Precise stepwise recovery of platinum group metals from high level liquid waste based on SDB polymer modified SiO_2

Kun Wu [a], Shunyan Ning [b,*], Xiangbiao Yin [b,*], Sizhi Xu [a], Yilai Zhong [a], Zengyuan Li [a], Lifeng Chen [b], Mohammed F. Hamza [b], Toyohisa Fujita [a], Yuezhou Wei [b,c]

[a]*State Key Laboratory of Featured Metal Materials and Life-cycle Safety for Composite Structures, MOE Key Laboratory of New Processing Technology for Nonferrous Metals and Materials, and School of Resources, Environment and Materials, Guangxi University, Nanning 530004, China.*

[b]*School of Nuclear Science and Technology, University of South China, 28 Changsheng West Road, Hengyang 421001, P.R. China.*

[c]*School of Nuclear Science and Engineering, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, China.*

*Corresponding author: Shunyan Ning

E-mail: ningshunyan@usc.edu.cn

Address: School of Nuclear Science and Technology, University of South China, 28 Changsheng West Road, Hengyang 421001, P.R. China.

ORCID: 0000-0002-9573-5960

*Corresponding author: Xiangbiao Yin

Email: yinxb@usc.edu.cn

Address: School of Nuclear Science and Technology, University of South China, 28 Changsheng West Road, Hengyang 421001, PR China.

ORCID: 0000-0003-2319-1789

3.2.1. Effects of HNO_3 concentration and temperature

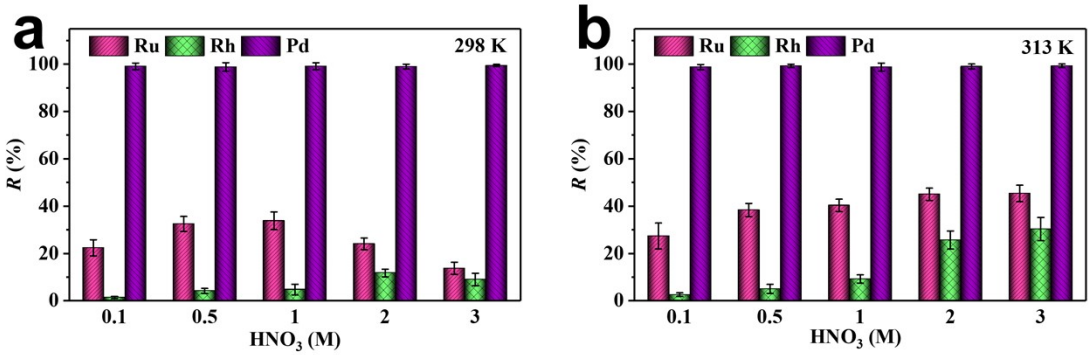


Fig. S1. Effect of HNO_3 concentrations on the adsorption of PGMs by dNbpy/SiO_2-P at 298 K (a), 313 K (b) (m/V = 0.02 g/mL, C_o: 1 mM, t = 24 h).

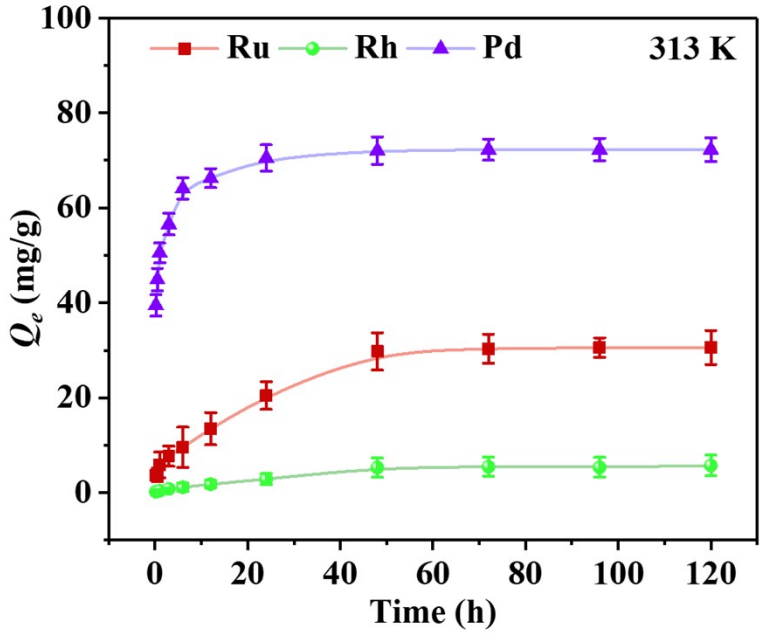
3.2.2 Kinetics study

Pseudo-first-order kinetics model: $\ln(Q_e - Q_t) = \ln Q_e - k_1 t$ **(S1)**

Pseudo-second-order kinetics model: $\frac{t}{Q_t} = \left(\frac{1}{Q_e}\right)t + \frac{1}{k_2 Q_e^{\,2}}$ **(S2)**

