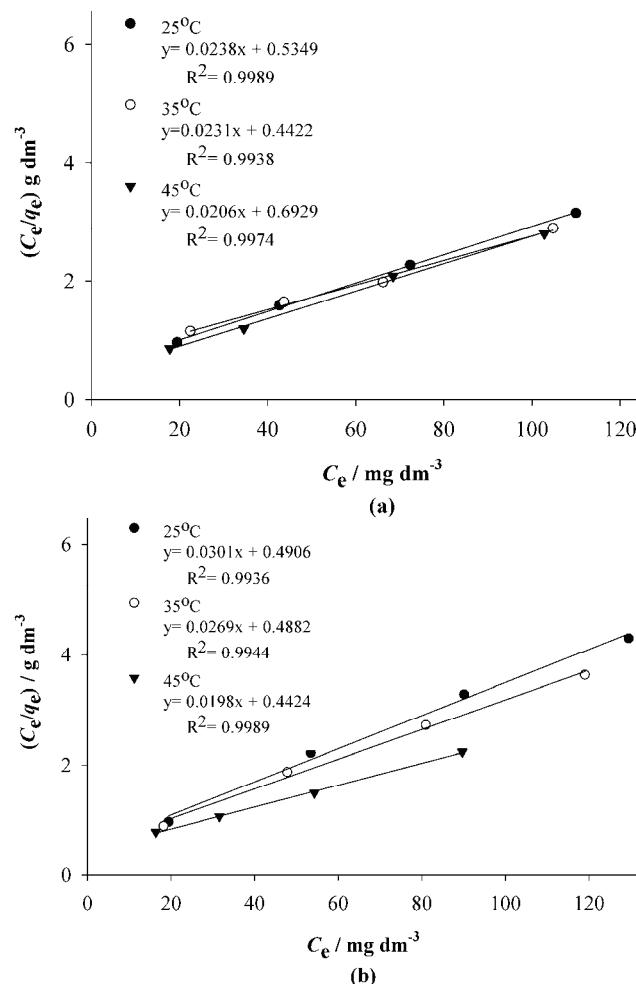


Fig. 7. The Langmuir isotherm of platinum adsorbed onto a) rice hulls and b) Lewatit TP 214 (20 mg sorbent, 60 min, 100 rpm, pH 1.5, and 5 mL solution of concentration 100–250 ppm).

TABLE II. Langmuir constants for the adsorption of platinum ions at various temperatures

T / °C	Rice hulls			Lewatit TP 214		
	K _L / dm ³ mg ⁻¹	Q _{max} / mg g ⁻¹	R ²	K _L / dm ³ mg ⁻¹	Q _{max} / mg g ⁻¹	R ²
25	0.04	42.02	0.9989	0.06	33.22	0.9936
35	0.05	43.29	0.9938	0.06	37.17	0.9944
45	0.03	48.54	0.9974	0.05	50.51	0.9989

The enthalpy change, ΔH° , and the entropy change, ΔS° , were calculated from the slope and from the intercept in linear plots of $\ln K_c$ vs. T^{-1} and are as shown in Fig. 8.

