Adsorption Behaviour of D201×4 Resin for Platinum(IV)

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The adsorption behaviour of D201×4 resin for Pt(IV) were investigated. The influences of medium pH, temperature, retention time on adsorption process are studied. Pt(IV) was quantitatively adsorbed by D201×4 resin in the medium of pH = 3.47. The statically saturated adsorption capacity is 567.5 mg/g. Pt(IV) adsorbed on D201×4 resin can be eluted by 0.1-2.0 mol/L NaOH. The rate constant is k_{298} = 9.13×10^{-5} s^{-1}. The Pt(IV) adsorption process on D201×4 resin obeys the Freundlich isotherm. The adsorption parameters of thermodynamic are as follows: enthalpy change (ΔH) =1.65 KJ/mol, Gibbs free energy change (ΔG) = -8.65 KJ/mol and entropy change (ΔS) = 34.57 J/(mol K). The apparent activation energy (E_a) is 11.93 KJ/mol. The coordination molar ratio of the functional group of D201×4 resin to Pt(IV) was 1:1.

Key Words: D201×4 resin, Platinum, Adsorption, Behaviour.

INTRODUCTION

In recent years, noble metals have not only been used as adornment and currency, they have been extensively applied in micro-electronics, aviation, atomic energy, chemical industry, environmental protection, military industry, medicine, *etc*. Platinum is characterized by corrosion resistance, steady thermo-electricity and excellent catalysis. With the rapid development of technology, platinum is increasingly required, which brings about the extensive exploration of its separation and refinement. Its traditional methods of separation and deposition have undergone several challenges[1-9]. Many efforts have been made to separate and concentrate certain metals by using ion exchange resin[10-16].

The adsorption of platinum has been investigated at present, but most of the adsorption materials have relative low adsorption capacity[17-19]. In this article, the capability and mechanism of platinum absorbed by the D201×4 resins in CH₃COOH-CH₃COONa medium are studied. A series of important parameters have been obtained, which supply the theory of platinum enriched and separated by the D201×4 resins.

EXPERIMENTAL

D201×4 resin (provided by Nankai university, activated before use). Standard solution of platinum(IV) prepared from K₂PtCl₆. Buffer solution with pH 2.63-5.73 prepared from acetic acid and sodium acetate (CH₃COOH-CH₃COONa). The other reagents were of AR grade.

723 spectrophotometer (the Third Analysis Instrument Factory of Shanghai); SartoriusPB-20 pH meter (Germany Sartorius Stock Company); SHZ-B temperature constant shaking machine (Shanghai Yuejin Medical Treatment Machine Factory); Perkin-Elmer683 FT-IR (American Nicolet Instrument Company).

Method: A solution containing lesser than 75 g of Pt(IV) was accurately added into a 25 mL colorimetric tube and then 5 mL of HCl solution and 5 mL 25 % SnCl₂ solution were added. After the addition of redistill water to the mark of the colorimetric tube, the absorbency was determined in a 1 cm colormetric vessel at a wavelength of 403 nm and compared with blank test.

General procedure

Adsorption equilibrium experiment: A desired amount of treated resin was weighed and added into a conical flask; then a desired volume of buffer solution with pH = 3.47 was added. After 24 h, a required amount of standard solution of Pt(IV) was added[20,21]. The flask was shaken in a shaker at constant temperature. The upper layer of clear solution was taken for analysis until the adsorption equilibrium was reached. The distribution coefficient (D) was calculated as follows:

$$D = \frac{Q_R}{\rho_e}$$

where $Q_R = (\rho_o - \rho_e)V/m$; ρ_o is the initial concentration of metal ion in solution, mg/mL; ρ_e is the equilibrium concentration of

metal ion in solution, mg/mL; V is the total volume of solution, mL; m is the mass of resin, g.

Elution test: 15 mg of resin was added into a mixed solution composed of pH = 3.47 buffer solution and desired amount of standard solution of Pt(IV). After the equilibrium was reached, the concentration of Pt(IV) in the aqueous phase was determined and then the adsorption capacity of the resin for Pt(IV) was obtained. The resin that has adsorbed Pt(IV) was separated from the aqueous phase and washed three times with pH = 3.47 buffer solution and the eluant was added to the resin. After the elution equilibrium was reached, the concentration of Pt(IV) in corresponding aqueous was determined and then the percentage of elution was obtained.