Where k_1 (h^{-1}) and k_2 ($mg \cdot g^{-1} \cdot h^{-1}$) are the adsorption rate constants of pseudo-first-order kinetics model and pseudo-second-order kinetics model, the equilibrium adsorption capacity and the adsorption quantity at time t (min), respectively, are Q_e ($mg \cdot g^{-1}$) and Q_t ($mg \cdot g^{-1}$).

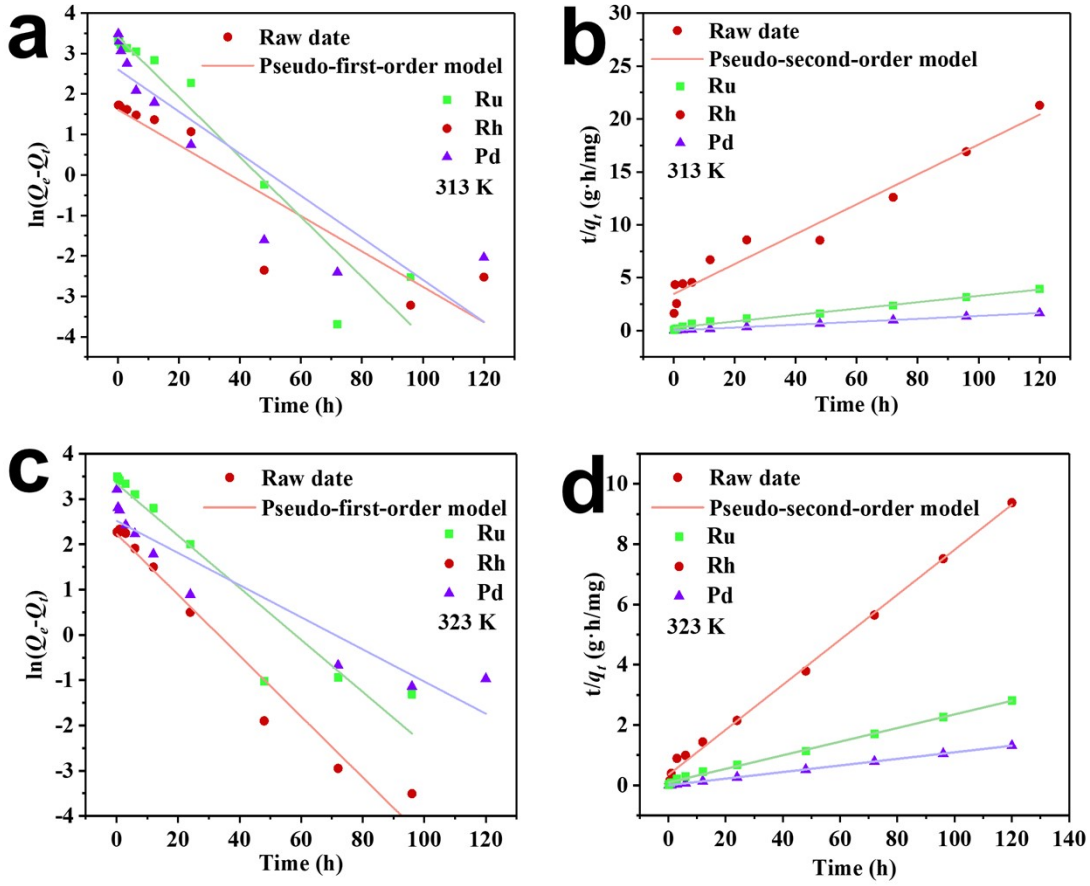
In this work, both pseudo-first-order kinetics model and pseudo-second-order kinetic model were applied to analyze the experimental data.



33

34 **Fig. S2.** Adsorption kinetics of PGMs on dNbpy/SiO_2-P at 313 K (m/V = 0.02 g/mL, $C_{Ru(III)}$: 10 mM,

35 $C_{Rh(III)}$: 5 mM, $C_{Pd(II)}$: 20 mM, C_{HNO3}: 3 mol/L).



36

37 **Fig. S3.** Adsorption kinetics fitting results of PGMs on dNbpy/SiO_2-P at 313 K (a, b) and 323 K (c, d)

(m/V = 0.02 g/mL, $C_{Ru(III)}$: 10 mM, $C_{Rh(III)}$: 5 mM, $C_{Pd(II)}$: 20 mM, C_{HNO3}: 3 mol/L).