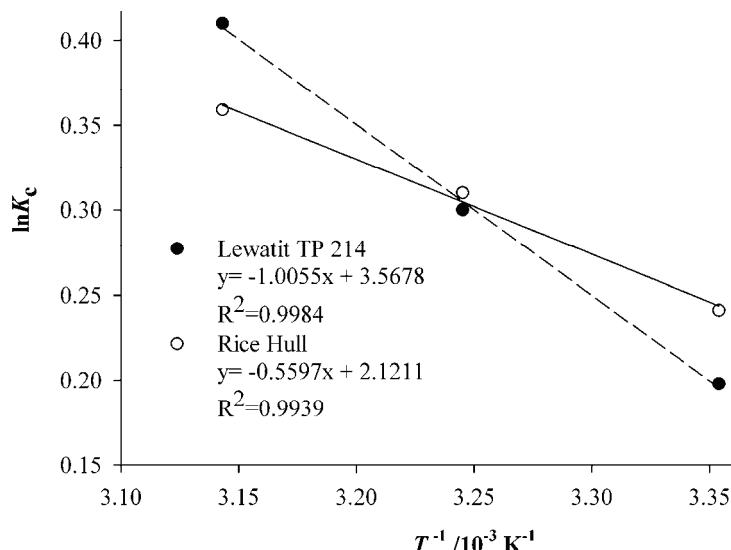


Fig. 8. $\ln K_c$ vs. $1000/T$ for platinum on Lewatit TP 214 and rice hulls (30 mg sorbent, 60 min, 100 rpm, pH 1.5 and 5 mL of 200 ppm solution).

The values of the thermodynamic parameters, ΔH° , ΔS° and ΔG° , for the platinum adsorption onto Lewatit TP 214 and the rice hulls were calculated using Eqs. (9)–(13) and are given in Table III.

TABLE III. Thermodynamic constants for the adsorption of platinum ions at various temperatures

T / K	Rice hulls			Lewatit TP 214		
	ΔG° kJ mol ⁻¹	ΔH° kJ mol ⁻¹	ΔS° J mol ⁻¹ K ⁻¹	ΔG° kJ mol ⁻¹	ΔH° kJ mol ⁻¹	ΔS° J mol ⁻¹ K ⁻¹
298	-0.60	4.65	17.6	-0.49	8.36	29.7
308	-0.79			-0.77		
318	-0.95			-1.08		

As shown in Fig. 5, an increase in the value of the adsorption percentage with increasing temperature indicates the endothermic character of platinum adsorption onto the sorbents. The value of $\Delta H^\circ_{298\text{ K}}$ for the platinum adsorption onto the rice hulls and Lewatit TP 214 were calculated to be 4.65 and 8.36 kJ mol⁻¹, respectively. The negative values of the free energy of specific adsorption ΔG° for the adsorption of platinum onto the sorbents, as shown in Table III, indicate that the process is spontaneous.³⁴ The value of ΔG° becomes more negative as the temperature increases, indicating an increasing driving force toward equilibrium, thereby resulting in a greater adsorption percentage at higher temperatures. The increase in the adsorption capacity of platinum onto the sorbents at higher temperature may be attributed to an enlargement of the pore size or to increased activation of the adsorbent surface. The greater extent of platinum adsorption at higher temperatures becomes apparent in an increase in the monolayer capacity. The process can only occur spontaneously if the entropy of the system increases and the value of $T\Delta S^\circ$ become greater than the value of ΔH° , yielding a negative value for the free energy of specific adsorption, ΔG° . The adsorption of platinum onto the sorbents is accompanied by an increase in the entropy of the overall system. The positive value of ΔS° indicates an increase in the randomness at the solid/solution interface during the adsorption of the metal ions onto the rice hulls and Lewatit TP 214. The results are in good agreement with those of other base metal ions adsorbed onto Lewatit TP 214⁴¹ and rice hulls.⁴²

CONCLUSIONS

This study demonstrated that both the commercially available rice hulls, an agricultural waste by-product, and Lewatit TP 214 can be effective for the adsorption of platinum ions from aqueous solutions. Equilibrium adsorption data were well fitted by the Langmuir model. The maximum monolayer adsorption capacities, Q_{\max} , at 25 °C of platinum ions onto rice hulls and Lewatit TP 214 were found to be 42.02 and 33.22 mg g⁻¹, respectively. Adsorption of platinum ions followed the pseudo-second-order rate equation, with a correlation coefficient of 0.99, rather than the pseudo-first-order rate equation. The kinetic rate of pseudo-second-order, k_2 , using 30 mg sorbent at 25 °C was found to be 0.0289 and 0.0039 g min⁻¹ mg⁻¹ for the rice hulls and Lewatit TP 214, respectively. The enthalpy change $\Delta H^\circ_{298\text{ K}}$ and the entropy change $\Delta S^\circ_{298\text{ K}}$ for this adsorption process for the rice hulls were calculated to be 4.65 kJ mol⁻¹ and 17.6 J mol⁻¹ K⁻¹, respectively, and the same quantities were calculated for Lewatit TP 214 to be 8.36 kJ mol⁻¹ and 29.7 J mol⁻¹ K⁻¹, respectively. Thus, the adsorption process was found to be endothermic.