RESULTS AND DISCUSSION

Influence of pH on the distribution coefficient (D): The test was carried out according to the above-mentioned method. The influence of pH on the adsorption behaviour of D201×4 resin for Pt(IV) is shown in Fig. 1. The results show that the distribution coefficient (D) was the highest at pH = 3.47. Thus, all the following experiments were carried out at pH = 3.47.
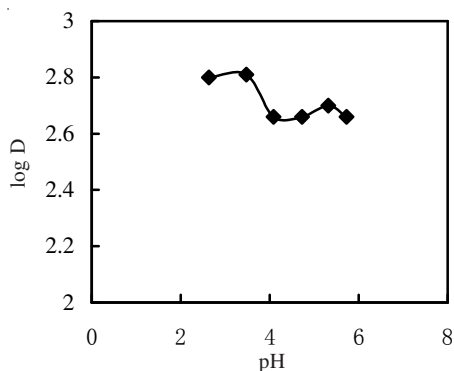
Fig. 1. Influence of pH on distribution coefficient. Resin 10 mg, 298 K, ρ_0 = 333 mg/L

Determination of t'$_{1/2}$: 20 mg of resin was weighted accurately. Under the experimental condition shown in Fig. 2, the upper layer clear solution was taken out of the total 40 mL solution at intervals for determining their concentrations, respectively. After their volume was corrected, a series of data was obtained and plotted as shown in Fig. 2. The result shows that t'$_{1/2}$ is equal to 4 h. Here, t'$_{1/2}$ is the time required to reach 50 % adsorption.
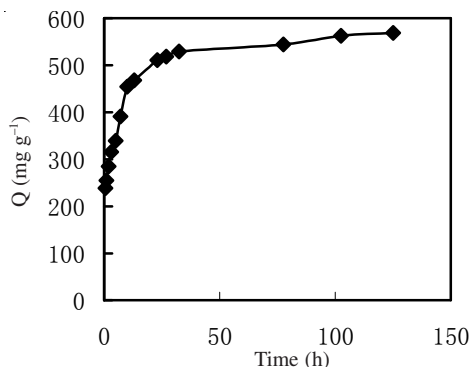
Fig. 2. Sorption rate curve of D201×4resin for Pt. pH = 3.47, 298 K, r_0 = 300 mg/L

Determination of the adsorption rate constant and apparent activation energy of D201×4 resin for Pt(IV): Four portions of 20 mg of resin were weighted accurately and put into conical flasks individually. The experiment was carried out using the above-mentioned method at 291, 298, 308 and 318 K. According to the experimental condition shown in Fig. 3, the upper layer clear solution was taken out of the 40 mL solution at intervals for determining their concentrations, respectively. After their concentration was kept constant and the volume was corrected, a series of data was obtained. According to the Brykina method[22], the adsorption rate constant k can be calculated from -ln (1-F) = kt, where F = Q_t/Q_∞ and Q_t and Q_∞ are the adsorption amounts at a certain time at equilibrium, respectively. The slope of straight line, which is made by plotting -ln (1-F) *versus* t (Fig. 3), yields the adsorption rate constant k and thus, the values of k at 291, 298, 308 and 318 K were obtained: k_{318} =12.56 × 10^{-5} s^{-1}, k_{308} = 10.34 × 10-5 s^{-1}, k_{298} = 9.13 × 10^{-5} s^{-1}, k_{291} = 7.85 × 10^{-5} s^{-1}. According to the Boyd liquid film spreading equation[23], it can be known from the linear relationship between -ln (1-F) and t that liquid film spreading is the predominant step of the adsorption process.
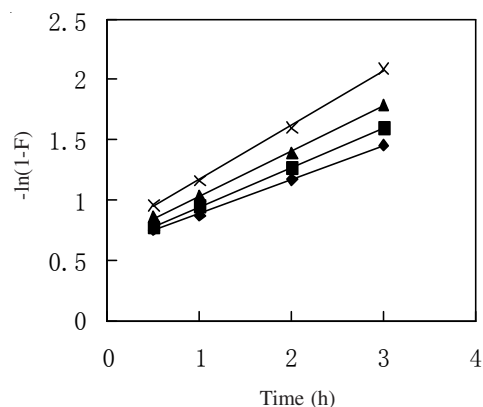
Fig. 3. Determination of rate content of D201×4 resin for Pt. ρ_0 = 300 mg/L, pH = 3.47

By plotting log k against 1/T (Fig. 4), the slope of straight line K_{slop} = -0.623. The correlation coefficient r = -0.9977 was achieved. According to Arrhenius equation:
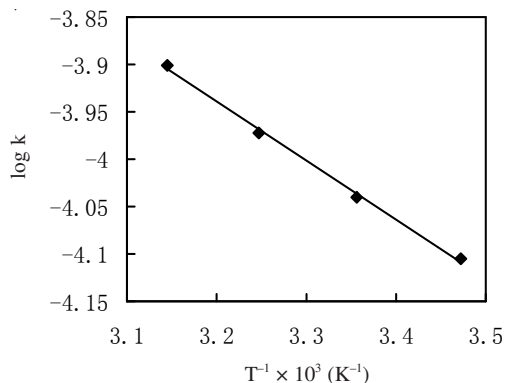
Fig. 4. Determination of activation energy of D201×4 resin for Pt

$$\log k = -\frac{E_a}{2.303RT} + \text{constant}$$

Thus, the apparent activation energy $E_a = -K_{slop} \times 2.303R$ = 11.93 kJ/mol. Adsorption reaction with apparent activation energy less than 40 kJ/mol is commonly named as the fast adsorption reaction, which completes easily at room temperature.