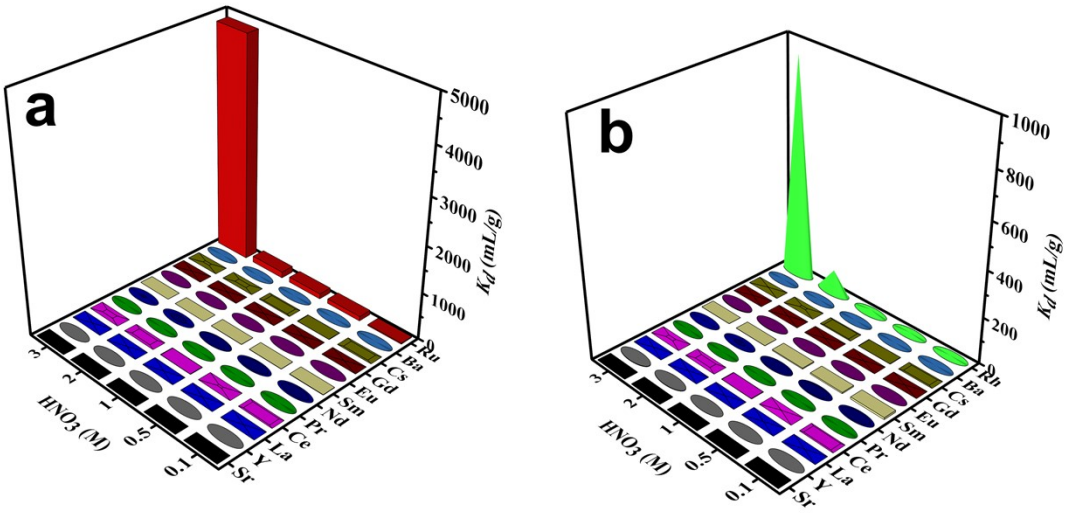


Fig. S4. Ru(III) (a) and Rh(III) (b) distribution coefficients.

Table S1 *SF* data for PGMs.

HNO_3/M	$SF_{Ru/M}$	$SF_{Rh/M}$	$SF_{Pd/M}$
0.1	33	4	543
0.5	170	9	930
1	188	59	1412
2	230	74	3716
3	1705	336	3805

3.2.3. Isotherm study

$$\text{Langmuir model: } Q_e = \frac{q_m \times K_L \times C_e}{1 + K_L \times C_e} \quad \textbf{(S3)}$$

$$\text{Freundlich model: } Q_e = K_F \times C_e^{\frac{1}{n}} \quad \textbf{(S4)}$$

where Q_e (mg·g^{-1}) and q_m (mg·g^{-1}) are the equilibrium and computed maximum adsorption capacities. C_e (mmol·L^{-1}) stands for equilibrium ions concentration. The constants in the Langmuir and Freundlich isotherm are K_L (L·mg^{-1}) and K_F (mg^{1-n}·L^n/g). Adsorption intensity is expressed as n.

Langmuir model (**Eq. S4**) assumes the process is single layer adsorption that all

the sites are evenly distributed and have the same adsorption ability. Freundlich model (**Eq. S5**) assumes a heterogeneous adsorption surface with sites having different adsorption energies.

3.2.4. Thermodynamic analysis

$$\text{Van't Hoff equation: } \ln K_d = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad \textbf{(S5)}$$

$$\text{Gibbs-Helmholtz equation: } \Delta G^o = \Delta H^o - \Delta S^o T \quad \textbf{(S6)}$$

where ΔG^o, ΔH^o, and ΔS^o are the changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol), entropy (kJ/K·mol), respectively. R is the universal gas constant 8.314 J/(K·mol) and K_d (mL/g) is the distribution coefficient. ΔS^o, ΔH^o are obtained according to the intercept and slope of **Eq. S6** ($\ln K_d$ versus $1/T$), while then ΔG^o at different temperature can btained according to **Eq. S7**.