This study demonstrates that platinum adsorption can successfully be achieved using rice hulls, which are abundantly available in Turkey, as an alternative to

more costly materials for the treatment of waste solutions containing heavy metal ions. These promising results suggest that platinum containing waste solutions, such as catalytic converter leach solutions, seasoned platinum plating solutions, anode slime solutions, *etc.* can be successfully treated with rice hulls. Best of all, this method does not involve the using of any chemicals; hence it does not generate any hazardous byproducts.

Acknowledgement. The authors thank the Istanbul Technical University, Turkey, for their financial support.

ИЗВОД

АДСОРПЦИЈА ПЛАТИНЕ НА ЉУСКАМА ПИРИНЧА И LEWATIT-У ТР 214 ИЗ РАСТВОРА ХЛОРОПЛАТИНСКЕ КИСЕЛИНЕ

M. H. MORCALI, B. ZEYTUNCU и O. YUCEL

*Istanbul Technical University, Faculty of Chemical and Metallurgical Engineering,
Maslak, 34469, Istanbul, Turkey*

Љуске пиринча, отпадна биомаса, и Lewatit TR 214, тиосемикарбазидни сорбент, испитивани су као адсорбенти за адсорпцију платине(IV) из разблаженог растовара хлороплатинске киселине. Љуске пиринча су окарактерисане методом ометене тоталне рефлексије са Фуријевом трансформацијом (ATR-FTIR). Испитивани су детаљно утицаји различитих адсорpcionих параметара: дозе сорбента, временена контакта, температуре и pH раствора на проценат адсорпције. Подаци добијени при адсорпцијоној равнотежи су најбоље фитовани Лангмировим моделом изотерме. Максимални капацитети монослоја, Q_{\max} , на 25 °C су били 42,02 и 33,22 mg g⁻¹ за љуске пиринча и Lewatit TR 214, редом. Термодинамички прорачуни у којима су коришћене измерене вредности за ΔH° , ΔS° и ΔG° указују да је адсорpcionи процес спонтан и егзотерман. Испитиване су једначине за брзине псеудо-првог реда и псеудо-другог реда; адсорпција јона платине на оба адсорбента је описана кинетичким моделом псеудо-другог реда. Константа брзине, k_2 , при коришћењу 30 mg сорбента на 25 °C је била 0,0289 и 0,0039 g min⁻¹ mg⁻¹ за љуске пиринча и Lewatit TR 214, редом. Резултати указују да се љуске пиринча могу успешно користити за уклањање платине из водених раствора.

(Примљено 12. септембра, ревидирано 1. децембра 2012)

REFERENCES

1. A. Wolowicz, Z. Hubicki, *Chem. Eng. J.* **197** (2012) 439
2. S. Aktas, M. H. Morcali, *Trans. Nonferrous Met. Soc. China* **21** (2011) 2554
3. A. Netzer, D. E. Hughes, *Water Res.* **18** (1984) 927
4. W. S. W. Ngah, C. S. Endud, R. Mayanar, *React. Funct. Polym.* **50** (2002) 181
5. K. Wang, B. Xing, *Chemosphere* **48** (2001) 665
6. K. H. C. Keith, M. Gordon, *Chemosphere* **60** (2005) 1141
7. K. C. Cheung, T. H. Venkitachalam, *Chemosphere* **41** (2000) 243
8. M. Rao, A. V. Parwate, A. G. Bhole, *Waste Manag.* **22** (2002) 821
9. E. Yildiz, *Sep. Purif. Technol.* **35** (2004) 241
10. C. A. Gray, A. P. Schwab, *Water, Air, Soil Pollut.* **69** (1993) 309
11. E. Guibal, T. Vincent, A. Larkin, J. M. Tobin, *Ind. Eng. Chem. Res.* **38** (1999) 4011