Isotherm adsorption curve: Certain amounts of the resin (10, 15, 20 and 25 mg) were weighted and put into conical flasks individually, in which 6 mL of the standard solution of Pt(IV) (2 mg/mL) and 34 mL of buffer solution with pH = 3.47 were added, respectively. The experiment was carried out using the above-mentioned method at 298 K and when the adsorption equilibrium was reached, the equilibrium concentration (ρ_e, mg/mL) was determined and the corresponding adsorption capacity (Q, mg/g) was calculated and plotted in Fig. 5. According to Freundlich formula $Q = a\rho^{1/b}$, *i.e.*, log Q = 1/b(log ρ) + log a, the correlation coefficient of straight line r = 0.9994 was achieved. Thus, the slope of the straight line in Fig. 5 was 1/b, and 1/b = 0.107, b = 9.35. The fact that the b value is between 2 and 10 indicates that Pt(IV) is easy to be absorbed[24].
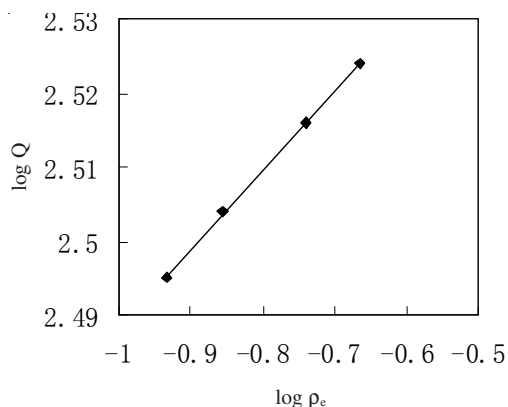
Fig. 5. Freundlich isotherm curve. pH = 3.47, 298 K, ρ_0 = 400 mg/L

Influence of adsorption temperature on the distribution coefficient and the determination of thermodynamic parameters: 10 mg of resin was accurately weighted. Under the experimental condition shown in Fig. 6, the distribution coefficient D of the resin for Pt(IV), over a range of temperature 291-318 K, was determined. log D is plotted against 1/T. The result obtained in Fig. 6 shows obviously that increasing temperature is favorable for the adsorption. It indicates that the adsorption process is an endothermic process. The correlation coefficient of straight line r = -0.9987 was achieved. The slope of the straight line in Fig. 6 is K_{slope} = -0.0862, S/R = 4.1578, according to

$$\log D = -\frac{H}{2.303RT} + \frac{S}{R}$$

where $\Delta H = -K_{slope} \times 2.303R = 0.0862 \times 2.303 \times 8.314 = 1.65$ kJ/mol, $\Delta S = 4.1578 \times 8.314 = 34.57$ J/(mol K). When T = 298K, $\Delta G = \Delta H - T\Delta S = 1.65-298 \times 0.03457 = -8.65$ kJ/mol.

Since H = 1.65 kJ/mol and there is less heat of adsorption, the adsorption reaction is considered to be physical adsorption.

Influence of various metal ions on the adsorption of D201×4 resin for Pt(IV): The results obtained are shown in
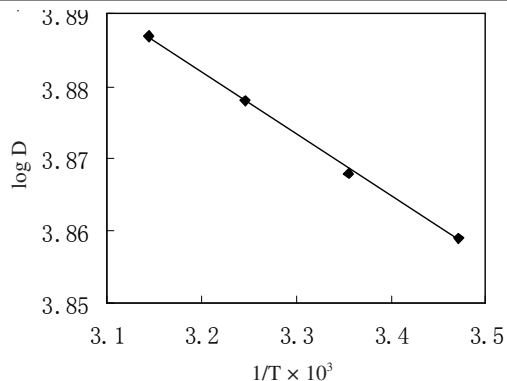
Fig. 6.   Influence of temperature on distribution ratio. pH = 3.47, ρ_0 = 333 mg/L