3.3.3 Slope analysis

$$M^{n+} + q\ NO_3^- + m\ [L] \rightleftharpoons [L]_m\ M\ (NO_3)_q^{-(q-n)} \quad \textbf{(S7)}$$

$$\text{Partition coefficient: } D = \frac{C_1}{C_a} = \frac{(C_2 - C_a)}{C_a} \times \frac{V_a}{V_1} = \frac{[L]m \bullet M\ (NO3 -)q}{Mn +} \quad \textbf{(S8)}$$

$$\text{Extraction equilibrium constant: } K' = \frac{[L]m \bullet M\ (NO3 -)q}{Mn +\ ⓾\ [L]m\ ⓾\ (NO3 -)q} \quad \textbf{(S9)}$$

$$\text{Slope analysis equation: } \log D = \log K' + q \log [NO_3^-] + m \log [L] \quad \textbf{(S10)}$$

Partition coefficient D was calculated using Eq. S9. C_1, C_2, and C_a represent the cation concentrations in the loaded oil phase, the initial aqueous phase before extraction, and the aqueous phase after extraction. V_a and V_1 denote the volumes of the aqueous and organic phases of the extraction experiment. Where M^{n+} represents the Ru,

Rh, and Pd, [L] represents dNbpy, m denotes the stoichiometric coefficient. log *D* can be transformed from **Eq. S9** and **Eq. S10** to **Eq. 11**.

3.3.4 Depth-profiling XPS analysis

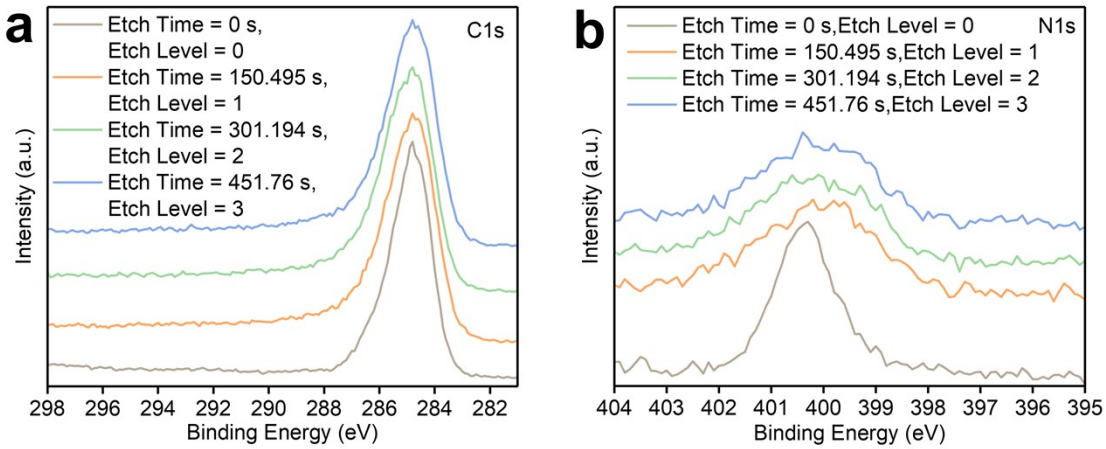


Fig. S5. Fine spectra of depth-profiling XPS etched C 1s (a), N 1s (b).

3.4. Column experiments

Table S2 Recovery yields of metal ions in the column experiment (a).

Elements	I (%)	II (%)	III (%)	IV (%)	Total (%)
Ru	0.00	99.57	0.00	0.10	99.67
Rh	0.00	99.83	0.00	0.07	99.9
Pd	0.00	0.08	0.03	99.58	99.69
Sr	0.00	99.99	0.00	0.00	99.99
Y	0.00	99.95	0.00	0.00	99.95
Cs	0.00	98.17	0.00	0.12	98.17
Ba	0.00	99.99	0.00	0.00	99.99
La	0.00	99.96	0.00	0.00	99.96
Ce	0.00	99.97	0.00	0.00	99.97
Pr	0.00	99.86	0.00	0.00	99.86
Nd	0.00	99.93	0.00	0.00	99.93
Sm	0.00	99.79	0.00	0.35	99.79
Eu	0.00	99.99	0.00	0.00	99.99

Gd	0.00	99.87	0.00	0.00	99.87

Table S3 Recovery yields of metal ions in the column experiment (b).

Elements	I (%)	II (%)	III (%)	IV (%)	Total (%)
Ru	0.00	9.43	0.00	90.35	99.78
Rh	0.00	60.92	0.00	15.37	76.29
Pd	0.00	0.00	0.00	0.00	0.00
Sr	0.00	99.32	0.00	0.07	99.39
Y	0.00	99.53	0.00	0.10	99.63
Cs	0.00	99.75	0.00	0.23	99.98
Ba	0.00	99.92	0.00	0.00	99.92
La	0.00	99.84	0.00	0.00	99.84
Ce	0.00	99.73	0.00	0.18	99.91
Pr	0.00	99.91	0.00	0.00	99.91
Nd	0.00	99.95	0.00	0.00	99.95
Sm	0.00	99.35	0.00	0.45	99.8
Eu	0.00	99.96	0.00	0.00	99.96
Gd	0.00	99.83	0.00	0.00	99.83