12. O. N. Kononova, T. A. Leyman, A. M. Melnikov, D. M. Kashirin, M. M. Tselukovskaya, *Hydrometallurgy* **100** (2010) 161
13. S. Aktas, M. H. Morcali, *Int. J. Miner. Process.* **101** (2011) 63
14. R. Chand, T. Watari, K. Inoue, H. Kawakita, H. N. Luitel, D. Parajuli, T. Torikai, M. Yada, *Miner. Eng.* **22** (2009) 1277
15. N. Thinakaran, P. Baskaralingam, M. Pulikesi, P. Panneerselvam, S. Sivanesan, *J. Hazard. Mater.* **151** (2008) 316
16. L. C. Romero, A. Bonomo, E. E. Gonzo, *Adsorpt. Sci. Technol.* **21** (2001) 617
17. Y. Bulut, Z. Tez, *J. Hazard. Mater.* **139** (2007) 35
18. A. Ozer, G. Dursun, *J. Hazard. Mater.* **146** (2007) 262
19. M. Valix, W. H. Cheung, G. McKay, *Chemosphere* **56** (2004) 493
20. C. Namasivayam, R. Radhika, S. Suba, *Waste Manag.* **21** (2001) 381
21. F. Banat, S. Al-Asheh, L. Al-Makhadmeh, *Process Biochem.* **39** (2003) 193
22. A. Hashem, A. A. Aly, A. S. Aly, A. Hebeish, *Polym.-Plast. Technol. Eng.* **45** (2006) 389
23. S. Rajeshwari, C. Namasivayam, K. Kadirvelu, *Waste Manag.* **21** (2001) 105
24. T. Robinson, B. Chandran, P. Nigam, *Environ. Int.* **28** (2002) 29
25. M. M. Mohamed, *J. Colloid Interface Sci.* **272** (2004) 28
26. R. L. Tseng, F. C. Wu, R. S. Juang, *Carbon* **41** (2003) 487
27. A. Mokhtar, Y. L. Nargess, M. M. Niyaz, S. T. Nooshin, *J. Hazard. Mater.* **135** (2006) 171
28. J. Tóth, *Adsorption: Theory, Modeling and Analysis*, Marcel Dekker, New York, USA, 2001, p. 251
29. D. M. Ruthven, *Principles of Adsorption and Adsorption Processes*, Wiley–Interscience, New York, USA, 1984, p. 177
30. C. Tasdelen, S. Aktas, E. Acma, Y. Guvenilir, *Hydrometallurgy* **96** (2009) 253
31. D. Ozcimen, A. Ersoy-Meriçboyu, *Adsorpt. Sci. Technol.* **28** (2010) 327
32. Y. S. Ho, G. McKay, *Chem. Eng. J.* **70** (1998) 115
33. R. G. Pearson, *Chemical Hardness*, Wiley–VCH, Weinheim, Germany, 1997, p. 43
34. G. Hussain, M. A. Khan, *J. Chem. Soc. Pak.* **33** (2011) 317
35. L. Zhou, J. Xua, X. Lianga, Z. Liub, *J. Hazard. Mater.* **182** (2010) 518
36. H. M. F. Freundlich, *J. Phys. Chem.* **57** (1906) 385
37. S. Y. Liu, J. Gao, Y. J. Yang, Y. C. Yang, Z. X. Ye, *J. Hazard. Mater.* **173** (2010) 558
38. I. Langmuir, *J. Am. Chem. Soc.* **40** (1918) 1361
39. H. Jaman, D. Chakraborty, P. Saha, *Clean: Soil, Air, Water* **37** (2009) 704
40. I. Kula, M. Ugurlu, H. Kaleaoglu, A. Celik, *Bioresour. Technol.* **99** (2008) 492
41. S. W. Won, J. Park, J. Mao, Y. S. Yun, *Bioresour. Technol.* **102** (2011) 3888
42. S. Naeem, U. Zafar, A. Altaf, A. Inayat, *J. Chem. Soc. Pak.* **31** (2009) 379.