Fig. 7. Under the condition of the same concentration of Cu(II), Zn(II), Ni (II), Co(II) and Pt(IV), at pH range of 2.63-5.73, Ni(II) is nearly not adsorbed and Zn(II), Cu (II), Co(II) are slightly adsorbed (the adsorption ratio is lower than 12 %); however, Pt(IV) is well adsorbed. At pH = 3.47, the adsorption ratio of Pt(IV) is 75.82 %. Therefore, under the condition of pH = 3.47, Pt(IV) can be completely separated from Ni(II) and can be well separated from Zn(II), Cu (II) and Co(II).
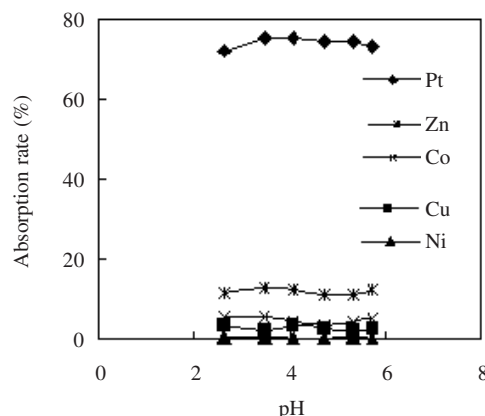
Fig. 7. Influence of various ions on the adsorption of D201×4 resin for Pt

Determination of the complex ratio

Equimolar method: Seven parts of different amounts of resins were accurately weighted and added into the conical flasks and then mixed with different amounts of Pt(IV). The total mole of D201×4 resin and Pt(IV) was kept as a constant at 145 μmol. Regardless of the molar ratio, the analysis was carried out according to the above-mentioned method. The adsorption amount *versus* $n_{Pt}/(n_{Pt} + n_R)$ yields a curve as shown in Fig. 8. The expected adsorption amount is the largest where the molar fraction of Pt(IV) is 0.48. It indicates that the molar ratio of functional group to Pt(IV) is 1:1.

Saturated method: 30 mg of resin was accurately weighted and under the condition of T = 298 K, ρ_0 = 400 mg/L, the experiment was carried out using the above-mentioned method. The adsorption capacity of the resin for Pt(IV) is 567.5 mg/g. The amount of the functional group and the capacity of the resin for Pt(IV) are calculated and shown in Table-1, which also indicates that the molar ratio of functional group to Pt(IV) is 1:1.

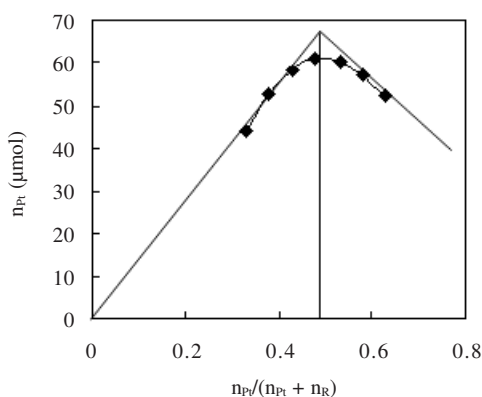| TABLE-1			
COMPLEX RATIO OF D201×4 RESIN FUNCTIONAL GROUP TO Pt(IV)			
N % of D201×4 resin (%)	Functional group capacity of D201×4 resin (mmol g^{-1})	Adsorption capacity of D201×4 resin (mmol g^{-1})	Complex molar ratio FG/Pt(IV)
4.15	2.97	2.91	1.02:1

Fig. 8. Equimolar series method. pH = 3.47, 298 K, total mole 145 μmol

Elution and recovery of platinum: The ratio of elution is shown in Table-2. The experimental result shows that the ratio of the second elution reaches more than 80 % when the concentration of NaOH is over a range of 1.0-2.0 mol/L. Thus, Pt(IV) adsorbed on D201×4 resin can be recovered quantitatively.

TABLE-2				
ELUTION TEST OF Pt(IV)				
Concentration of NaOH (mol L^{-1})	0.1	0.5	1.0	2.0
Second elution ratio (%)	58.2	65.8	83.1	88.6

Conclusion

Experimental results show that the static saturated adsorption capacity of D201×4 resin for Pt(IV) is 567.5 mg/g at pH = 3.47 in the medium of CH$_3$COOH-CH$_3$COONa. The ratio of the second elution reaches 88.6 % when the concentration of NaOH is 2.0 mol/L. The adsorption behaviour of D201×4 resin for Pt(IV) obeys the Freundlich isotherm and that the b value is between 2 and 10 indicates that Pt(IV) is easy to be absorbed. The rate constant $k_{298} = 9.13 \times 10^{-5}$ s^{-1}. The apparent activation energy E_a is 11.93 kJ/mol. The adsorption parameters of thermodynamics under 298 K: enthalpy change (ΔH) = 1.65 kJ/mol, Gibbs free energy change (ΔG) = -8.65 kJ/mol, entropy change (ΔS) = 34.57 J/(mol K). The molar ratio of functional group to Pt(IV) is 1:1.

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